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## "Brief Communications"

*SOME* technical journals maintain a "Communications to the Editor" section, in which brief technical reports may be published without delay. This JOURNAL has a "Technical Notes" section for short research papers, but the manuscripts are reviewed as thoroughly as longer papers, so that, if the time lapse from receipt to publication is under the average, it is only because of the brevity. The JOURNAL also publishes occasional "Letters to the Editor," but these are customarily not technical reports, but rather letters of criticism, comment, or suggestion, and they appear in the Current Affairs section.

It frequently has been suggested that the JOURNAL make provision for the publication of short technical reports which are of timely or current interest, which do not need to receive lengthy review, and which do not involve JOURNAL responsibility with respect to details in the same sense that full technical articles do. The latest suggestion of this type has come from a scientist who is not a member of The Electrochemical Society, but who is now completely vulnerable to the wiles of the Membership Committee. His proposal is clear and concise, and has impressed the Publication Committee. Consequently, the JOURNAL will undertake to publish "Brief Communications" which seem to be appropriate.

The rules will be as follows, subject to change from time to time: Material will be limited to 600 words, with a figure or short table counting as 100 words. The report may summarize high lights of material to be published in the future; may present new facts which warrant current distribution but otherwise could not appear for a long time; may cover bits of research which the author cannot pursue but which may be of use to others; etc. Letters of discussion or of polemical nature will be specifically excluded. "Brief Communications" will be reviewed by one or two members of the Editorial Board, but every effort will be made to send them, if accepted, to the printer at the next monthly deadline after receipt. Controversial material will, of course, be rejected, or subjected to more lengthy review.

The first "Brief Communication" appears in this issue, at the end of the Technical Section (see p. 432). It is an example of the type of communication which we think suitable; according to the rules described above, it is about 60 words too long. The time lapse from receipt to publication should be typical; in a favorable case the time might be two weeks less.

Of course, this type of publication has its dangers. Some authors are far more enthusiastic about their own work than anyone else; some reviewers are pessimistic about the value of brief reports or the need for rushing them into print. Well-conceived reports of this type can be useful, and will get attention. There is no doubt that many readers look for the short items first, postpone the longer articles for future study.

—CVK

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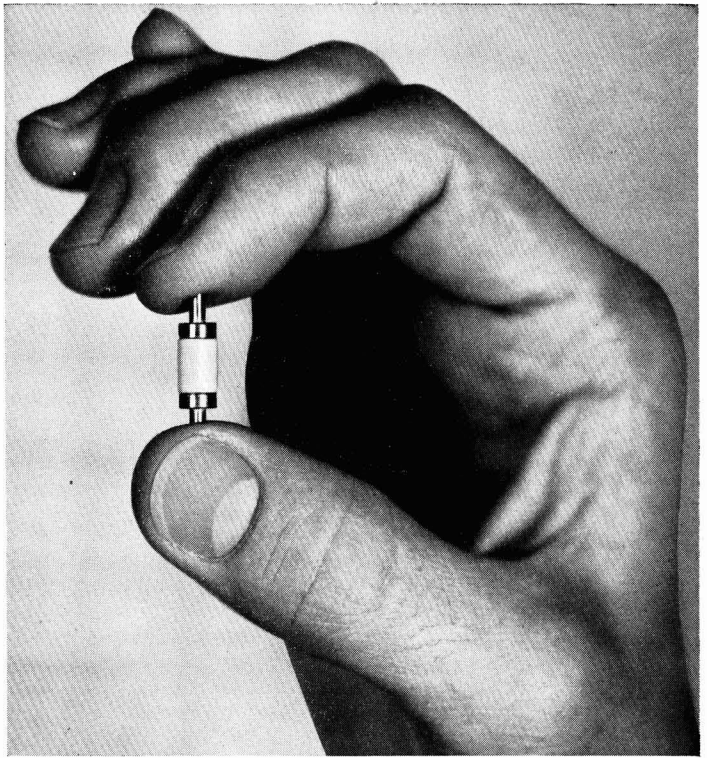
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AT 6,000,000,000 C. P. S.

How the radio art can be improved through solid state science is illustrated by a recent development at Bell Telephone Laboratories. To make voice signals travel by microwaves they must first be "converted"—caused to vibrate at billions of cycles per second. To date, it has been possible to accomplish this conversion only at the cost of appreciable loss of signal energy. Could a more efficient converter be provided?

In the field of solid state science it was known—as a laboratory curiosity—that semiconductor diodes can be made not only to convert the frequency of signals, but also to amplify them. At Bell Laboratories Dr. Arthur Uhlir, Jr., and his associates calculated that this amplifying action could be put to practical use. They proved the point by developing a junction diode converter which can deliver up to 40 times as much signal energy as previous converters.

This efficient new converter will be applied in a new Bell System microwave highway able to transmit thousands of telephone conversations and a dozen television programs simultaneously at six billion cycles per second. In other forms it is being developed, under Signal Corps contract, for radar and military communications where more efficient frequency conversion can also be used to advantage.

This development is an example of the many different ways in which Bell Laboratories works to improve your telephone service and communications at large.



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# Electrochemical Properties of PbO<sub>2</sub> and the Anodic Corrosion of Lead and Lead Alloys

Paul Rüetschi and Boris D. Cahan

*The Electric Storage Battery Company, Philadelphia, Pennsylvania*

## ABSTRACT

The total amount of anodic corrosion of Pb and Pb-Sb alloys in sulfuric acid under conditions of O<sub>2</sub> evolution can be evaluated by measuring the length of the potential plateau (transition time) during the electrochemical reduction of the PbO<sub>2</sub> layers, with a constant current, taking into account self-discharge and degree of utilization of the PbO<sub>2</sub>. Using high resolution techniques, a characteristic step in the potential plateau during discharge of the PbO<sub>2</sub> layer was discovered. This step can be attributed to a difference in discharge overvoltage between  $\alpha$ - and  $\beta$ -PbO<sub>2</sub>. For alloys of the Pb-Sb system, constant current corrosion increases slightly with increasing Sb concentration, whereas oxygen overvoltage decreases and constant potential corrosion strongly increases with increasing Sb concentration.

Precise electrode potential measurements of the  $\alpha$ -PbO<sub>2</sub>/PbSO<sub>4</sub> and the  $\beta$ -PbO<sub>2</sub>/PbSO<sub>4</sub> couple gave 1.7085  $\pm$  0.0005 v and 1.7015  $\pm$  0.0005 v, respectively, vs. H<sub>2</sub> in 4.40M sulfuric acid at 31.8°C. These two oxides have different oxygen overvoltage characteristics.

Removal of oxygen from  $\beta$ -PbO<sub>2</sub> results in a new crystalline compound PbO<sub>x</sub> with  $x$  1.4 to 1.6, with a pseudo-face-centered cubic orthorhombic lattice. This new compound is a nonconductor. The influence of the oxygen content of the lead oxides on their electrochemical behavior is discussed.

A constant current technique has been used recently to study anodic corrosion of lead and lead alloys in H<sub>2</sub>SO<sub>4</sub> (1). It involves evaluating the amount of PbO<sub>2</sub> formed during anodization by measuring the transition time for the discharge of the PbO<sub>2</sub> layer. Very small amounts of corrosion products can be determined accurately this way, therefore, and the corrosion resistance of an alloy can be evaluated in a relatively short time. The major corrosion product produced on lead and lead alloy anodes under conditions of oxygen evolution is  $\alpha$ -PbO<sub>2</sub>, a new crystalline modification of lead dioxide. This new compound has been found independently in several laboratories (1-6).

The electrochemical properties of the corrosion layers depend on the relative amounts of the two lead dioxide modifications and on their oxygen content. The present paper is a study of the electrochemical properties of the corrosion layers and of their oxygen content.

It is well known that PbO<sub>2</sub> never has the stoichiometric composition but always shows an oxygen deficiency. Palmaer (7) measured the electric properties of tetragonal ( $\beta$ )-PbO<sub>2</sub> obtained by electrodeposition and found a resistivity of  $(0.95 \pm 0.03) \cdot 10^{-1}$  ohm cm, with a positive temperature coefficient of 0.06%/degree in the range of 22°-84°C. The chemical analysis indicated that these samples had a composition PbO<sub>1.99</sub>. The analytical results here, however, always show a lower oxygen content for both  $\beta$ - and  $\alpha$ -PbO<sub>2</sub>, namely PbO<sub>1.91</sub> to PbO<sub>1.96</sub>.

Thomas (8) has reported values of the resistivity of tetragonal  $\beta$ -PbO<sub>2</sub> produced electrolytically in a

hard and dense form. He found a value of  $0.94 \cdot 10^{-4}$  to  $4.05 \cdot 10^{-4}$  ohm cm, with a temperature coefficient of 0.07%/degree of the room temperature value in the range -190° to -90°C. According to Thomas, the Hall coefficient is  $-3.7 \cdot 10^{-2}$  to  $-1.7 \cdot 10^{-2}$  cm<sup>3</sup>/coulomb. The negative sign of the Hall coefficient indicates that the carriers are electrons. The high concentration of free electrons in PbO<sub>2</sub> arises from the departure from the stoichiometric composition in the direction of oxygen deficiencies, although it is not firmly established whether PbO<sub>2</sub> is a metal excess or an anion defect type of conductor.

It has been reported that oxygen can be removed by thermal decomposition *in vacuo* to PbO<sub>1.99</sub> (9) or to PbO<sub>1.9</sub> (10) without phase change. If these results are correct, it should be possible to make PbO<sub>2</sub> even more conducting by heating *in vacuo*. Kittel, however, has shown (11) that the conductivity decreases as oxygen is removed by thermal decomposition. At the same time the Hall coefficient increases, indicating a decrease in the "free electron concentration." Kittel's data are summarized in Table I.

These results indicate the formation of a new insulating lattice as oxygen is removed. The fact that a phase change occurs has been described by several authors (11-16), although their interpretations are not at all in agreement.

According to Kittel the mean electric resistance of PbO<sub>2</sub> is  $1.18 \cdot 10^{-1}$  ohm cm and the temperature coefficient in the range between -180° and 20°C is about 0.07%/degree. The mean value for the Hall coefficient is  $-7.8 \cdot 10^{-3}$  cm<sup>3</sup>/amp sec. Oxygen over-

Table I. Conductivity and Hall coefficient of lead dioxide as a function of amount oxygen removed (in per cent of the initial oxygen content), Kittel's data

Oxygen removed in % of initial amount of oxygen present	Sample No.	Conductivity ohm <sup>-1</sup> cm <sup>-1</sup>	Hall coefficient cm <sup>2</sup> /amp sec
0	1	0.74 · 10 <sup>4</sup>	-7.8 · 10 <sup>-3</sup>
	2	0.89	-8.6
	3	0.74	-8.5
	4	1.01	-7.7
	5	0.82	-8.0
0.4	4	0.13 · 10 <sup>4</sup>	-13.5 · 10 <sup>-3</sup>
	5	0.24	-14.4
2.4	1	0.34 · 10 <sup>4</sup>	-10.7 · 10 <sup>-3</sup>
	2	0.26	-11.3
3	3	0.16	-12.4
	4	0.10 · 10 <sup>4</sup>	-15.7 · 10 <sup>-3</sup>
	5	0.22	-13.2
4.4	2	0.22 · 10 <sup>4</sup>	-11.6 · 10 <sup>-3</sup>
	3	0.12	-13.7
6.3	1	0.24 · 10 <sup>4</sup>	-13.5 · 10 <sup>-3</sup>
8.0	2	0.16 · 10 <sup>4</sup>	-13.1 · 10 <sup>-3</sup>
	3	0.10 · 10 <sup>4</sup>	-14.5 · 10 <sup>-3</sup>
13	3	0.04 · 10 <sup>4</sup>	-20.2 · 10 <sup>-3</sup>

voltage and anodic corrosion are related to the oxygen content of the PbO<sub>2</sub> layers during anodization, as shown below.

### Experimental

The electrolytic cell, the electric circuit, and the sample preparation for anodization and polarization studies have been described (1). Anodic corrosion was evaluated by recording the potential of PbO<sub>2</sub> layers formed at 3 ma/cm<sup>2</sup> for 20 hr at 30°C in H<sub>2</sub>SO<sub>4</sub>, sp gr 1.225 (at 20°C) during discharge with constant current, using a Minneapolis-Honeywell ½ second recorder, Model Y 153X (19)V-X-156, operated in conjunction with a General Radio Voltmeter amplifier type 1230-A. Potentials were measured against a H<sub>2</sub> electrode in the same electrolyte at the same temperature. Alloy samples for the corrosion experiments were cast, applying identical casting conditions for all the alloys, namely, a metal temperature of 900°F and a mold temperature of 400°F. It is known that grain size is an important factor in anodic corrosion of lead alloys (17).

An RCA electron microscope, type EMU-3, was used to study the surface structure of the corrosion layers. Portions of the corrosion products were stripped by imbedding in low molecular weight polystyrene. These samples were lightly covered with an evaporated carbon film to hold the crystals together. The polystyrene was dissolved with toluene and samples of corrosion products of approximately 1 mm<sup>2</sup> area were collected on copper screens for investigation under the electron microscope.

A series of batteries containing some grid alloys of Table II were built and SAE overcharge life tests were run.<sup>1</sup>

Baker C.P. tetragonal (β-)PbO<sub>2</sub> was used for the thermal decomposition experiments. Samples of about 2 g were heated in 7 mm Pyrex tubing in an

electric tube furnace. Temperatures were controlled to ±2°C using a Sola CVH-500VA constant voltage transformer and a Variac, and measured with an iron-constant an thermocouple. Samples were heated for 3 hr at 1 mm or at 3 atm of oxygen pressure, and then removed from the furnace and air cooled. No change in the oxygen content of any sample was observed after cooling and storage in a dry atmosphere.

Samples were chemically analyzed for active oxygen by thiosulfate titration of the iodine liberated from a KI solution in sodium acetate (18). Evaporation of the liberated iodine was prevented by continuous addition of thiosulfate as the iodine was liberated by the reaction. The results of the analysis were reproducible to ±0.3%.

Small samples of the prepared oxides were mounted in collodion on a glass slide and x-rayed with a GE-XRD-3 Geiger diffractometer.

For electrode potential measurements, samples were pressed into a strip of perforated lead sheet, with a pressure of 80,000 lb/in.<sup>2</sup> using a Carver Laboratory Press. The holes in the lead strip were spaced 1.5 mm and had a diameter of 1.2 mm. The prepared and immersed part of the strip was about 1 cm<sup>2</sup>. The electrode potentials were measured in H<sub>2</sub>SO<sub>4</sub>, sp gr 1.225 (at 20°C), prepared from C.P. H<sub>2</sub>SO<sub>4</sub> and triple distilled water. The potentials were measured with a Rubicon Type B high precision potentiometer, against a hydrogen electrode in the described electrolyte.

Electrode potentials of pure orthorhombic (α)PbO<sub>2</sub> and pure tetragonal (β)PbO<sub>2</sub> were measured by the same technique. α-PbO<sub>2</sub> was prepared by electrolysis on a Pt screen of a concentrated solution of KOH, saturated with Pb(OH)<sub>2</sub> at a current density of 1 ma/cm<sup>2</sup>. The adhering film sample was ground, washed with hot ammonium acetate solution and with conductivity water. Baker C.P. tetragonal (β)PbO<sub>2</sub> was used for the electrode potential measurements of β-PbO<sub>2</sub>.

Electrode potentials of electrodeposited layers of α- and β-PbO<sub>2</sub> were also measured. The layers were electrodeposited on a Pt wire, which was rigidly mounted between the ends of a U-shaped glass rod to prevent vibration and cracking of the PbO<sub>2</sub> film. The wire had a diameter of 0.6 mm; the length exposed to the electrolyte was 2.5 cm.

The α-PbO<sub>2</sub> layer was electrodeposited in a two compartment cell at 50°C, at 1 ma/cm<sup>2</sup> for 20 hr. After this time period the layer had reached a thickness of about 0.1 mm. β-PbO<sub>2</sub> layers were deposited at the same current for the same time period but at 30°C. Electrode potentials were measured after washing the electrodes and immersing them in 4.40M acid.

β-PbO<sub>2</sub> was prepared by electrodeposition from 30% perchloric acid saturated with litharge, according to the procedure described by Thomas (8). The electrolytic bath for deposition of α-PbO<sub>2</sub> was prepared by adding 50 cc of water, 50 cc of saturated sodium acetate solution, and 10 cc of saturated lead acetate solution to 100 cc of carbonate-free, saturated KOH solution.

<sup>1</sup> In this SAE test, a 100 amp-hr, 6 v automotive battery is overcharged at 100°F at a rate of 9 amp for a total of 1000 amp-hr each week. At the end of each week, the battery is discharged at 300 amp at 100°F. The battery has reached the end of life when the capacity is less than 0.5 min.



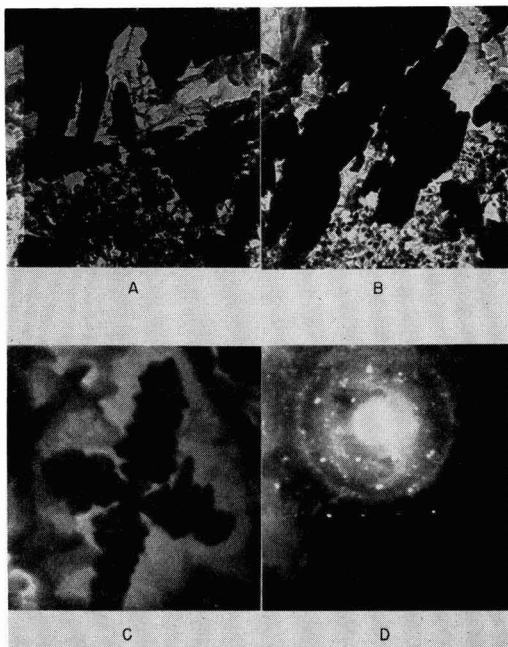


Fig. 1. Electron microscope pictures of an anodized lead surface at 30,000  $\times$  magnification.

Oxygen overvoltages were measured on these electrodeposited layers of  $\alpha$ - and  $\beta$ - $\text{PbO}_2$  in  $\text{H}_2\text{SO}_4$  under very pure conditions.

### Results

The corrosion products formed by anodization of lead and lead alloys were in a fine crystalline state. Figure 1 shows electron microscope pictures of crystals of the corrosion products at 30,000  $\times$  magnification. The pictures of Fig. 1 refer to a pure lead

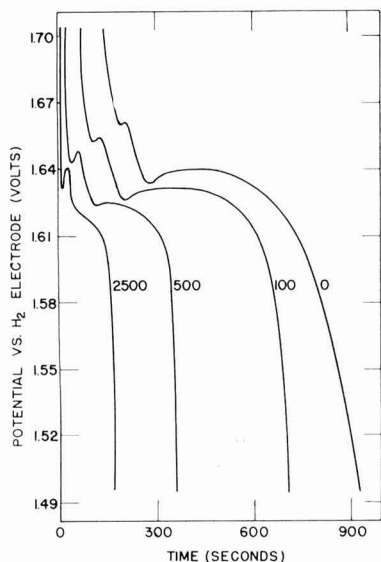


Fig. 2. Electrode potential transients during discharge at 0, 100, 500, and 2500  $\mu\text{A}/\text{cm}^2$  of  $\text{PbO}_2$  layers formed at 3  $\text{mA}/\text{cm}^2$  for 20 hr in 53M  $\text{H}_2\text{SO}_4$  at 30°C.

sample which had been anodized for 4 hr with 3  $\text{mA}/\text{cm}^2$  at 30°C in  $\text{H}_2\text{SO}_4$ , sp gr 1.225. Single crystal diffraction patterns were obtained by selected area diffraction. Figure 1D shows such a pattern for the remarkable cross-shaped lead sulfate crystal shown in Fig. 1C. The crystal can be recognized in the background of Fig. 1D. With selected area diffraction the material of microscopic crystals can be identified. More work using this technique for studying corrosion products is anticipated.

Figure 2 shows the potential transients during discharge with 0, 100, 500, and 2500  $\mu\text{A}/\text{cm}^2$  of  $\text{PbO}_2$  layers which were produced by anodization for 20 hr at 3  $\text{mA}/\text{cm}^2$  of a lead alloy containing 11% Sb [alloy #8 in reference (1)]. Due to the high resolution of the potential recording equipment, interesting details of the discharge process are revealed. On interruption of the anodizing current and start of the discharge, the potential drops from the oxygen overvoltage value to a first minimum. This initial minimum has also been observed by other investigators (19). During the time period from start of discharge to the first minimum, the excess oxygen on and in the layer is desorbed. The potential then recovers to a first plateau and drops thereafter to a second plateau, about 30 mv below the first plateau. It is shown later that the two plateaus could possibly correspond to the two modifications of lead dioxide, the tetragonal  $\beta$ - $\text{PbO}_2$  and the orthorhombic  $\alpha$ - $\text{PbO}_2$ .

Discharge curves as shown in Fig. 2 were taken and the discharge times (down to a fixed potential of 1.55 v vs.  $\text{H}_2$ ) were measured at 0, 100, 500, and 2500  $\mu\text{A}/\text{cm}^2$  discharge current for a large series of lead alloys of the binary system PbSb (alloys No. 1 to 8) and of other lead alloys containing the elements Ca, Sb, Sn, As, and Ag (alloys No. 9 to 14). The chemical analyses of all the alloys are given in Table II.

The technique for evaluating the total amount of corrosion has been described (1). The product  $i \times t$ , where  $i$  is the discharge current and  $t$  is the discharge time, increases with decreasing discharge time. Extrapolation to zero discharge time gives the total available capacity since self-discharge is then eliminated (1, 20). The amount of  $\text{PbO}_2$  left in the layer after discharge was determined by microtitration. This amount of  $\text{PbO}_2$  increased only very slightly with decreasing discharge time for all of the alloys, and it was easy to extrapolate the values to zero discharge time. Adding the extrapolated values for the available capacity and the amount of  $\text{PbO}_2$  left in the layer after discharge gave the total amount of corrosion. The total extrapolated capacity (total amount of corrosion) expressed in amp sec/ $\text{cm}^2$ , after anodization at 3  $\text{mA}/\text{cm}^2$  for 20 hr at 30°C in 1.225 sp gr  $\text{H}_2\text{SO}_4$ , is shown for the binary system Pb-Sb (alloys No. 1 to 8) as a function of the Sb-concentration in Fig. 3. Constant current corrosion increases slightly with increasing Sb-concentration for Sb-concentrations above 1%, although the discharge time decreases with increasing Sb-concentration particularly at small discharge currents, as shown in Fig. 4. This decrease in discharge time

Table II. Analysis of lead alloys used for corrosion studies

Alloy No.	Per cent by weight									
	Sb	As	Sn	Cu	Bi	Ag	Fe	Ni	Ca	
1	0.0001	—	0.0001	0.0001	0.0005	0.0001	—	0.0001	—	
2	1.08	—	0.0001	0.003	0.05	0.0003	0.0005	0.0003	—	
3	2.16	0.008	0.0001	0.003	0.01	0.0004	0.0005	0.0003	—	
4	3.48	0.03	0.0001	0.003	0.018	0.0005	0.0005	0.0003	—	
5	5.76	0.025	0.0002	0.01	0.015	0.004	0.0005	0.0003	—	
6	7.26	0.015	0.0001	0.008	0.008	0.005	0.0005	0.0008	—	
7	8.76	0.015	0.0001	0.01	0.003	0.004	0.0005	0.001	—	
8	10.98	0.015	0.0001	0.005	0.008	0.002	0.0005	0.001	—	
9	0.0001	—	0.0001	0.0001	0.0005	0.0001	—	0.0001	0.0495	
10	0.0001	—	0.0001	0.0001	0.0005	0.0001	—	0.0001	0.0785	
11	5.70	0.48	0.22	0.003	0.020	0.009	0.0005	0.0005	—	
12	5.70	0.48	1.70	0.003	0.020	0.009	0.0005	0.0005	—	
13	5.94	0.48	0.27	0.005	0.022	0.112	0.0005	0.0005	—	
14	4.14	0.48	0.26	0.005	0.022	0.116	0.0005	0.0005	—	

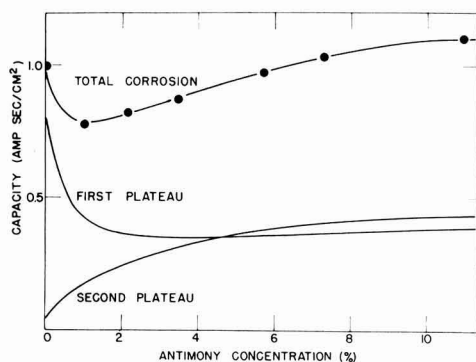


Fig. 3. Constant current corrosion of Pb-Sb alloys as a function of the Sb concentration. The amount of corrosion product is expressed in terms of equivalent capacity in amp sec/cm<sup>2</sup>.

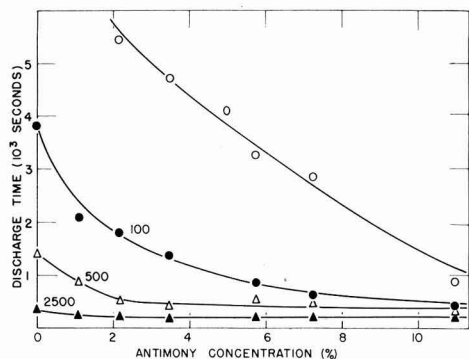


Fig. 4. Total discharge time at discharge currents of 0, 100, 500, 2500  $\mu\text{a}/\text{cm}^2$  of  $\text{PbO}_2$  layers formed at 3  $\text{ma}/\text{cm}^2$  for 20 hr in 4.53M  $\text{H}_2\text{SO}_4$  at 30°C.

with increasing Sb-concentration is due to an increased rate of self-discharge with increased Sb-concentration.

It is important to keep in mind that the corrosion values shown in Fig. 3 correspond to constant current conditions. A comparison at constant voltage would show a stronger increase of corrosion with increasing Sb-concentration. This can be shown from the curve of oxygen overvoltage vs. Sb-con-

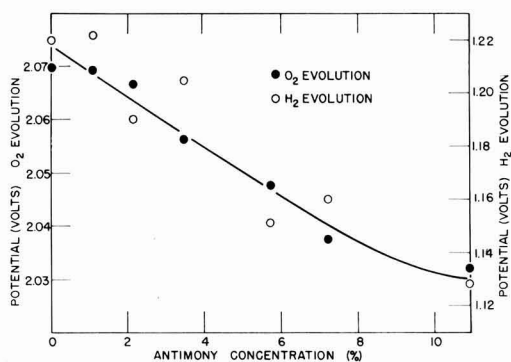


Fig. 5. Hydrogen overvoltage and oxygen overvoltage of Pb-Sb alloys at 3  $\text{ma}/\text{cm}^2$  in 4.53M  $\text{H}_2\text{SO}_4$ . Potentials are given vs. H<sub>2</sub>.

centration. The solid circles in Fig. 5 show oxygen overvoltage values at 3  $\text{ma}/\text{cm}^2$  after anodization for 20 hr at 30°C in  $\text{H}_2\text{SO}_4$ , sp gr 1.225. The sample containing 11% Sb corroded at a potential which was about 40 mv less positive than the potential of a pure lead sample at the same current density and after the same time period. Since corrosion increases with increasing electrode potential, more corrosion would have been observed for the 11% Sb alloy if it had been maintained at a potential identical to that of the pure lead sample.

It is interesting to compare the length of the various parts of the potential transient during discharge, as they vary with Sb-concentration and discharge current. The capacity corresponding to the time period from start of discharge to the first minimum is practically independent of the Sb-concentration. The electrode process prevailing during this time period is accompanied by a relatively small self-discharge rate. As will be discussed later, the potential-determining reaction during this period may be the removal of excess oxygen from the surface.

For a given alloy, the electrode process of the first plateau is accompanied by a higher rate of self-discharge than the electrode process corresponding to the second plateau. This is evident from the fact that the capacity during discharge decreases more

strongly with increasing discharge time for the first plateau than for the second plateau. The total available capacity as determined by extrapolation to zero discharge time has been obtained for both plateaus and has been plotted in Fig. 3. The total available capacity from the first plateau decreases with increasing Sb-concentration, whereas the amount of available capacity from the second plateau increases with increasing Sb-concentration. The rate of self-discharge of both plateaus increases with increasing Sb-concentration.

If the two plateaus are due to the presence of two different corrosion products, the product corresponding to the first plateau has a smaller discharge overvoltage (higher exchange current) and a higher rate of self-discharge than the product corresponding to the second plateau. From the fact that oxygen overvoltage and the relative amount of product corresponding to the first plateau decreases with increasing Sb-concentration, one cannot necessarily anticipate that this product has a higher oxygen overvoltage than the product corresponding to the second plateau. Figure 5 shows that hydrogen overvoltage decreases with increasing Sb-concentration. This decrease is due to free Sb metal which has a low hydrogen overvoltage. Polarization was started immediately after immersion of the microtomed metallic surface into the electrolyte in order to prevent adsorption of sulfate ions (1). Tafel slopes and  $i_0$  values for oxygen and hydrogen overvoltage on lead and lead alloys were reported earlier (1).

The total amount of corrosion after anodization for 20 hr at 3 ma/cm<sup>2</sup> as determined by the extrapolation technique is plotted for a series of alloys in Fig. 6. A good correlation exists between the corrosion figures and the overcharge life of batteries containing the various alloys in the positive grids, as determined by the standard SAE overcharge test. Figure 6 demonstrates that the SAE overcharge life test is a fair measure of anodic constant current corrosion.

In order to study the influence of the oxygen concentration in more detail, a large series of lead oxides with varying oxygen content were prepared by

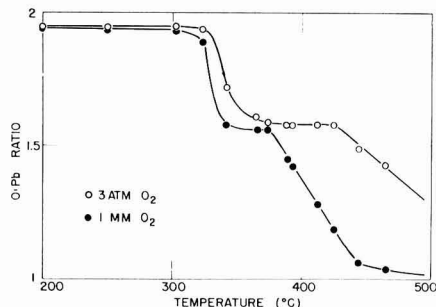


Fig. 7. Thermal decomposition of  $\beta\text{-PbO}_2$ . Oxygen content of the decomposition product as a function of temperature. Open circles refer to samples heated under an oxygen pressure of 3 atm; solid circles refer to samples heated at 1 mm oxygen pressure.

thermal decomposition of tetragonal ( $\beta$ ) $\text{PbO}_2$ . Figure 7 shows the oxygen content of samples which were heated for 3 hr at the indicated temperatures.

The decomposition temperature of  $\text{PbO}_2$  strongly depends on the oxygen pressure. A first loss of oxygen occurs at about 330°C. A compound with the composition  $\text{PbO}_{1.37}$  seems to form. This composition corresponds to a compound  $\text{Pb}_3\text{O}_9$ , or more accurately to  $\text{Pb}_3\text{O}_{11}$ . This composition has also been found by Holtermann and Lafitte (15). At higher temperatures apparently no equilibrium was established and the oxygen content decreased continuously down to  $\text{PbO}_{1.0}$ . Figure 8 shows the relative amounts (%) of the observed compounds in the heated samples as determined by x-ray analysis. Small samples of the prepared oxides were finely ground and mounted in collodion on a glass slide and x-rayed with a GE XRD-3 Geiger diffractometer. The  $\text{PbO}_2$  patterns had completely disappeared after removal of oxygen down to  $\text{PbO}_{1.6}$ . Instead, a new pattern became apparent. This new pattern corresponds to a crystalline compound with a pseudo-face-centered cubic, orthorhombic lattice. This compound has a composition  $\text{PbO}_x$  with  $x = 1.6$  to 1.4 (Fig. 8). X-ray analysis shows that it undergoes a change in the lattice parameters as the oxygen content in the sample decreases below  $\text{PbO}_{1.5}$ . It appears that this new crystalline compound has a variable oxygen content as indicated by the shift in the lattice constants. Samples with oxygen contents smaller than  $\text{PbO}_{1.1}$  showed the lines of  $\text{Pb}_3\text{O}_9$ , and finally  $\text{PbO}$  simultaneously with the patterns of  $\text{PbO}_x$ . Figure 8 also shows the colors of the produced oxide samples.

Electrodes were prepared by pressing the oxides in perforated lead foil. Electrode potentials of the prepared samples were measured in 1.225 sp gr  $\text{H}_2\text{SO}_4$  against a hydrogen electrode at 20°C in the same solution. The electrode potentials usually increased over a period of 1-4 hr for several millivolts and dropped then at a slowly increasing rate to less positive potentials. This drop in potential became increasingly faster with decreasing oxygen content in the sample. Figure 8 shows the maximum positive electrode potentials reached by the various samples.

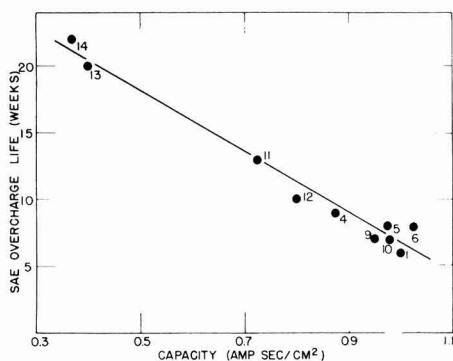


Fig. 6. Corrosion of various lead alloys vs. SAE overcharge life of batteries. The numbers identify various alloys from Table II. The ordinate gives the number of weeks a battery will perform on the SAE overcharge test. The abscissa gives the capacity of the corrosion film built up in 20 hr at 3 ma/cm<sup>2</sup> at 20°C in 4.53M  $\text{H}_2\text{SO}_4$ .

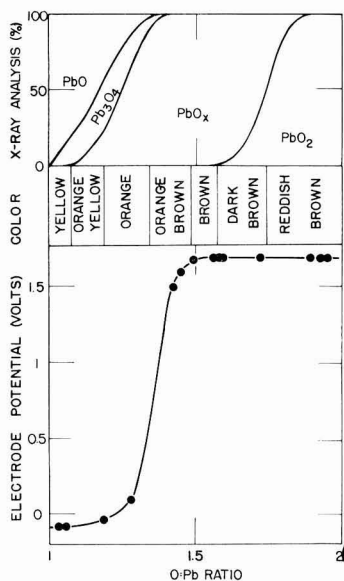


Fig. 8. Electrode potentials, colors, and x-ray analysis data of lead oxide samples with varying oxygen content produced by thermal decomposition of  $\beta$ - $\text{PbO}_2$ .

It is interesting to note that a sample with an oxygen content as low as  $\text{PbO}_{1.5}$ , which showed no sign of the presence of  $\text{PbO}$  in the x-ray pattern, still showed a  $\text{PbO}_2$  potential, although only for a relatively short time. It was also observed that the maximum potential measured on samples with low oxygen content  $\text{PbO}_{1.4}$  to  $\text{PbO}_{1.6}$  was 1.698 v vs.  $\text{H}_2$  or several millivolts higher than the value observed on pressed electrodes with untreated  $\beta$ - $\text{PbO}_2$  (1.692 v vs. No. 2).

In order to explain this phenomenon a sample of  $\text{PbO}_{1.45}$ , obtained by heating  $\beta$ - $\text{PbO}_2$  at 1 mm oxygen pressure at  $389^\circ\text{C}$ , was ground in a mortar and was placed in  $\text{H}_2\text{SO}_4$ , sp gr 1.225, for a period of 2 days. The sample was then carefully washed with hot and cold concentrated ammonium acetate solution in order to dissolve the lead sulfate. X-ray examination of the sample after this treatment showed that the  $\text{PbO}$  pattern which was originally observed had disappeared completely and had been replaced by a pattern of  $\alpha$ - $\text{PbO}_2$ . It can be concluded that the compound  $\text{PbO}_x$  undergoes a disproportionation in  $\text{H}_2\text{SO}_4$  into  $\text{PbSO}_4$  and  $\alpha$ - $\text{PbO}_2$ . The experiment described above suggests a simple method of preparation of  $\alpha$ - $\text{PbO}_2$  by heating  $\beta$ - $\text{PbO}_2$  in *vacuo* at  $390^\circ\text{C}$  and treating the product with  $\text{H}_2\text{SO}_4$ . The higher electrode potential of the heat treated sample is due to the fact that  $\alpha$ - $\text{PbO}_2$  has a higher electrode potential than  $\beta$ - $\text{PbO}_2$ . Potential measurements in  $\text{H}_2\text{SO}_4$  more dilute than sp gr 1.225 indicated that self-discharge strongly increased with decreasing acid concentration. The electrode potentials started to drop soon after immersion of the electrodes into the electrolyte.

Precise electrode potential measurements of  $\text{PbO}_2$  electrodes are very difficult because of passivation due to self-discharge. Electrode potentials of

$\alpha$ - $\text{PbO}_2$ , stable to  $\pm 1$  mv over a period of 12 hr, were obtained by pressing powdered  $\alpha$ - $\text{PbO}_2$  into perforated pure lead sheet. However, these electrodes suffered self-discharge and the potential dropped rapidly after 2 days. The highest potential for  $\alpha$ - $\text{PbO}_2$  obtained by this technique was  $1.707 \pm 0.001$  v. This potential was measured in  $\text{H}_2\text{SO}_4$ , sp gr 1.225, against a hydrogen electrode in the same solution at a temperature of  $25^\circ\text{C}$ .

Electrodeposition of  $\alpha$ - $\text{PbO}_2$  on a Pt wire according to the procedure described in the experimental section lead to a stable electrode potential of  $1.7085 \pm 0.0005$  v against a hydrogen electrode at  $31.8^\circ\text{C}$  in 4.40M  $\text{H}_2\text{SO}_4$ . This potential can be considered as a very reliable value for  $\alpha$ - $\text{PbO}_2$ .

Electrode potential measurements of  $\beta$ - $\text{PbO}_2$  using pressed lead dioxide in perforated lead strips were not stable over extended time periods and showed a high rate of self-discharge. Maximum potentials of  $1.692 \pm 0.002$  v were obtained in  $\text{H}_2\text{SO}_4$ , sp gr 1.225. This value might be too low because of self-discharge effects. Generally it was observed that electrodes showing a low electrode potential were only stable over short time periods.

Electrodeposited layers of  $\beta$ - $\text{PbO}_2$  on Pt wires showed electrode potentials of  $1.7015 \pm 0.0005$  in 4.40M  $\text{H}_2\text{SO}_4$  against a hydrogen electrode in a  $31.8^\circ\text{C}$  temperature bath. The potential was stable over extended time periods and can be considered to be a reliable value for  $\beta$ - $\text{PbO}_2$ . The electrode potential of the electrodeposited  $\alpha$ - $\text{PbO}_2$  electrode showed excellent stability. After anodization or partial discharge, the potential always returned to the stable value given above. After standing in  $\text{H}_2\text{SO}_4$  for periods of several weeks the potential was observed to drop. Microscopic examination revealed a surface layer of well-developed lead sulfate crystals. After stripping the sulfate layer with ammonium acetate the potential returned to its original value. After prolonged anodization of the electrodeposited  $\beta$ - $\text{PbO}_2$  electrode, the potential dropped very slowly on open circuit and did not show a distinct plateau at the reversible potential (1.7015 v). However, after stripping the sulfate layer from the electrode with ammonium acetate the potential returned to the reversible value. It is interesting to note that these results show a higher electrode potential for  $\alpha$ - $\text{PbO}_2$  than for  $\beta$ - $\text{PbO}_2$  under the conditions described above, the difference being 7 mv.

The electrode potential of  $1.7015 \pm 0.0005$  v for  $\beta$ - $\text{PbO}_2$  agrees with the data given by Hamer (21). If his values are extrapolated to 4.40M  $\text{H}_2\text{SO}_4$  and  $31.8^\circ\text{C}$ , a potential of 1.701 v is calculated.

The temperature dependence of the potential difference between  $\alpha$ - and  $\beta$ - $\text{PbO}_2$  will be studied in the future in order to determine entropy and enthalpy for the  $\beta$ - $\alpha$  transition. The reversibility for the couples  $\alpha$ - $\text{PbO}_2/\text{PbSO}_4$  and  $\beta$ - $\text{PbO}_2/\text{PbSO}_4$  will be determined by measuring discharge overvoltages.

Figure 9 shows oxygen overvoltage data at  $31.8^\circ\text{C}$  on the electrodeposited layers. Voltages given in Fig. 9 refer to the theoretical reversible oxygen electrode in the same electrolyte as the  $\text{PbO}_2$  electrode, namely 4.40M  $\text{H}_2\text{SO}_4$ . The reversible oxygen

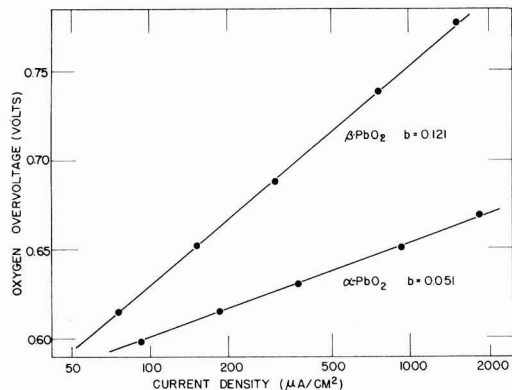


Fig. 9. Oxygen overvoltage data for  $\alpha$ - and  $\beta$ -PbO<sub>2</sub>.

potential in this electrolyte is 1.260 v vs. H<sub>2</sub>. The Tafel slope is 0.121 for  $\beta$ -PbO<sub>2</sub> and 0.051 for  $\alpha$ -PbO<sub>2</sub>, indicating a different mechanism for the oxygen evolution reaction on the two different PbO<sub>2</sub> modifications. These oxygen overvoltage measurements were performed in highly purified solutions. The high acid concentration prevented errors due to ohmic resistance. The curves shown were followed in both directions and were very reproducible.

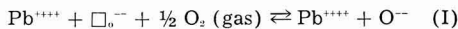
The "exchange currents"  $i_0$  for oxygen evolution calculated from the data shown in Fig. 9 are  $1.7 \cdot 10^{-10}$  amp/cm<sup>2</sup> for  $\alpha$ -PbO<sub>2</sub>, and  $6.2 \cdot 10^{-10}$  amp/cm<sup>2</sup> for  $\beta$ -PbO<sub>2</sub>. Results for  $\beta$ -PbO<sub>2</sub> are in close agreement with the overvoltage data for anodized lead samples (1), indicating that oxygen is evolved primarily on the  $\beta$ -PbO<sub>2</sub> sites.

### Discussion

The high electrical conductivity of PbO<sub>2</sub>, approaching that of metallic conductors, is caused by an apparent oxygen deficiency producing free electrons. It is possible that this is caused in part by OH groups replacing oxygen in the lattice. This viewpoint is supported by the observation that small amounts of water are produced on heating PbO<sub>2</sub> samples. However, this could be adsorbed water on the surface of the sample. Further work is anticipated on this problem.

The thermodynamically stable form of PbO<sub>2</sub> at room temperature apparently departs from its nominal composition. Chemical analysis shows a composition of PbO<sub>1.91</sub> to PbO<sub>1.96</sub>. During anodization under conditions of oxygen evolution the PbO<sub>2</sub> corrosion layers must contain a higher oxygen content than at equilibrium. It has been shown that oxygen overvoltage is related to the strength of the bond M-O or M-OH in the oxide (22). The strength of this bond decreases with increasing amount of oxygen in the surface. This decreased bond strength is the cause of the high oxygen overvoltage on PbO<sub>2</sub>. This interpretation of the overvoltage corresponds to the thermodynamic point of view, i.e., the formation of an intermediate oxide with a higher free energy. Thermodynamic considerations of electrochemical properties of oxide electrodes with varying oxygen content have been given by various authors (23-25).

From the thermodynamics of ordered mixed phases it is possible to derive how the number of oxygen defects in PbO<sub>2</sub> should depend on the oxygen pressure. Assuming that the stoichiometric oxygen deficiency is caused by vacancies, the formation of the thermodynamically stable lead dioxide (at room temperature and atmospheric pressure oxygen content PbO<sub>1.96</sub>) can be expressed by the equation:



where Pb<sup>4+</sup> are four valent lead ions and  $\square_{\text{o}}^{-}$  are the oxygen vacancies. If the chemical potential of each of the components of (I) is given by

$$\mu_i = \mu_i^{\circ} + RT \ln C_i \quad (\text{II})$$

(using to a first approximation concentrations instead of activities), the concentration of oxygen vacancies is given by

$$[\square_{\text{o}}^{-}] = \frac{1}{P_{\text{O}_2}^{1/2}} \exp\left(\frac{\Delta g}{Z RT}\right) \quad (\text{III})$$

where  $P_{\text{O}_2}$  is the oxygen gas pressure and  $\Delta g$  is the free enthalpy for reaction (I). Thus the oxygen vacancy concentration in PbO<sub>2</sub> is not very sensitive to O<sub>2</sub> pressure. Figure 7 shows that the oxygen content of PbO<sub>2</sub> and PbO<sub>x</sub> depends slightly on the oxygen pressure.

Removal of oxygen below a Pb/O ratio of 1.94 results in a decrease in conductivity due to the formation of a new, nonconductive compound. The decrease in conductivity is accompanied by an increase in the negative Hall coefficient, due to a decrease in the free electron concentration. The new compound has a variable oxygen content (PbO<sub>x</sub> with  $x = 1.4$  to 1.6), and the x-ray lattice parameters change with oxygen content. A high self-discharge rate and fast passivation are observed with electrodes consisting largely of this compound. The electrode potential for these electrodes is established by the presence of  $\alpha$ -PbO<sub>2</sub> produced by disproportionation of the original PbO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>. This  $\alpha$ -PbO<sub>2</sub> is rapidly passivated by the PbSO<sub>4</sub> formed during the reaction. The fact that  $\alpha$ -PbO<sub>2</sub> is formed is very interesting. Note that the lattice structures of  $\alpha$ -PbO<sub>2</sub> and PbO<sub>x</sub> are quite similar. Both compounds form an orthorhombic lattice; PbO<sub>x</sub> is a distorted  $\alpha$ -PbO<sub>2</sub> lattice. Thermal decomposition of  $\beta$ -PbO<sub>2</sub> probably starts with a transition to an  $\alpha$ -PbO<sub>2</sub> lattice which then loses oxygen. It seems that oxygen might be removed from  $\alpha$ -PbO<sub>2</sub> down to an oxygen content of PbO<sub>1.4</sub> without a drastic phase change.

According to Bode and Voss (3) the tetragonal ( $\beta$ )PbO<sub>2</sub> has a higher electrode potential than the orthorhombic ( $\alpha$ )PbO<sub>2</sub>. Our measurements definitely show a higher electrode potential for  $\alpha$ -PbO<sub>2</sub>. Discharge overvoltages for  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> are unknown at the present time, however, and further proof seems necessary to decide definitely if the first plateau corresponds to the discharge of  $\alpha$ -PbO<sub>2</sub> and the second plateau to the discharge of  $\beta$ -PbO<sub>2</sub>. Since the first plateau shows a higher self-discharge rate, one could anticipate that the material corresponding

to this plateau is in more immediate contact with the underlying metal.

The mechanism of formation of the two oxides must be different.  $\alpha$ - $\text{PbO}_2$  is formed in alkaline solution by anodic deposition on inert electrodes and in  $\text{H}_2\text{SO}_4$  solution by direct oxidation of the metallic lead.  $\beta$ - $\text{PbO}_2$  is formed in acid solution by anodic deposition. It is possible that in the formation of  $\alpha$ - $\text{PbO}_2$  an intermediate complex of tetravalent lead with (OH) groups is formed, whereas formation of  $\beta$ - $\text{PbO}_2$  proceeds over a complex of tetravalent lead with other groups such as  $\text{SO}_4$ . The size of the participating group probably determines which oxide modification is formed. The presence of any nuclei of either modification at the beginning of formation can also have an influence (3).

It has been observed that formation of positive storage battery plates begins at the surface of the grid members. This is to be expected since the active material of an unformed plate has extremely low conductivity. As formation progresses,  $\text{H}_2\text{SO}_4$  is liberated at the formation boundary (the interior of the plates remains basic even after prolonged immersion of the plates in  $\text{H}_2\text{SO}_4$ ) and becomes available for sulfation of  $\text{PbO}$  and basic lead sulfates. In plates made from sublimed litharge or in thoroughly conditioned plates (no free lead) formation of  $\alpha$ - $\text{PbO}_2$  is not observed. It is to be concluded that the formation of  $\alpha$ - $\text{PbO}_2$  in the interior of storage battery plates is probably not nucleated by  $\text{PbO}$  but rather by the direct oxidation of metallic lead particles. That further production of  $\alpha$ - $\text{PbO}_2$  is induced by these nuclei is evident from the fact that even after prolonged periods of cycling  $\alpha$ - $\text{PbO}_2$  is found in the plates.

The oxygen overvoltage data on  $\alpha$ - and  $\beta$ - $\text{PbO}_2$  shown in Fig. 9 indicates that a different mechanism takes place on the two oxides.  $\alpha$ - $\text{PbO}_2$  shows a Tafel slope of 0.05, like a large series of electrodes in alkaline solution. This slope corresponds to a process where two electronic charges are involved when the rate-determining reaction occurs once (22).  $\beta$ - $\text{PbO}_2$  has a Tafel slope of 0.12 indicating that only one electronic charge is involved in the rate-determining reaction. Therefore,  $\alpha$ - $\text{PbO}_2$  in  $\text{H}_2\text{SO}_4$  behaves like an oxygen-evolving electrode in alkaline solution, where  $\beta$ - $\text{PbO}_2$  shows the normal Tafel slope of 0.12 like most of the other electrode materials in acid solution. This difference is apparently due to a difference in the lattice spacing of two oxides,  $\alpha$ - $\text{PbO}_2$  having the smaller spacing.

Anodic corrosion in the potential region where oxygen is evolved increases strongly with the electrode potential (26). Therefore, electrodes with a low oxygen overvoltage should withstand corrosion better under constant current conditions. Certain additives to the electrolyte such as  $\text{Co}^{2+}$  ions can reduce oxygen overvoltage and anodic corrosion. Oxygen overvoltage is, of course, not the only factor determining the rate of anodic corrosion. In particular, the nature of the electrode material has a strong influence (27). The fact that constant current corrosion increases with increasing Sb concentration for Pb-Sb alloys has also been described by Krivolapova and Kabanov (28).

Oxygen overvoltage and anodic corrosion are influenced by the amount of  $\text{SO}_4^{2-}$  ions adsorbed on the electrode surface. Since in all of these corrosion experiments the anodizing current was kept at 3 ma/cm<sup>2</sup> the electrode potential during the period of anodic corrosion was considerably higher than the zero-charge potential, according to Fig. 5, always above 2 v. At this potential the electrode surface is covered with specifically adsorbed anions (29). The zero charge potential on a lead dioxide electrode has been determined at 1.80 v by Kabanov, et al. (30).

The relative ratio of the amounts of  $\alpha$ - and  $\beta$ - $\text{PbO}_2$  in the corrosion layer changes with the time of anodization. X-ray examination shows that as anodization progresses the  $\alpha$ - $\text{PbO}_2$  pattern becomes more and more pronounced. At the same time oxygen overvoltage decreases.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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## A Contribution to the Theory of Stress Corrosion in Al-4% Cu Alloys

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### ABSTRACT

Stress cracking of Al-4% Cu alloys was found to be greatly influenced by exposed area of the specimen (small areas showed long time-to-failure). Experiments with grain boundary-grain center couples showed that neither potentials nor couple current were influenced sufficiently by stress to account for the acceleration of failure by stress. At constant applied anodic current, however, stress was found to direct the attack perpendicular to applied stress. The theory of Champion and Logan is substantiated. A refinement is suggested in which the last stages of failure result from direct and rapid local attack on film-free metal.

Many theories have been proposed to account for the conjoint action of stress and corrosion in destroying metals and alloys. These have been reviewed adequately in the corrosion literature (1-4). One notes in examining these theories that there is general agreement on the mechanism of the beginning of the attack; there is lack of agreement, however, centered around the role of the stress in the mechanism of failure. It was the purpose of this study to shed some light on the mechanism of the stress effect.

The general approach was first to show that a susceptible alloy, 2024, exhibited an area effect (the dependence of the time to stress-corrosion failure on the amount of area exposed to the corrodent). It was felt that the establishment of this property would give information regarding the nature of the corroding cell. The phenomenon has been noted in other alloys (5-7). The second phase of the study was to make certain electrochemical measurements on cells in which the anodes were separated from the cathodes and to determine the effect on these measurements of certain variables: stress, H<sub>2</sub>O<sub>2</sub> concentration, relative areas, etc. A mechanism is proposed to account for the results obtained in the study; it is essentially that suggested by Champion (8) and Logan (9), with some refinement.

### Area Effect in 2024 Al

*Apparatus and materials.*—Four-point loading was selected as the means for stressing  $\frac{3}{4}$  in. x 3% in. x 0.035 in. (1.9 cm x 8.6 cm x 0.089 cm) speci-

mens. This type of loading places the surface of the specimen between the inner supports in a state of uniform stress (10). The method is simple in load application and calculation of stress.

Figure 1 shows the test fixture, constructed almost entirely of Lucite. It consists of two inner knife-

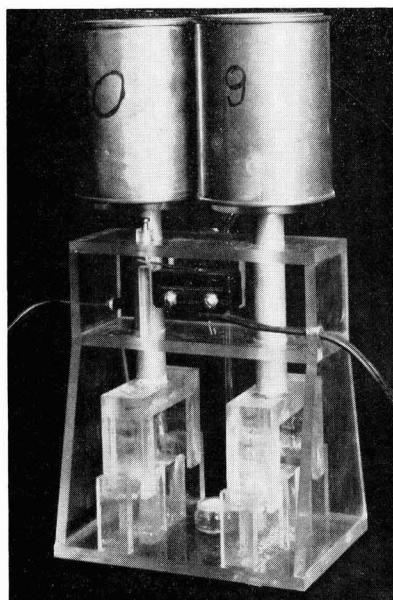


Fig. 1. Stress corrosion fixture

Table I. Compositions of alloys

	Cu	Mg	Mn	Fe	Si	Al
H. P. Al.	0.000	0.001	—	0.001	0.002	Bal.
Al-4 % Cu	4.07	0.001	<0.001	0.001	0.006	Bal.
2024	4.70	1.20	0.94	0.16	0.08	Bal.

edge supports cemented to the base of the fixture 1 in. (2.54 cm) apart. The outer knife-edges, 3 in. apart (7.62 cm), are inverted and fixed to the weight stage by a post. These apply the load to the specimen. The switch, actuated by the weight stage, shuts off a timer when the specimen deflection increases by a certain increment due to corrosion. These increments were either  $\frac{1}{4}$  in. (0.63 cm) or  $\frac{1}{8}$  in. (0.31 cm) and were defined as "failure" for the purpose of this work. Loads were calculated from the equation

$$S = \frac{3Lx}{bd^2}$$

where  $S$  is the stress in the outer fibers,  $L$  is the load,  $x$  is the distance between inner and outer supports (1 in. with the fixture shown),  $b$  is the specimen width, and  $d$  is the specimen thickness.

The fixtures (each accommodating two specimens) were placed in individual glass troughs when a variable in composition of corrodent was being observed, or in a long Lucite trough when variables other than the medium were being studied. When using the long trough, the solution was circulated from a 12-gal reservoir which was kept at constant temperature.

Commercial 2024 alloy was used in most of the experiments reported in this work; however, a few experiments involved high-purity aluminum and a high-purity aluminum-copper alloy. The compositions of these are shown in Table I. The high-purity alloys were furnished by Aluminum Research Laboratory, Aluminum Company of America; the H. P. Al as 0.064 in. sheet, and the Al-4% Cu as  $1\frac{1}{2}$  in. forged bars, which were first hot and then cold rolled to 0.035 in. strip. The 2024 alloy was purchased as 0.032 in. annealed sheet.

Experiments were conducted to determine the correlation, if any, between the total area exposed on a stressed specimen and the time to failure. Sensitized specimens were masked completely on the bottom surfaces; the top surfaces were partially masked to expose certain areas. The masking material was a commercial plating stop-off compound. Quadruplicate specimens were used for each area. These specimens were stressed in the fixtures to 80% yield strength (Y.S. was 42,500 psi) and placed in the trough with 53 g/l NaCl + 2.5 g/l  $H_2O_2$  at room temperature (72°F). The results of the run are shown in Fig. 2 (upper curve) and indicate a definite correlation between area exposed and time to failure.

Failure mechanisms based on mechanical considerations only have been proposed to explain area effect. To show that the effect is electrochemical in

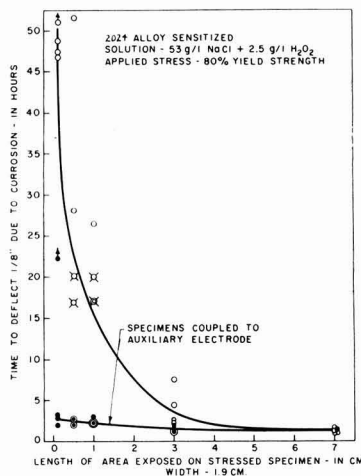


Fig. 2. Area effect for 2024 alloy and the influence of an auxiliary electrode.

nature the above experiment was conducted in the same manner, but with each specimen electrically connected to an unstressed immersed specimen. The unstressed specimen was masked to expose an area such that the total area (stressed plus unstressed) was 13.3 cm<sup>2</sup> (equal to the largest specimen of the previous run, 7 x 1.9 cm). The results of this experiment are shown as the lower curve in Fig. 2. It should be noted that the area effect is no longer in evidence, and all specimens failed in essentially the same time, namely, that of the 7 x 1.9 cm stressed and uncoupled specimen.

It appears from the results shown in Fig. 2 that time to failure is a function of the total area exposed (stressed plus unstressed). This would be difficult to explain purely on mechanical grounds. Electrochemically, the results are a confirmation of the fact that the corroding cell is under cathodic control. The total attack is strongly dependent on the total cathodic area, stressed or unstressed; that is, where large cathodic areas are exposed, attack is great, where small cathodic areas are exposed, attack is less. Since grain centers constitute the bulk of specimen surface, the cathodic area can be taken as being roughly equal to the total area.

#### Effect of Hydrogen Peroxide on Time to Failure

Early in the program it was found that the hydrogen peroxide concentration fell rapidly during a test. Investigation showed that the peroxide decomposed at a rate proportional to specimen size when 2024 was involved, but that pure aluminum caused no detectable peroxide loss. It was quickly established that the peroxide decomposition was catalyzed by cupric ion, produced by the corrosion of the 2024. This is a well-known effect sometimes neglected in corrosion testing.

The dependence of the time to failure on peroxide concentration was determined. Sensitized 2024 specimens, masked to expose 7 x 1.9 cm, were stressed to 80% yield strength and each fixture (carrying duplicate specimens) was placed in a

<sup>1</sup> Sensitizing treatment for 2024 specimens consisted of holding specimens at 350°F for 6 hr after solution treatment (910°-930°F: cold water quenched).



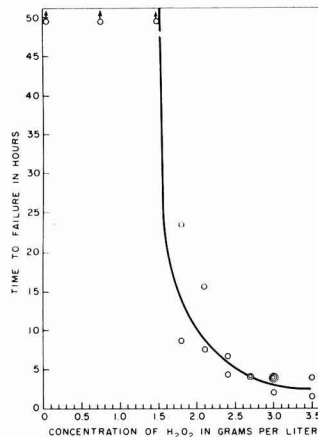


Fig. 3. Effect of  $H_2O_2$  concentration on time to failure in 53 g/l NaCl. Specimens were 2024 alloy, quenched and aged at 350°F for 6 hr, stressed to 80% yield strength.

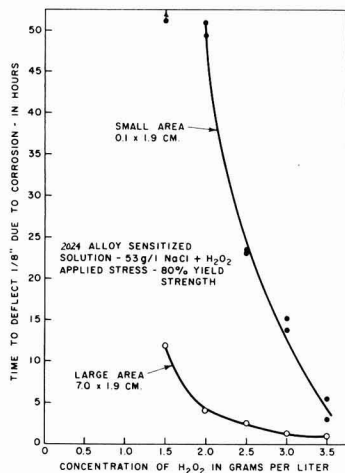


Fig. 4. Influence of  $H_2O_2$  concentration on area effect

separate glass trough. Each trough was filled with 53 g/l NaCl, with varying concentrations of  $H_2O_2$ . The results of the experiment are shown in Fig. 3. Great sensitivity to the peroxide concentration in the range 1.5-3.0 g/l is noted. Above this critical range, specimens failed in a few hours; below about 1.5 g/l, the failure time increased rapidly.

The data illustrate the importance of good peroxide concentration control during the course of a stress corrosion test, a factor which may not have been fully recognized in earlier work.

The fact that the time to failure is sensitive to peroxide concentration (a cathodic depolarizer) is further verification that the cell is under cathodic control.

Runs were made using oxygen gas instead of peroxide in an effort to stabilize the depolarizer concentration. The gas dispenser can be seen in Fig. 1. No failure was noted after exposure of 337 hr (14 days). This result is consistent with other experience (11) in which oxygen saturation has been

found equivalent to about 0.02 g/l  $H_2O_2$ . Referring to Fig. 3 and 4, it is seen that this level is well below that causing rapid failure. The use of peroxide was therefore continued.

#### Influence of $H_2O_2$ on Area Effect

Having shown the critical dependence of time to failure on peroxide concentration, the area effect was reinvestigated as a function of peroxide concentration. Large (7.0 x 1.9 cm) and small (0.1 x 1.9 cm) sensitized specimens were exposed to different concentrations of peroxide, stressed at 80% yield strength. Figure 4 shows the results of these runs. As might be expected, the area effect became more pronounced as the depolarizer concentration was decreased. Due to the long times to failure, the region below 1.5 g/l  $H_2O_2$  was not investigated. Runs identical with those shown in Fig. 2, substituting 2.0 g/l  $H_2O_2$ , were made; the largest area (7.0 x 1.9 cm) failed in a few hours; the smaller areas had not failed in 65 hr (confirming the data of Fig. 4).

#### Grain Boundary-Grain Center Cell Study

Mears, Brown, and Dix studied the area effect for a magnesium base-6Al alloy (5). They concluded that cracking time was controlled by the total available cathodic activity. The area effect for 2024 described above was approached from the same point of view. Studies were made of potentials and currents involved in the corrosion process. These were followed by a set of experiments designed to clarify the role of stress in the mechanism of failure.

*Specimen preparation.*—The example of the classical experiments of Dix and associates (12) was followed in this phase of the study. Grain boundaries and grain centers were masked on identical specimens of copper-aluminum binary alloy (composition shown in Table I).

The high purity of the alloy permitted easy growth of large grains by the strain-anneal method. Final grain size was in the range  $\frac{1}{2}$ -1 cm<sup>2</sup>. Following grain growth, specimens were given a caustic pickle and solution treated. Anode specimens were sensitized following solution treatment; cathode specimens were used in the solution-treated condition. Following heat treatment, all specimens were etched in Flick's reagent<sup>2</sup> and then masked.

Masking compound was made by thinning Duco<sup>3</sup> cement with Cellosolve<sup>1</sup> and colored with fuchsin dye. Masking of grain boundary specimens was performed under a low power microscope (30X) so that exposed grain boundary zones could be held to 0.5 mm. Since the grain center specimens were used in the solution-treated condition, it was felt that the entire surface of the specimen would be sufficiently homogeneous to obviate the need for masking the grain boundary zones. Electrical connections were made by peening the bared end of 30 gauge Teflon-covered wire into a slit in the specimen; the entire joint was then covered by stop-off.

<sup>2</sup> HCl (conc.) 15 ml, HF (48%) 10 ml, H<sub>2</sub>O 90 ml.

<sup>3</sup> E. I. du Pont de Nemours & Co.

<sup>1</sup> Carbide & Carbon Chemical Co.

*Effect of Hydrogen Peroxide, Anode Area, and Cathode Area on Current and Potential*

Pairs of specimens prepared as described above (anode and a cathode) were exposed unstressed to media containing various peroxide concentrations plus 53 g/l NaCl, a fresh pair of specimens for each peroxide concentration. Open-circuit potentials of grain boundary and grain center specimens were measured and then shorted through an electronic self-balancing zero-resistance ammeter (13). The current was observed until it reached a steady value (about 1 min). Data derived from these experiments are shown in Fig. 5 and 6.

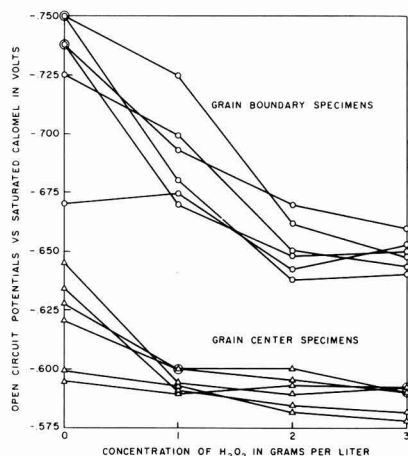


Fig. 5. Open-circuit potentials of grain center and grain boundary specimens in solutions containing 53 g/l NaCl and various levels of  $H_2O_2$ .

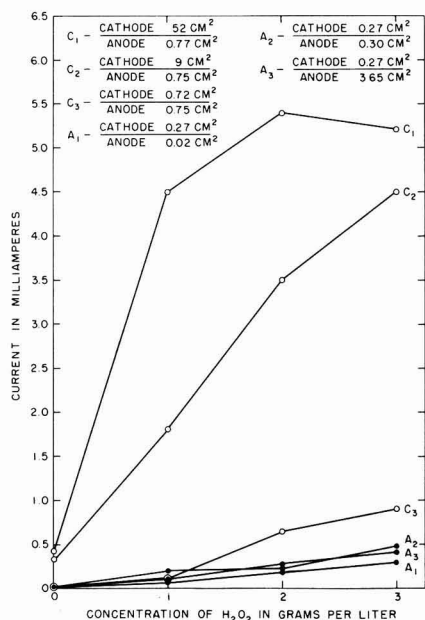


Fig. 6. Current flow between various areas of anode and cathode specimens at different  $H_2O_2$  concentrations and 53 g/l NaCl.

Several observations may be made from the data shown in Fig. 5. It is to be noted that in all cases the grain boundary specimens showed open-circuit voltages more anodic than those of the grain centers. This indicates clearly that grain boundaries are anodic to grain centers at all concentrations of peroxide.

It is interesting to note that the anode curves shift in the cathodic direction with increasing peroxide concentration. This shift might be caused by a depolarization of the local cathodes on the anode specimen (the 0.5 mm exposed width would include considerable cathode area); it might also be caused by a passivation of the anode regions by the oxidizing peroxide. The cathode curves show a much less marked change in open-circuit potential with increasing peroxide. The spread of the potentials at zero peroxide for both anodes and cathodes is characteristic of aluminum in straight salt solutions.

Figure 6 shows the current flowing between various areas of anodes and cathodes at different peroxide concentrations. The  $C_1$ ,  $C_2$ , and  $C_3$  curves vary in cathode area (with fixed anode area); the  $A_1$ ,  $A_2$ , and  $A_3$  curves vary in anode area (with fixed cathode area). It should be noted that in all cases the couples are under cathodic control. Thus, with actual corroding specimens a greater total current (hence more rapid penetration) would be expected for large area specimens than for small area specimens, in agreement with the experimental data of Fig. 2.

*Effect of Peroxide Concentration on Polarization of Anodes and Cathodes*

It has been shown that the magnitude of the couple current in the above cells is strongly dependent on the concentration of the cathodic depolarizer, hydrogen peroxide. To assess this effect quantitatively, polarization curves ( $E$  vs.  $I$ ) were determined for the anode and cathode specimens prepared as described above, using three different peroxide concentrations, 0, 1.5, and 3.0 g/l  $H_2O_2$ .

Potential measurements were made using a saturated calomel reference cell equipped with a small tubulus. The opening was placed just above the

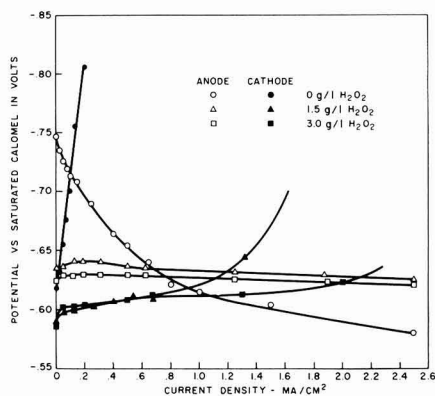


Fig. 7. Potential vs. current curves for anode and cathode specimens for various  $H_2O_2$  concentrations with 53 g/l NaCl (Cu-Al binary alloy).

specimen, held in the stress jig but not stressed. Current was obtained from a voltage divider connected across a 6-v battery. Grain boundary specimens were polarized anodically and grain center specimens cathodically. The inert electrode was a platinum screen.

The polarization curves are shown in Fig. 7. The depolarization effect of peroxide is seen to be great in the case of the cathode.

The anode open-circuit potentials show a shift in the cathodic direction with increasing peroxide and, surprisingly, anode polarization is found to be less at the higher peroxide levels.

Thus, the corrosion process is stimulated by peroxide, acting chiefly as a cathodic depolarizer. This effect is most pronounced in the low concentration range (0-1.5 g/l).

#### Effect of Stress on Polarization of Anodes and Cathodes at Varying Peroxide Concentrations

Having established the polarization curves for unstressed anodes and cathodes, the question then arises as to the effect of stress on these curves and in turn on the couple current. The experiments used to obtain the curves in Fig. 7 were repeated; in this case, however, both grain boundary and grain center specimens were stressed to 80% yield strength. The results of these runs are shown in Fig. 8 for 0, 1.5, and 3.0 g/l  $H_2O_2$ .

The difficulty of obtaining accurate data on polarization curves of this type limits the extent to which they can be interpreted quantitatively. It is possible, however, to reach certain general conclusions from the data Fig. 8: (a) anodic activity ap-

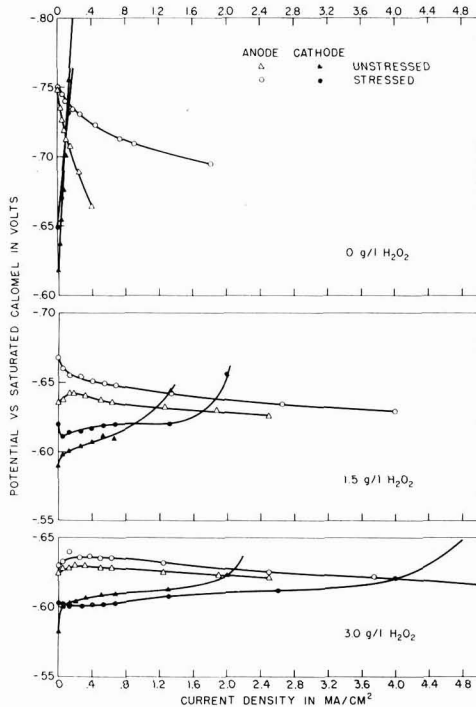


Fig. 8. Effect of stress on the curves of Fig. 7

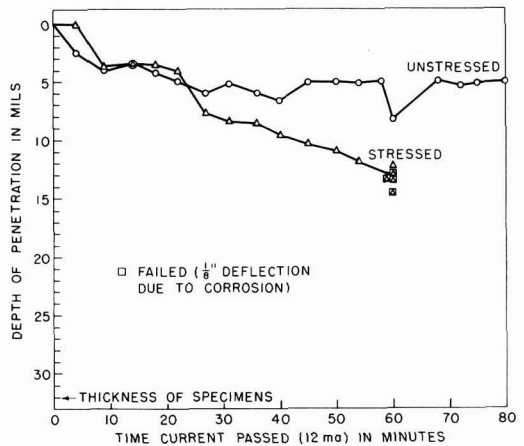


Fig. 9. Effect of stress on rate of penetration of 2024 specimens by applied anodic current (53 g/l NaCl).

pears to be increased consistently by stress at all peroxide levels; the cathodic effect is not clear cut; (b) the increase in anodic activity produced by stress does not appear to be sufficient to account for the very marked effect of stress on the penetration rate in actual stress corrosion.

#### Effect of Stress on Rate of Penetration

The data presented thus far have shown that the stress does not increase the corrosion current sufficiently to account for the marked acceleration of failure. To further clarify the role of stress, the rate of penetration was measured.

Specimens of sensitized 2024 alloy masked to expose  $0.3 \times 1.9$  cm areas were made anodic in a solution of 53 g/l NaCl. The anodic current was held constant at 12 ma, and both stressed and unstressed specimens were exposed. Specimens were removed after certain times of exposure, and cross sections were examined metallographically to determine the depth of penetration. The results are shown in Fig. 9.

The curves for both stressed and unstressed specimens follow the same course up to 25 min, at which point the unstressed specimens suffer no further penetration, while the stressed specimens undergo continued penetration, reaching failure at about 60 min. It should be remembered that "failure" is defined as an increase in deflection—due to cor-

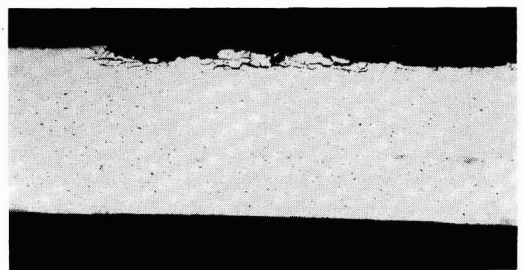


Fig. 10. Sensitized unstressed 2024 specimen after exposure to 53 g/l NaCl with 12 ma anodic current for 54 min.

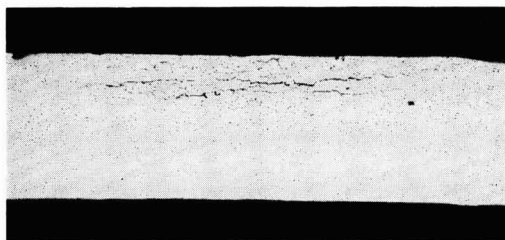


Fig. 11. Sensitized, stressed 2024 specimen after exposure to 53 g/l NaCl with 12 ma anodic current for 54 min.

rosion—of  $\frac{1}{8}$  in. This observation has been noted by others (6, 7, 14), viz, the stress is important only in the latter stages of exposure.

Photomicrographs of the unstressed and stressed specimens after 54-min exposure (just before failure of the stressed specimen) are shown in Fig. 10 and 11, respectively. These microstructures show the greater penetration for the stressed specimen and, although not too clearly, the greater total attack in the case of the stressed specimen. Both stressed and unstressed specimens were exposed to the same (externally applied) current for the same time, but it was observed that hydrogen was evolved from the stressed specimen only. This indicates that local action was initiated by the stress and accounts for the greater total attack of the stressed specimen.

Some workers (1, 4, 5) feel that this local action is induced by the creation of essentially film-free metal in the base of the crack, which, because of its greatly increased anodic activity, increases the couple current between the cathodic specimen surface (or crack walls) and the base of the crack. It seems more likely, however, that, if film-free metal is produced in the crack, the nature and site of the cathodic action are altered to include reduction of  $H^+$  to  $H$  in the crack apex, as well as the reduction of peroxide on the crevice walls. This is discussed further below.

A similar experiment was performed using the high-purity binary alloy. The penetration-time curve for a stressed specimen is shown in Fig. 12. It should be noted that complete penetration occurred in 5 min as compared to 60 min for failure of stressed 2024 specimen. Figure 13 shows the unetched microstructure of the binary specimen just before complete penetration.

The differences in cracking time and in appearance between the 2024 and the high-purity binary alloy are possibly due to differences in grain size and grain boundary purity.

### Discussion

The above experiments demonstrate that the stress corrosion cracking of Al-4% Cu type of alloys is dependent on the area exposed to the corrosion medium. This area effect is electrochemical in nature and has been related to the total cathodic activity of the corrosion cell. Furthermore, hydrogen peroxide has a great influence on the time to failure of these alloys and at high concentrations tends to minimize the effect of area.

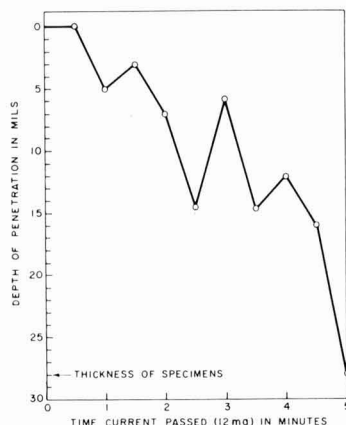


Fig. 12. Penetration of stressed Al-4% Cu binary alloy by applied anodic current.



Fig. 13. Stressed Al-4% Cu binary alloy after exposure to 53 g/l NaCl with 12 ma anodic current for  $4\frac{1}{2}$  min.

Experiments with partially masked specimens showed that the grain boundaries of sensitized alloy are anodic to the grain centers at all concentrations of peroxide tested. It was also shown that the grain boundary/grain center cell is under cathodic control. Hydrogen peroxide functioned as an active cathodic depolarizer, but had little effect on anodic action. Saturation by molecular oxygen was found to be far less effective in depolarization than peroxide.

Some increase in anodic activity was observed when stress was applied, but the effect was relatively small compared to the cathodic effect produced by peroxide. It appeared that the stress exerted no influence on the rate of penetration of the specimen until about half the total time-to-failure had elapsed.

The course of attack of a stressed specimen might be as follows: when first immersed in the medium, a cell is set up between the grain centers and grain boundaries of the piece. The magnitude of the current flow depends on the area of cathode, its composition, composition of the anode, and the composition of the medium. As the current flows, the grain boundaries are oxidized preferentially, resulting in the formation of trenches. As the trenches deepen with time and their apices become sharper, the stress increases due to notch effect. When the yield strength of the grain boundary (depleted zone) is reached, the specimen rapidly fails.

It is the mechanism of the last stage of the cracking process (when the effect of stress is noted) that is felt to be inadequate in present theories. Most of

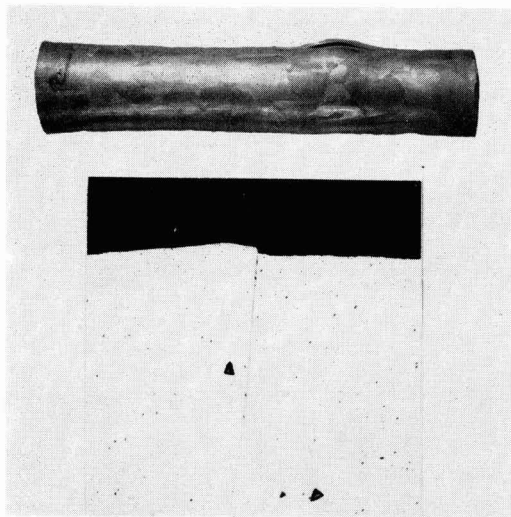


Fig. 14. Tube of Al-4% Cu alloy, quenched and sensitized, subjected to hydraulic internal pressure to bursting. Above, full size photograph before reduction for publication. Note greater deformation in grain boundaries than in grain centers. Below, photomicrograph of a grain boundary near the failure zone. Note grain boundary deformation. Etchant: 20 parts HNO<sub>3</sub>, 20 parts HF, 60 parts glycerin. Magnification 150X before reduction for publication.

these postulate an increase in grain boundary-grain center couple current, due to film rupture or metal rupture which expose fresh unfiled metal.

In the present work, however, the effect of stress on the anodic polarization curves for grain boundary zones does not appear sufficiently great to support the above mechanism. An alternative mechanism is suggested which appears to fit better the observed effect of stress on cracking rate.

Champion (8) and Logan (9) suggest that when the yield strength of the grain boundary material is exceeded (by the stress concentration effect), plastic flow begins which ruptures the film. This suggestion is reasonable since it has been demonstrated adequately elsewhere that in sensitized alloys the grain boundary zones are depleted in copper and magnesium, and, further, that alloys with lower copper contents show lower yield strength and higher ductility than those with the nominal 2024 composition (15). Evidence of this fact is shown in Fig. 14, where grain boundary flow<sup>5</sup> is obvious.

When the 2024 specimen reaches the stage where the grain boundaries begin to flow, the film will be broken, thus exposing fresh metal. There will be a constant tendency to refile this naked metal. If the flow is slow (low stress), the metal will remain relatively inactive due to rapid healing of its oxide film. If the deformation is rapid, however, the medium will be unable to maintain the film, the grain boundary metal will go into solution with evolution of hydrogen, and the crack will propagate rapidly.

Thus, in effect, the propagation of a crack consists of a continuous reaction in which extremely

<sup>5</sup> Grain boundary flow in this study refers to flow of the depleted metal adjacent to the grain boundary.

active aluminum is exposed through film rupture and oxidized by direct reaction with the corrosion medium. This occurs only after electrochemical attack has proceeded to the point where the notch effect has increased the stress level in the grain boundary zones beyond the yield strength of the depleted zone. When the strain rate in this region is sufficient to prevent film maintenance, the extremely rapid (almost explosive) penetration occurs. It is felt that hydrogen evolution largely replaces peroxide reduction as the cathodic reaction during this phase of cracking.

Summarizing then, penetration by stress-corrosion occurs by two mechanisms; first, a galvanic dissolution of the depleted grain boundaries in which the rate depends on the area and composition of the anodes and cathodes, and second, a hydrogen evolution type of dissolution of the depleted grain boundary beginning when the strain rate of the grain boundary is too great to permit refileing, this stage being independent of cathodic area. The triggering of the second mechanism, whose rate is much faster than the first, depends on the orientation of grain boundaries relative to the direction of stress application and the sharpness of the grain boundary trench apices.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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## Grain Growth and Flecking in Electroplated Copper Caused by Cyclic Stress

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### ABSTRACT

Microscopic investigation has been made on microflecks produced by cyclic stress on the surface of electroplated copper. Examination of the surface and cross section of the plated copper after stressing reveals that some of the micrograins constituting the plated metal grow to a considerable size.

It is ascertained that the flecks are always produced when grain growth occurs in the plated metal and can never be produced when grain growth does not occur.

The electroplating method originated by one of the present authors proved useful for an accurate determination of the surface stress (1). The method is based on the sensitive color change on the surface of a copper-plated specimen made by microflecks produced by cyclic stress. There is little information available on the detailed process as to how flecks are produced by cyclic stress. For an improvement of the electroplating method, however, it is most essential that the mechanism of producing the flecks be found.

### Experimental

*Conditions for deposition.*—Specimens used in this experiment are conical rods of carbon steel. They are prepared by treatment in dilute  $H_2SO_4$  and caustic alkali after a fine polishing and then receive a preliminary deposit of copper from a cyanide copper vat.

The conditions for deposition are as follows:

Solution: $CuSO_4 \cdot 5H_2O$	250 g
$H_2SO_4$	80 g
$H_2O$	11

Current density: 3 amp/dm<sup>2</sup>; temperature: 23°C; Bath voltage: 0.5 v; duration of deposition: 15 min.

*Microscopic examination.*—Examining the surface of a specimen undergoing color change, as shown in Fig. 1, by microscope, microgroups of fine flaws mixed among the flecks are found and these flaws run almost parallel to the planes of maximum shear (2).<sup>1</sup> Figure 2 is a micrograph of the flaws produced on the surface of a specimen by rotary bending test; Fig. 3 is a micrograph of flaws produced by torsion test; the arrows indicate the axial direction of the specimens. Close examination shows that a fleck

is not a mass of flaws and that the group of flaws is not always situated exactly in a fleck.

When a specimen is exposed to a flow of hydrogen gas at 300°C during the comparatively short interval of 5 min, the flecks disappear, leaving only a trace, while the groups of flaws suffer no change whatever. Figure 4 is an original fleck and Fig. 5 its trace deoxidized by a flow of hydrogen gas. When a specimen is exposed to a flow of carbon dioxide at the same temperature, the flecks suffer no change. This indicates that the flecks are not produced by a mechanical change on the surface as are the flaws, but that they are produced by a chemical change occurring in the surface layer of the plated metal.

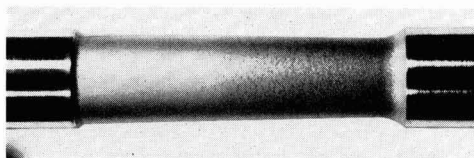


Fig. 1. Test piece partially changed in color

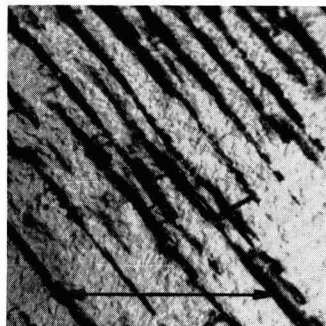


Fig. 2. Flaws, rotary bending (1000X)

<sup>1</sup> Similar flaws are also found when brass is used as the ground metal instead of steel.

Being only in the surface, the flecks are readily removed by slight electropolishing.

*Grain growth in plated metal.*—Microscopic examination of the surface and cross section of a specimen having been color-changed, electropolished, and etched, reveals the nature of grain growth in the plated metal. Figures 6 and 7 are cross sections of specimens showing the initial status of grain growth, namely, the number of repetitions of cyclic stress has been below one million, the flecks have not as yet appeared, and the surface of the specimen has not changed in color, while the physical change as shown in the figures is already found in the plated metal.

With sufficient increase in the number of repetitions of cyclic stress, the grains grow up to the sur-

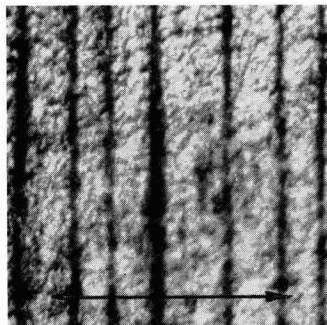


Fig. 3. Flaws, torsion (1000X)



Fig. 4. Fleck, before deoxidation (330X)

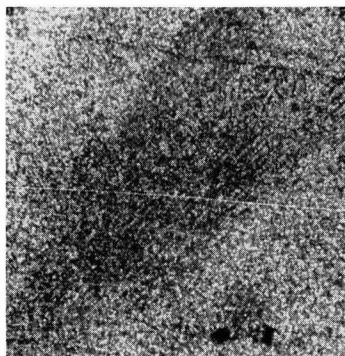


Fig. 5. Fleck deoxidized in hydrogen gas (330X)

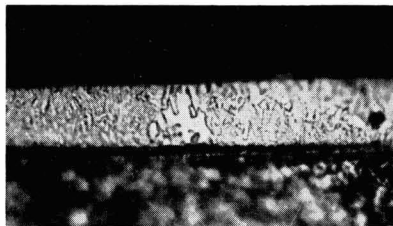


Fig. 6. Initial status of grain growth, after direct stress of  $\pm 18$  kg/mm<sup>2</sup> for  $9 \times 10^6$  cycles (1000X).



Fig. 7. Initial status of grain growth, after direct stress of  $\pm 18$  kg/mm<sup>2</sup> for  $9 \times 10^6$  cycles (1000X).

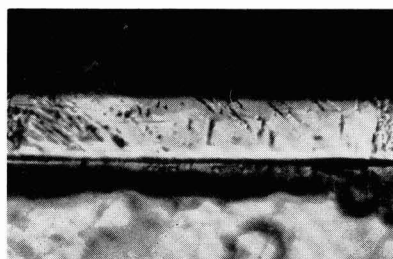


Fig. 8. Grown grain, after direct stress of  $\pm 18$  kg/mm<sup>2</sup> for  $5 \times 10^6$  cycles (1000X).

face of the plated metal, as shown in Fig. 8 and 9, and the flecks are produced.

Figures 10 and 11 are micrographs, the former of a fleck and the latter of a figure on the etched surface after slight electropolishing. By means of etching, one can distinguish easily between the part changed in physical constitution and the remaining part, namely, between a large grown grain and the neighboring micrograins.

Comparison of the x-ray patterns before and after stressing also suggests grain growth in the plated metal. X-ray patterns are shown in Fig. 12 and 13.

These results show that, when a specimen plated with copper is submitted to reversals of cyclic stress, if the magnitude of the stress exceeds the "proper stress",<sup>2</sup> some of the micrograins in the plated metal gradually grow to a considerable size with increase of the number of repetitions. Then the microgroups of fine flaws appear on the surface of these grown grains.

<sup>2</sup> In a previous paper, the limit value of the cyclic stress within which the flecks are not produced by fatigue is termed "proper stress" of the plated metal. The value of the proper stress, however, is a nominal one and is not the true value of the stress arising in the plated metal since it is calculated from the bending moment or the twisting moment acting on a specimen and ignores the difference between the elastic moduli of copper and steel; the value of the proper stress is based on the elastic modulus of the underlying steel. The proper stress is usually much smaller than the endurance limit of the steel.

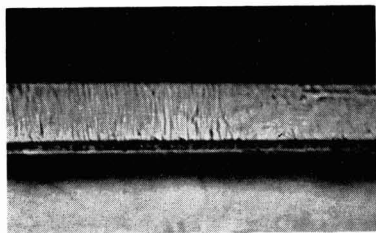


Fig. 9. Grown grain, after direct stress of  $\pm 20$  kg/mm<sup>2</sup> for  $5 \times 10^6$  cycles (1000X).

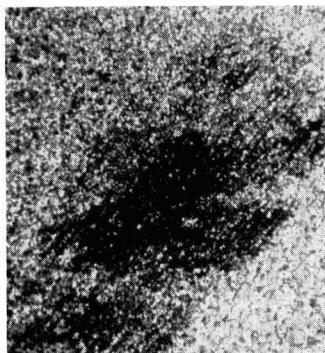


Fig. 10. Fleck (330X)

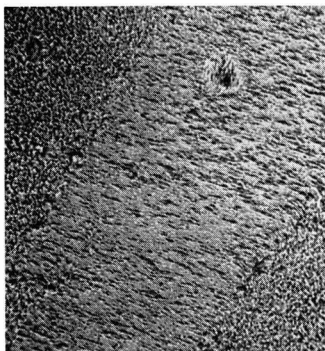


Fig. 11. Etched figure after electropolishing, showing a grown grain and the neighboring micrograins (330X).

*Size of grown grains.*—The size of grown grains is almost equal to the size of flecks and often to the grain size of the underlying steel. The grain size of the ground metal may affect the size of grown grains, but the definite relation between them is not yet known.

The size of grown grains is considerably affected by various conditions even though the same ground steel is used, for example by a slight difference in plating solution, by the temperature of deposition, by the heat treatment of specimens, and other factors.

The size of grown grains is much smaller when the plating solution is made with cupric oxide instead of commercial copper sulfate, when the temperature of deposition is much higher than room temperature, and when specimens are annealed at a temperature near 250°C.

In cases where the size of grown grains is quite small, the grain growth generally occurs at a lower value of cyclic stress than usual and the value of the proper stress is appreciably reduced. The microgroups of fine flaws described usually are not found in this case.

Figure 14 is a surface view showing grown grains in the plated metal when the plating solution is made with commercial grade copper sulfate. Figures

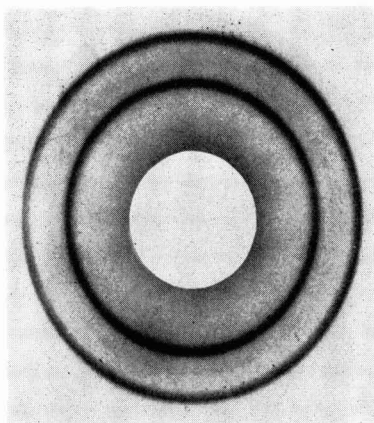


Fig. 12. X-ray pattern, before stressing

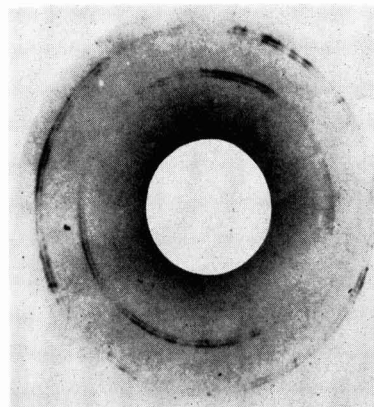


Fig. 13. X-ray pattern, after direct stress of  $\pm 22$  kg/mm<sup>2</sup> for  $16 \times 10^6$  cycles.

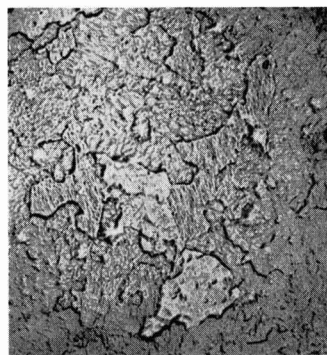


Fig. 14. Grown grains, plating solution made with cupric oxide (330X).



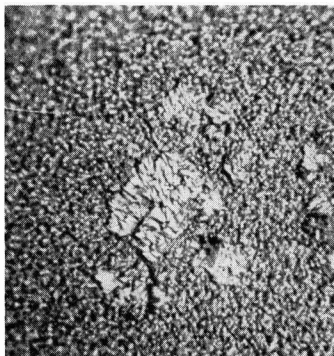


Fig. 15. Annealed at 250°C, before stressing (1000X)

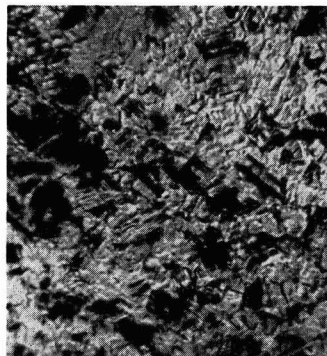


Fig. 18. Annealed at 350°C, after stressing (1000X)

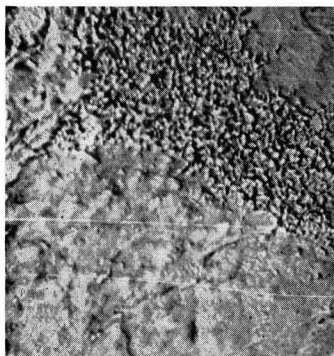


Fig. 16. Annealed at 250°C, after stressing (1000X)



Fig. 19. Annealed at 600°C, before stressing (1000X)

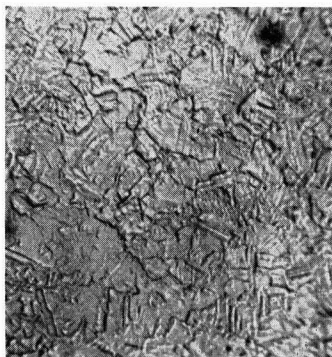


Fig. 17. Annealed at 350°C, before stressing (1000X)

15 and 16 are surface views showing the constitution of the plated metal before and after stressing, respectively, when the specimen is annealed at 250°C for 1 hr in vacuum. As is shown in Fig. 15, the recrystallization of copper occurs in part by the heat treatment. Comparing Fig. 14, 16, and 11, it would appear that the size of grown grains becomes much smaller than in the usual case.

*Effect of heat treatment.*—Figures 17 and 18 show the surface of the plated metal annealed at 350°C before and after stressing, respectively. In this case, since the progress of recrystallization of copper is considerably advanced, the grain growth caused by cyclic stress does not occur and the flecks described

are not produced. The surface of a specimen submitted to cyclic stress, however, becomes tarnished owing to the appearance of microflaws, as shown in Fig. 18.

Figures 19 and 20 are views of the surface and cross section of the plated metal annealed at 600°C, where the recrystallization of copper is complete. The endurance limit of annealed copper (3) almost agrees with the true value of the proper stress of the plated metal. Consequently, when the magnitude of the cyclic stress passes the proper stress, fatigue cracks appear instead of the flecks, as shown in Fig. 21.

### Conclusion and Remarks

The experimental results described indicate that the flecks are produced only when the grains constituting the plated metal develop in sufficient size to reach its surface and can never be produced when grain growth does not occur.

The mechanism of the flecking and the substance which causes the chemical change creating the flecks have not been definitely known until now. It may be concluded that the chemical change is due to some substance contained in the plated metal and not to oxygen in the atmosphere. This is verified by the fact that, when a specimen is isolated from the air by a coating of vinyl prior to stressing, it changes as usual in color while there is no discernible change in the appearance of the flecks.

As was described in a previous paper, the predominant stress producing the flecks is shearing

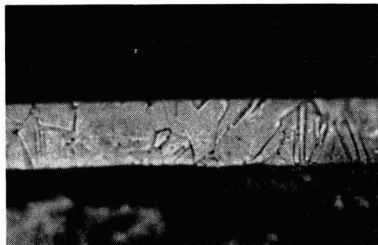


Fig. 20. Annealed at 600°C, before stressing (1000X)



Fig. 21. Annealed at 600°C, after stressing (1000X)

stress (4). Consequently, the physical change in the constitution of the plated metal can be attributed to the reversals of shearing strain.

It is known that a very small quantity of gelatine mixed in the plating solution raises the value of the proper stress remarkably (4). The gelatine, mixed

with the micrograins of the plated metal, prevents the grains from growing and resists orientation of flecks.

The temperature rise on the plated metal during stressing has been measured by Kikuchi<sup>3</sup> by means of the electrostrain gauge. According to his findings, the temperature rise begins at the point of proper stress, but amounts to only several degrees even for stressing in considerable excess over the proper stress. It is concluded that such a small temperature rise cannot be the cause of grain growth, which then must be attributed to a purely mechanical cause.

#### Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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<sup>3</sup> S. Kikuchi, graduate student at Nagoya University.

## Surface Phenomena Associated with Application of Organic Films to Phosphor Screens

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#### ABSTRACT

The production of aluminized screens for cathode ray tubes involves the formation of a temporary organic barrier film on the phosphor coating on which the aluminum may be deposited. Defects in this film produce undesirable blemishes on the finished screen. Certain inherent defects encountered when employing a "flow filming" technique are described, and the fundamental factors governing their formation and prevention are considered.

The use of aluminized cathode ray tube screens has become almost universal in the manufacture of television picture tubes and to a lesser extent in the manufacture of instrument and radar tubes. The well-known technique of aluminizing screens involves the production of a temporary organic barrier layer or film upon which the reflecting aluminum coating may be deposited, usually by evaporation in vacuum. The success of the aluminizing process depends largely on the production of this

organic film free from variations in thickness and imperfections which would allow the aluminum to penetrate round the phosphor crystals and so cause local undesirable reductions in the light output from the screen. It is also necessary for this layer to be extremely thin (less than  $1\mu$ ) and to be composed of a material that may be removed from the screen during subsequent baking treatment. Nitrocellulose and methacrylic resins have been found to be suitable film forming materials.

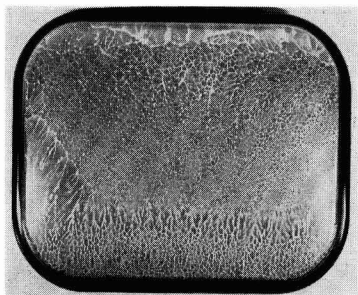


Fig. 1. General appearance of lace pattern in the lacquer film on a 14-in. screen.

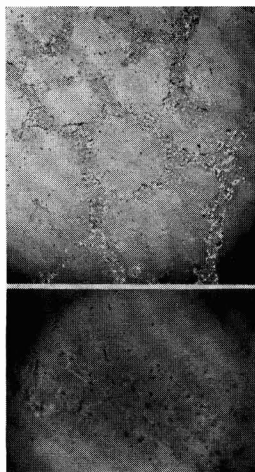


Fig. 2. Areas of laced film showing tendency to globulization and lens formation. Magnification, top 50X, bottom 100X before reduction for publication.

The barrier layer has been prepared by several different techniques, each presenting its own particular problems and producing characteristic defects. It is proposed to limit this paper to a brief description of a "flow filming" technique, as it has come to be called, and to a study of some associated surface phenomena.

Although a complete quantitative explanation of all aspects of the phenomena has not been possible, an outline will be given of the fundamental factors involved, together with appropriate results of more empirical investigations. In the investigations, phosphor screens have been produced by a potassium silicate settling process with barium nitrate as the precipitant and electrolyte.

#### Flow Filming Process

The flow filming technique consists essentially of the following operations:

1. An excess of a dilute solution or lacquer of a film forming resin in a water immiscible solvent, for example butyl methacrylate in toluene, is spread over the surface of the water-moistened screen. A water-moistened screen is here considered to be a screen wherein the capillaries between the phosphor grains are filled or partially filled with water or other aqueous solution.

2. Excess lacquer is drained off.
3. The resultant liquid film is allowed to solidify by evaporation of the solvent, thus forming a solid film.

#### Defects in the Film Structure

When the lacquer is applied under specific conditions of screen wetness and substrate pH and also when particular lacquers are used, the liquid film so produced breaks up and the resultant solid film forms a lacelike pattern, as shown in Fig. 1. These patterns consist of regions of varying film thickness or absence of film and vary in size from small starlike shapes to large irregular areas. A closer examination of solid films removed from screens indicates that the regions of laced films do themselves consist of a minute structure of thick and thin film as shown in Fig. 2.

It has been found that this structure does not occur on phosphor screens only, but may be produced with the same materials on any porous surface such as moistened filter papers and sintered glass plates.

#### Basic Theoretical Considerations

Factors governing the stability of surface films of one liquid on another have been studied by many workers (1-5). Consider the conditions that govern the spreading of a liquid A of surface energy  $\gamma_A$  per unit area on a denser liquid B of surface energy  $\gamma_B$  per unit area. Liquid A spreads spontaneously, producing a liquid-liquid interface of energy  $\gamma_{BA}$  per unit area and a liquid-gas interface of energy  $\gamma_A$  per unit area if

$$\gamma_B > \gamma_{BA} + \gamma_A$$

Further, if the volume of liquid A is not so great as to maintain gravitational spreading, liquid A contracts to a lens leaving only a nonduplex thin film (probably a monolayer) at the original interface of energy  $\gamma_{BA}$  per unit area if

$$\gamma_{BA} < \gamma_A + \gamma_{BA}$$

All known liquid pairs having  $\gamma_B > \gamma_{BA} + \gamma_A$  have  $\gamma_{BA} < \gamma_A + \gamma_{BA}$ . The tendency is therefore for all spreading liquids to contract to a lens-monolayer equilibrium of minimum free energy.

If it were possible to find suitable liquids having initially

$$\gamma_B > \gamma_A + \gamma_{BA}$$

and finally

$$\gamma_{BA} > \gamma_A + \gamma_{BA}$$

then liquid A would remain in stable equilibrium as a duplex film of multimolecular thickness.

Consider the relation between these fundamental factors and the flow filming technique. When the wetted screen is flow filmed, spreading is achieved initially by an excess of lacquer flowing over the surface. That is, the spreading of a multimolecular liquid film is promoted by gravitational forces. When the excess lacquer is drained off and the solvent begins to evaporate the tendency will be for the still fluid system to resolve into the state of minimum free energy, that is, a lens-monolayer state in the case of an initially spreading lacquer or a lens only in the

case of a nonspreading lacquer. The degree to which this is accomplished and the particular form it takes depends on the magnitude of the resultant contractile forces, the viscosity of the lacquer, and the structure and water content of the phosphor screen.

### Influence of Water Content

The quantity of water held in the screen has an important influence on the stability of the film of liquid lacquer. The two extreme conditions are (a) a screen in which the phosphor crystals are coated with a thin film of water only, as shown in Fig. 3(a), and (b) a screen in which the majority of the phosphor crystals are submerged in water, as shown in Fig. 3(b).

In the first condition, the lacquer is held in the screen capillaries; if only contraction occurs, it is within the capillaries. In the second condition, the lacquer film should contract, while it is still fluid, to a single lens in equilibrium with a monolayer. Between these two extremes there is "lacing," the formation of a multitude of lens-monolayer or lens systems of varying sizes.

Further, as shown in Fig. 3(a) condition (a) provides a much larger lacquer-water interface area than is provided by condition (b), (see Fig. 3a and 3b). This also has an important influence on the stability of the lacquer film.

Assuming that the surface of the lacquer is substantially at the same level initially with respect to the phosphor for all conditions of wetness of the screen, then the surface area of the lacquer will be constant.

Thus, if the ratio of the interface area to the surface area is  $m$ , then initially the free surface energy  $E_1$  of a completely spread duplex film of area  $S$  is given by

$$E_1 = S(\gamma_A + m\gamma_{BA})$$

where  $\gamma_A$  is the surface energy of lacquer per unit area;  $\gamma_{BA}$  is the interfacial energy of lacquer per unit area.

If the film contracts to an area  $(S - S')$  leaving a monolayer at the original interface of area  $S'$   $m$  then the free energy  $E_2$  is now given by

$$E_2 = (S - S')(\gamma_A + m\gamma_{BA}) + S'm\gamma_{BA}$$

where  $\gamma_{BA}$  is the monolayer energy per unit area. Contraction to a lens-monolayer equilibrium will not occur if

$$E_2 > E_1$$

i.e.,

$$(S - S')(\gamma_A + m\gamma_{BA}) + S'm\gamma_{BA} - S(\gamma_A + m\gamma_{BA}) > 0$$

or

$$m\gamma_{BA} > \gamma_A + m\gamma_{BA}$$

That is,

$$\frac{\gamma_{BA}}{\gamma_{BA}} > 1 + \frac{\gamma_A}{m\gamma_{BA}}$$

By increasing the water content, which reduces  $m$ , contraction to a lens-monolayer formation and therefore lacing should be more likely to occur.

In practice these findings are confirmed. Screens drained for different times before filming with a lacquer known to be prone to lacing are found to exhibit lacing to a varying degree as shown in Fig. 4. It is therefore desirable to work with the

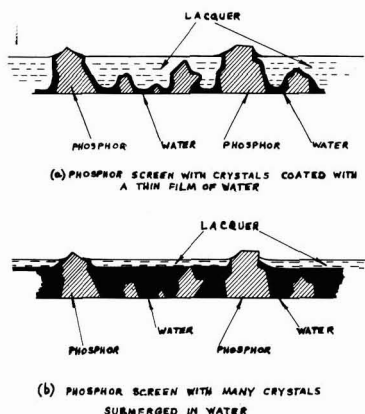


Fig. 3. Diagram of section of screen structure indicating the effect of the quantity of water held in the screen on the lacquer/water interface area.

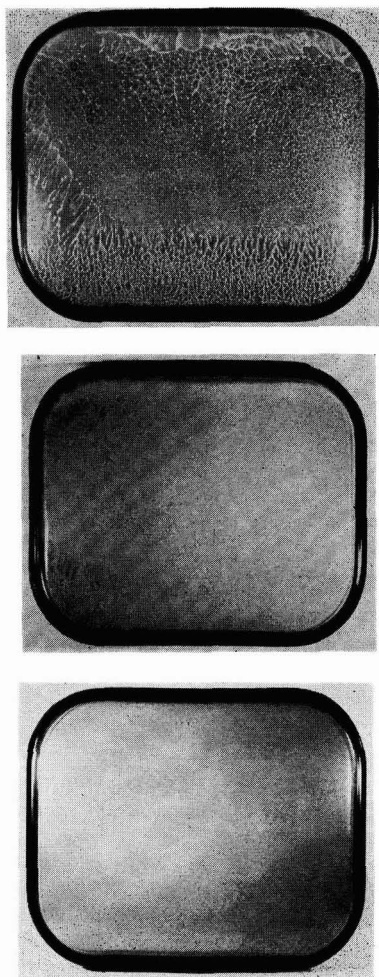


Fig. 4. Effect of water draining time on the lacing of lacquer films: top, 20 min draining; center, 1½ hr draining; bottom, 6 hr draining.

longest possible draining time, provided a state is not reached when too little water is present, which results in lacquer penetrating the phosphor layer and thus screen darkening after aluminizing. A compromise between these two conflicting requirements is generally necessary.

#### Influence of Lacquer Viscosity and Composition

Immediately the lacquer has spread on to the surface of the moistened screen the solvent commences to evaporate and the viscosity of the still fluid film increases. It is desirable that the viscosity of the lacquer film should rise to a level sufficient to prevent migration of the lacquer and the formation of lace patterns. This may be achieved either by working with a high solid concentration, for example greater than 10% resin in solvent, or by using a polymeric resin of high molecular weight. The latter is preferable as it possesses the advantage of being able to achieve the high viscosity at low concentrations which in turn produces dried films of low thickness, a desirable feature when considered in relation to the subsequent bake-out and processing of the tube.

The constitution of the lacquer and also of the substrate has been found to influence the degree of the lacing defect. For example, a lacquer composed of iso-butyl methacrylate, toluene, and a poly-alkylene glycol derivative plasticizer was found to lace to a very much greater extent than the same lacquer plasticized with dibutyl phthalate or tri-cresyl phosphate. Additions of a nonionic surface active agent such as polyethylene glycol monoleate or an ionic surface active agent such as dioctyl sodium sulfosuccinate (Aerosol OT) to the lacquer caused very bad lacing and in the extreme cases an apparent complete inability of the lacquer to wet the screen surface. An example of such a case is shown in Fig. 5. This probably occurs because a very thin film of the surface active constituent spreads out rapidly over the moistened surface of the screen and in so doing reduces the surface energy  $\gamma_A$  to an extremely low value so that initial spreading of the lacquer is prevented.

#### Influence of pH

Water substrates of different pH produce different degrees of lacing; the higher the pH the less is the tendency toward lacing. This is shown in the difference in the results obtained when filming is carried out on either nondried silicate settled screens after decanting or on screens rewetted with de-ionized water. In the former case at pH 11 the lacing is less than in the latter case at pH 8. Depression of the pH to below 4 by the use of buffer solutions for rewetting produces an even greater tendency toward lacing.

The interfacial tension of toluene-butyl methacrylate lacquers on substrates of varying pH has been determined, according to Antonow's rule, from the difference between the surface tensions of the mutually saturated phases, the surface tensions being measured by the well-known capillary rise method. The interfacial tension is found to decrease as the pH increases, as shown in Fig. 6. From earlier

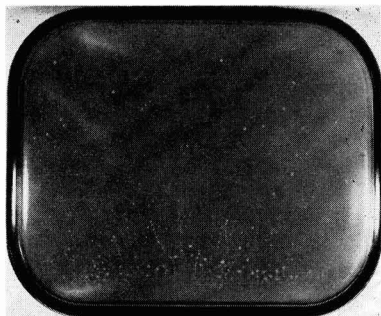


Fig. 5. Effect of the addition of surface active agents to lacquer showing the nonwetting of the moistened screen by the lacquer.

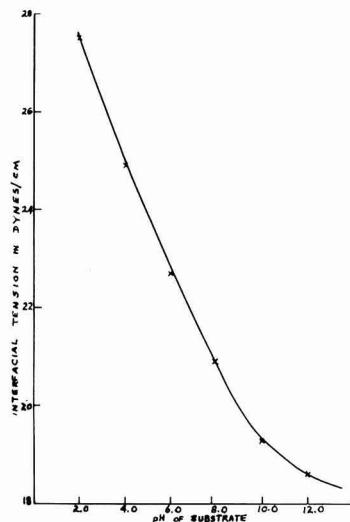


Fig. 6. Variation in interfacial tension of 8% butyl methacrylate in toluene with increasing pH of substrate.

considerations this would be expected to promote spreading of the lacquer. Changes in the monolayer energy might likewise be expected, but measurements of the monolayer tension have been rendered difficult and the results unreliable on account of the presence of solid resin which produces rigid layers. The mechanism of the reduction in interfacial energy is likely to be similar to that reported by Zisman (6) on the spreading of oil drops containing long chain acids.

#### Surface Tension of Substrate

Changes in the surface tension of the rewetting water due to accidental or intentional contamination would be expected to alter two factors: (a) the quantity of water held in the screen capillaries, and (b) the spreading characteristics of the lacquer. These two factors would be expected, as indicated previously, to affect lacing. In order to confirm this the surface tension of the rewetting water was reduced by adding a detergent, Teepol X (Shell Chemicals) and ethyl alcohol, respectively.

Addition of 1% by volume of Teepol X, resulting in a drop in the surface tension of the water to 34 dynes/cm, was found to cause very bad lacing and inability of any lacquer to wet the surface.

The following observations were made on normally nonlacing lacquers applied on rewetting water containing various concentration of ethyl alcohol.

Surface tension of water/alcohol solution, dynes/cm	Observations
52	No lacing observed
45	Slight tendency toward lacing and globulization
37	Very bad lacing and considerable globulization
30	Lacquer did not appear to wet surface at all and remained as globules.

### Spreading of Lacquers on Aqueous Substrates

The foregoing considerations and a study of the lacing defect indicate that it is allied to the problem of the spreading of lacquers on free aqueous surfaces. In order to study the spreading properties of lacquers more closely, known small volumes of various lacquers have been spread on the surface of various aqueous solutions. The diameter of the liquid lens produced has been considered a guide to the spreading properties of the system.

Considering the conditions when a drop of liquid A of volume  $V$  is spread on the surface of a liquid B of surface area  $S$ . If  $\alpha$  is the initial surface area of the drop resting almost on B and  $F(g)$  its initial gravitational energy, then the initial free energy of the system is given by

$$E_1 = \alpha\gamma_A + S\gamma_B + F(g) \quad (I)$$

where  $\gamma_A$  is the surface energy of A per unit area and  $\gamma_B$  is the surface energy of B per unit area. If, on spreading, the lens is assumed to approximate to a flat cylinder, i.e., its radius is large compared with its height, then if  $H$  is the height of and  $\alpha'$  the area of the lens,

$$V = h\alpha'$$

and the final free energy  $E_2$  is given by

$$E_2 = (S - \alpha')\gamma_{BA} + \alpha'(\gamma_A + \gamma_{BA}) + f(g) \quad (II)$$

where  $\gamma_{BA}$  is the surface energy of a monolayer of A on B and  $f(g)$  the final gravitational energy of the lens. Then the free energy decrease  $\delta E$  is  $E_2 - E_1$ . Therefore

$$\delta E = S(\gamma_B - \gamma_{BA}) + \alpha\gamma_A + F(g) - f(g) - \alpha'(\gamma_A + \gamma_{BA} - \gamma_{BA}) \quad (III)$$

For equilibrium

$$\frac{d(\delta E)}{d\alpha'} = 0$$

i.e.,

$$-\frac{df(g)}{d\alpha'} - (\gamma_A + \gamma_{BA} - \gamma_{BA}) = 0 \quad (IV)$$

but  $f(g) = (V\rho gh)/2$  and  $h = V/\alpha'$  where  $\rho$  = density of liquid A

$$\therefore f(g) = \frac{V^2\rho g}{2\alpha'} \text{ and } \frac{df(g)}{d\alpha'} = \frac{-V^2\rho g}{2\alpha'^2} \quad (V)$$

from Eq. (IV) and (V)

$$\gamma_A + \gamma_{BA} - \gamma_{BA} - \frac{h^2\rho g}{2} = 0$$

Thus it is seen that the thickness of the lens is dependent on the surface, interface, and monolayer energies, and anything that alters these energies would be expected to alter the height and therefore the diameter of the lens.

Numerous experiments were carried out to determine in practice the effect of changes in these parameters. It was noted that in all cases where the surface of the water was not previously contaminated, a thin film (probably a monomolecular layer) spread out in front of the main body of lacquer. The latter in many cases spread considerably initially but then contracted to a stable lens in equilibrium with the confined monolayer. Other lacquers spread more slowly initially but retained a larger lens diameter without contraction. It was found that lacquers prone to lacing exhibited the phenomena of initial spreading followed by contraction to a small diameter lens, whereas nonlacing lacquers spread without contraction to a lens of much greater diameter. Spreading was found to be greater on aqueous solutions of high pH than on solutions of low pH.

Spreading was greatest when the atmosphere over the lens and monolayer was saturated with solvent vapor.

These effects serve to indicate, without considering their mechanism, the type of phenomena that may be expected when changes are made in the various parameters of the system.

### Summary and Conclusions

Some of the problems relating to the formation of stable films have been outlined.

It has been shown that these problems are fundamental to the nature of the materials involved. The development of a satisfactory filming process depends on the choice of the solvents, resins, and aqueous substrates having the correct surface energy characteristics and on the control of the water content in the screen. The importance of avoiding contamination from surface active impurities has been shown.

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# Melted Layer Crystal Growth and Its Application to Germanium

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## ABSTRACT

Single-crystal material of constant impurity distribution may be grown conveniently from a doped melted layer maintained above solid retained in a crucible. As crystal is withdrawn from the melt, fresh material is supplied to the melted layer by moving the melted layer downward through the solid. A single crystal may be grown using direct high-frequency coupling to heat the melted layer if fluctuating components of the field are removed. Data are given for resistivity profiles of germanium crystals doped with antimony and grown with manual operation of the heaters.

The growing of a single-crystal material is usually performed to obtain "good" crystal containing the desired concentrations of specific impurities. The Czochralski method (1) for growing crystals from a melt yields "good" crystal. With doping, however, the fraction of crystal containing a certain range of impurity concentration is governed by the segregation coefficient. This fraction of crystal is smaller, the smaller the allowable range of impurity concentration for a particular use and the smaller the segregation coefficient for the impurity. The problem becomes particularly acute if one desires a high concentration of an impurity with a very small segregation coefficient, for in such a case a significant fraction of the material grown may be polycrystalline.

A more uniform distribution of impurity may be obtained by zone levelling in a boat (2) or by the floating zone (3) procedure. Single-crystal germanium grown in a boat appears to require special annealing in order to reduce the number of crystalline imperfections introduced by constraint by the boat during growth (3). These studies also indicate that the after-anneal may drastically reduce the lifetime. The properties of germanium render diffi-

cult the application of the floating zone technique for single-crystal growth although this technique would obviate the problems involved in using boats and crucibles. With the availability of crucible materials that do not react with the molten semiconductor, such as quartz or graphite for germanium, the unconstrained growth of a crystal having an impurity distribution such as is realized by zone levelling may be obtained by a "melted layer" procedure.

In the melted layer arrangement, shown diagrammatically in Fig. 1, homogeneous solid is retained in a vertical crucible. A layer of melt is established at the top of the original solid. This may be inoculated with one or more impurities. A monocrystal seed is introduced into the melt and, after attention to making a good splice, a single crystal of the material is withdrawn gradually. As crystal is withdrawn, the volume of melt is regulated by melting the solid below the melted layer. This is readily accomplished by lowering the heating coils.

The principles governing the distribution of impurities follow those described by Pfann (2). Attention must be given to impurities present accidentally or intentionally in the solid as well as to those that may be added intentionally to the melt. In the application of the principles of zone levelling to the melted layer procedure, allowance must be made for the fact that the crystal will in general be smaller in diameter than the original solid. In practice, the diameter of the growing crystal is surprisingly constant for a given diameter of crucible and for a particular rf coil arrangement; it appears to be controlled by the rounded shape of the melt surface rather than by growth rate or power input. The fact that the diameter of the growing crystal is quite insensitive to factors other than those arising out of the original design is convenient for programming the rate at which the rf coil must move downward in order to maintain a constant volume of melt. The rate,  $L$ , for downward movement of the coil may be derived from simple considerations to be

$$L = \frac{P}{(D^2/d^2) - 1}$$

where  $P$  is the linear rate at which the crystal is raised and  $D$  and  $d$  the diameters of the crucible and crystal, respectively. This relation is adequate if the

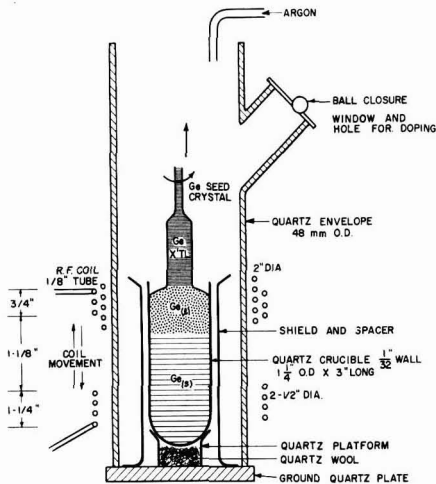


Fig. 1. Schematic arrangement of parts for growing crystal by a "melted layer" procedure.

segregation coefficient is very small (e.g.,  $< 0.01$ ). The rate must be reduced if the segregation coefficient is large enough that the concentration in the crystal reduces substantially the concentration in the melt. This situation can also be taken care of by using a conical shaped crucible. In practice in order to maintain a constant melt volume it has been found necessary to decrease the power or reduce the rate of coil movement as the melted layer approaches the bottom of the crucible.

### Experimental

There are several problems encountered in conducting the melted layer procedure satisfactorily; two arise from the use of rf power for melting and the other from the expansion of germanium on freezing if a quartz crucible is used. Quartz is particularly convenient to use when programming by viewing. With automatic programming, a graphite crucible is satisfactory and then this problem peculiar to the use of quartz is obviated. The problem of obtaining a good splice is more difficult using directly coupled rf heating rather than conventional radiative heating. The seed crystal (usually small) is relatively cold. Of several ways to overcome this difficulty the easiest is to raise the melt temperature substantially. This can be done without increasing the width of the melted layer by temporarily increasing the rf power and raising the rf coils at the same time. A second difficulty arising from the use of ordinary rf power is the agitation of the melt which is usually severe enough to prevent single-crystal growth. By filtering the rf output of a standard electronic oscillator with a choke-capacitor combination, most of the fluctuating components of the rf field are removed, and agitation of the melt is reduced to a degree where there is no interference to single crystal growth.

In order to start with homogeneous solid in the crucible, it is desirable to freeze rapidly the initially molten charge. When quartz is used this ordinarily results in cracking of the crucible. No cracking need be experienced if the solid is maintained at a temperature at which it is plastic, for germanium above about  $600^{\circ}\text{C}$  (5). This situation may be realized by winding the single rf coil in two sections, a tightly wound portion for maintaining the melted layer, and an auxiliary section of more open winding to keep the solid in its plastic temperature range.

### Procedure and Results

Although the crystal pulling and rotation mechanism is automatic, the mechanism for moving the rf coils—a simple screw thread—was operated manually. The power source was a standard 5KW 450kc General Electric oscillator with the output filtered as described, using a 5000 v, d-c, 20.5  $\mu\text{f}$  capacitor and large choke coil of several henrys. A typical charge for the crucible was 300 g of zone-refined germanium. After melting and rapid freezing, a melted layer approximately  $\frac{1}{8}$  in. wide was established. The volume of melt was readily estimated from the diameter of the crucible. The amount of doping was computed on the simple basis that  $C = KC_c$ , where  $C_c$  is the concentration of added im-

purity necessary in the melt to produce the concentration,  $C$ , of that impurity in the solid, and  $K$  is the segregation coefficient. After doping, the seed is introduced into the melt and crystal growth initiated. As the crystal is grown, the coil is lowered at a rate to preserve the width of the melted layer. The width of the layer was estimated from visual observation and consequently fluctuations were of the order of  $\pm 1/16$  in.

Two typical results will be reported that have a bearing on (a) the quality of crystal, and (b) the uniformity of impurity distribution under a normally adverse condition of high concentration of impurity for which the segregation coefficient is small.

In order to check that crystals grown by the melted layer procedure are substantially the same as those grown by the Czochralski method, zone-refined germanium was grown into a single crystal without any doping. The lifetime of crystal grown under the melted layer condition ranged from 1.2  $\mu\text{sec}$  near the splice to 850  $\mu\text{sec}$  in the region just prior to normal growth. Crystals grown by the standard Czochralski method on this material bracketed closely 1  $\mu\text{sec}$  for lifetime. To the extent that lifetime is an index for crystal perfection at a given level of purity, there does not appear to be any significant difference between the quality of crystals grown by the melted-layer procedure or by the Czochralski method. The lifetime of these crystals is substantially better than those reported grown in a boat with after anneal (4).

Using antimony ( $K = 0.001$ ) as the doping agent, in obtaining a concentration of about  $3 \times 10^{17}$  carriers/cm in a crystal grown by the Czochralski method, approximately the last third of the crystal is usually polycrystalline. Figure 2 shows resistivity plotted as a function of the crystal length for two crystals grown by the melted layer procedure in which the melted layer was doped with antimony to produce 0.01 ohm-cm germanium. In the crystal A, although mechanical difficulty was encountered, 75% of the crystal shows a variation of  $\pm 20\%$  in resistivity. Twenty-seven grams or about 10% of the initial 300 g was lost due to polycrystalline material. This situation is to be compared (dashed line) with the 30% loss by normal growth and the

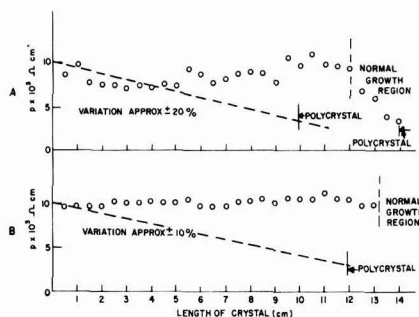


Fig. 2. Resistivity profiles for antimony-doped germanium crystals. Open circles experimental, melted layer growth; dashed line estimated for normal growth from melt.



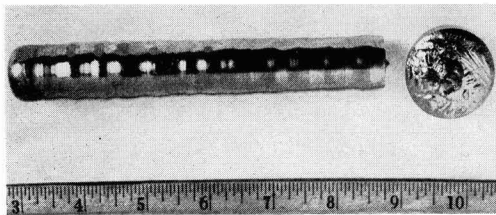


Fig. 3. Photograph of typical crystal from melted layer growth.

fact that only 50% of the original germanium would yield crystal within a factor of two for resistivity. In (B) of Fig. 2 is shown a resistivity plot for crystal grown reflecting only the variations introduced by manual operation of the coils. It may be seen that about 75% of this crystal has no more than a

$\pm 10\%$  variation in resistivity. A photograph of crystal B is seen in Fig. 3.

#### Acknowledgments

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## A Study of the Molded Nickel Cathode

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#### ABSTRACT

Research work on the molded nickel cathode is described. Results are given regarding the effects on emission and life of variations in nickel powder, alkaline-earth carbonates, reducing agents, sintering, and aging. Data on pulsed emission are presented.

This paper describes testing methods used in the evaluation of molded nickel cathodes and discusses the effect on cathode emission and life of various materials and processing techniques. Some of the early work on such cathodes was done by MacNair, Lynch, and Hannay (1). These authors discussed the fabrication of the cathodes, some of the useful properties, and gave a comparison between the emission of the molded cathode, oxide cathodes, and L cathodes. Other studies on the molded cathode were reported by Beck, Brisbane, Cutting, and King (2), Bell and Brewer (3), and by Haas and Jensen (4). In spite of the considerable previous work, only meager results have been presented regarding materials, processing, or life.

#### Description of Molded Cathode

The structure of a typical molded nickel cathode is shown in Fig. 1. The cathode sleeve is a nickel cylinder having an outer diameter of 0.125 in., a length of about 0.33 in., and a wall thickness of 0.004 in. The cathode pellet is composed of two layers. The lower layer, about 0.045 in. thick, contains nickel powder and an activator ( $ZrH_2$ ) in the weight proportions of 99:1. The upper part of the pellet, which is 0.003 to 0.005 in. thick, contains nickel powder (69% by weight), alkaline earth carbon-

ates (30%) and an activator (1%). The nickel powder is fired at 600°C for 15 min in a hydrogen atmosphere ( $-10^\circ\text{C}$  dew point). All powders are thoroughly dried before use.

The cathode pellet is formed and pressed into the sleeve at a pressure of 80 tons/in.<sup>2</sup> in a single step by use of a hardened steel die and hydraulic press. Active material is then removed from the edge of the cathode sleeve by rubbing with aluminum-oxide

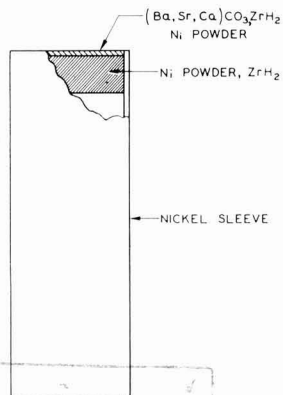


Fig. 1. Structure of a molded nickel cathode

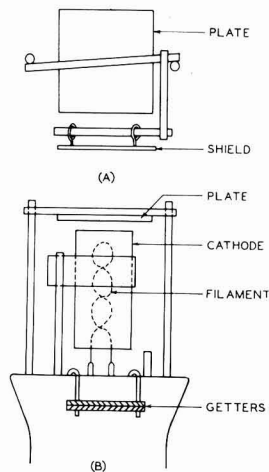


Fig. 2. Construction of test diode

paper. The most important step in the processing of the cathode is sintering, which is discussed in detail later. After sintering, the cathodes are stored in evacuated ampules until ready for use.

### Test Diode

Figure 2 is a drawing of the test diode used for emission measurements on molded nickel cathodes. The cathode is welded to a tantalum strip which, in turn, is welded to a stem lead. The plate, which is a flat piece of nickel or tantalum, is mounted at a suitable distance above the cathode so that the spacing between them is about 0.015 in. when the cathode is hot. The upper surface of the plate is sand-blasted to promote radiation.

A tantalum evaporation shield [shown only in Fig. 2(A)] is mounted between the cathode and the glass envelope to keep the glass clean. This shield can be moved aside to permit pyrometric observation of the cathode temperature through the glass. Temperatures are measured near the top of the nickel cathode and are not corrected for either the emissivity of the nickel or the transmission of the glass. The temperatures quoted are, therefore, close to brightness temperatures.

No attempt is made to achieve an extremely high vacuum in the test diode. A typical evacuation schedule, which is more or less characteristic of industrial techniques, is given below.

1. The tube is baked at a temperature of 400°C for ½ hr.
2. All metal parts are heated by radio-frequency induction.
3. Heater voltage is applied in half-volt steps, each held long enough to insure that the pressure does not exceed  $10^{-4}$  mm Hg. The maximum temperature to which the cathode is raised is 1000°C (brightness); this temperature is maintained until the pressure falls below  $10^{-6}$  mm Hg.
4. With the cathode temperature at 1000°C (brightness), the plate voltage is slowly increased to 50 v. The plate is held at this maximum voltage for about 15 min, at the end of which time the cathode-current density is about 0.5 amp/cm<sup>2</sup>.

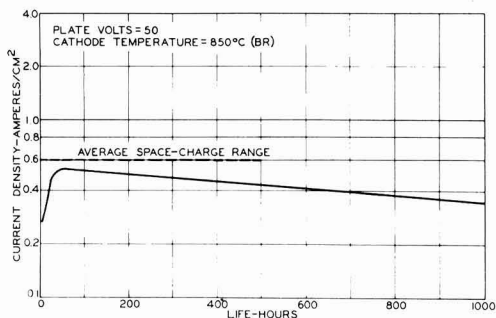


Fig. 3. D-C emission during life

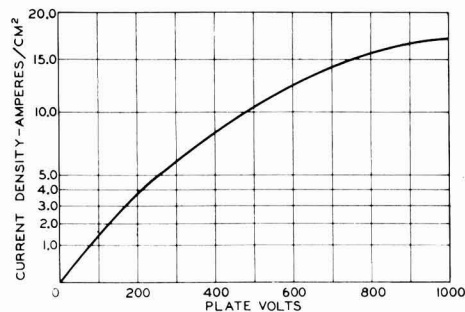


Fig. 4. Pulse-emission characteristics

5. All voltages are removed, the getter is partially fired, the tube is sealed off, and the getter is then completely fired.

After the tube is removed from the exhaust system, the cathode is aged for about 15 min at a temperature of 1000°C (brightness) and a plate voltage of 50 v. The effect of aging schedules is described later.

### D-C Life Test and Pulse Emission

All cathodes are life-tested for 1000 hr at a cathode temperature of 850°C (brightness) and a plate voltage of 50 v. Figure 3 shows the typical current densities during 1000 hr of life. The average space-charge-limited current, calculated from the dimensions of the tube by means of elementary space-charge theory, is also indicated. The average current density throughout life is about 0.4 amp/cm<sup>2</sup>, which is slightly less than that predicted by space-charge theory.

The life test is interrupted periodically, and the pulse emission of the cathodes is measured at a cathode temperature of 850°C (brightness), a peak plate voltage of 1000 v, a pulse length of 2.5 μsec, and a repetition rate of 60 pulses/sec. Figure 4 shows the peak current density as a function of peak plate voltage. At the 1000-v measuring condition, the field at the cathode is clearly accelerating. Field-free emission is less than the 1000-v emission by a factor which varies between 2 and 6, depending on the activity of the cathode and the cathode-plate spacing. For many cathodes, the maximum peak emission throughout life (usually reached after 24 to 100 hr) is between 16 and 20 amp/cm<sup>2</sup> at the 1000-v condition. These values are equivalent,

therefore, to an emission of about 2 to 10 amp/cm<sup>2</sup> under field-free conditions.

Bell and Brewer (3) discussed the necessity of preventing emission which can result from high fields at the edges of the active cathode pellet. Because the pellet they used extended beyond the cathode sleeve, they shielded the cathode edges by an additional electrode structure held at cathode potential. No such shield is necessary with the cathode shown in Fig. 1 because the active cathode material does not migrate appreciably to the edge of the cathode sleeve, as evidenced by the fact that the emission never exceeds that predicted by space-charge theory. Furthermore, if a space-charge plot is made at moderate voltages, a straight line results, with a slope which indicates that only about 70% of the surface is emitting.

Some comment is in order on the result that only about 70% of the cathode surface emits, a conclusion also reached by Beck, *et al.* (2), but obtained by different experimental techniques. It is believed that at least two sources of emission are required to explain the above fact: (a) alkaline-earth-oxides contained within the pores of the matrix; (b) a monolayer of alkaline-earth-oxide (probably barium oxide), which has migrated onto a small area of the nickel which surrounds each pore. The following facts are cited to support this explanation.

1. From geometrical considerations and the proportions of carbonate and nickel used in the active pellet, one concludes that less than 70% of the active surface is composed of alkaline-earth-oxide.

2. The pulsed emission of the cathode is greater than the d-c emission, but by a factor much smaller than that usually reported for an alkaline-earth-oxide cathode.

### Cathode-Pellet Composition

Although a complete study of cathode pellet materials was not made, various compositions were tried. The most useful emissive material is a triple carbonate, designated RCA-33C-311-B, containing 57% by weight barium carbonate, 39% strontium carbonate, and 4% calcium carbonate. Cathode pellets were also made from a triple carbonate containing 13% calcium carbonate and from barium carbonate alone. Satisfactory emission was obtained from all the cathode pellets, but the ones containing barium carbonate alone were somewhat gassy.

Three nickel powders having particles of different sizes were tried: Type B carbonyl nickel (1-3 $\mu$ ), standard carbonyl nickel (9-14 $\mu$ ), and Sherritt-Gordon nickel (60 $\mu$ ). Although the emission from cath-

odes using type B material was best, the difference was not necessarily significant.

Three reducing agents were tested as activators: zirconium hydride, carbon, and titanium hydride. Carbon is gassy and results in short-lived emission. Zirconium hydride gives satisfactory results and is used in the cathodes for which data are reported. Titanium hydride is satisfactory but has no particular advantage over zirconium hydride.

### Sintering and Aging

The most important step in the processing of molded nickel cathodes is sintering. During this process, the cathodes are held in a nickel boat within a Vycor tube, which in turn is within a muffle furnace. Nitrogen and hydrogen are passed in series through a deoxidizer, an electrolyzer, a liquid-nitrogen trap, and finally the Vycor tube. The hydrogen flows at the rate of 200 cm<sup>3</sup>/sec, the nitrogen at 50 cm<sup>3</sup>/sec. The time-temperature schedule during sintering, which is quite critical, is given in Table I.

Figure 5 shows pulse current density (measured periodically during life) as a function of hours of life for both sintered and unsintered cathodes. The remarkable improvement in life performance due to sintering is obvious.

The mechanism of the sintering process is not completely understood. Presumably it includes deoxidization of the nickel powder, decomposition of the zirconium hydride, and diffusion of a small amount of free zirconium into the nickel matrix. The zirconium which diffuses into the matrix later diffuses out and acts as a reducing agent throughout the life of the emitter. During sintering, at least part of the carbonate is broken down, as evidenced by the fact that sintered cathodes give off considerably less gas during exhaust than unsintered ones.

The effect of aging on cathodes is shown in Fig. 6. Pulse emission is plotted as a function of life for cathodes which are (a) not aged, (b) aged for 15 min, and (c) aged for 30 min. The best performance was obtained with cathodes aged for 15 min. However, uncontrolled variations in construction and processing of cathodes may require different aging times for optimum results. The optimum aging time can be determined by observation of the current during aging. Most cathodes show a slump of current during initial phases and then recover. The

Table I. Time-temperature schedule during sintering

Temp, °C*	Atmosphere	Time (min)
Room to 600	H <sub>2</sub>	8
600 to 1000	N <sub>2</sub>	7
1000 to 600	N <sub>2</sub>	7
600 to Room	H <sub>2</sub>	8
Room	N <sub>2</sub>	10

\* Temperature is held constant during change of atmosphere from one gas to another, which may take as much as a minute.

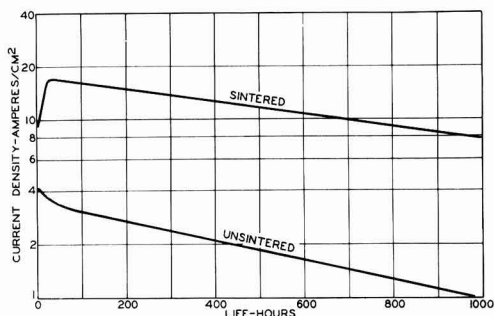


Fig. 5. Life performance of sintered and unsintered cathodes

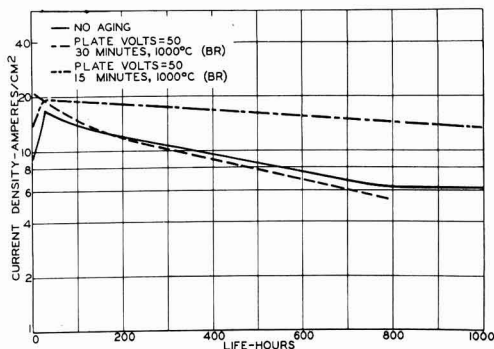


Fig. 6. Effect of aging on life

optimum aging time is reached when the recovery is essentially complete.

### Applications

Molded nickel cathodes have been used in several practical applications. Their use is most advantageous when the cathode must be exposed to air (as in demountable systems) or when it is expected to deliver large amounts of current in the presence of positive ion bombardment, a poor vacuum, or a large electric field. A comparison between the performance of molded nickel cathodes and that of oxide-coated cathodes in three applications demonstrated the superiority of the molded cathodes.

In the first application, a typical cathode ray gun was mounted in a demountable vacuum system for the purpose of evaluating phosphors. Cathode-current requirements are fairly low, about  $1.5\mu\text{a}$ . However, the demountable system is opened to air several times a day for varying periods of time. A typical molded nickel cathode survives 80-100 such cycles and is still able to deliver the required current. In contrast, typical oxide-coated cathodes last only 10-20 cycles.

In the second application, a similar electron gun was mounted in a demountable vacuum system for the purpose of evaluating electron-optical structures. In this gun, however, the beam current was about  $150\mu\text{a}$ . A molded nickel cathode performed satisfactorily through about 30 openings of the demountable system, but an oxide cathode lasted through about 3 such openings. In this application, the cathode is not heated while the system is open to air, as described by Haas and Jensen (4).

In the third application, a molded nickel cathode was used in a developmental projection kinescope. In this structure, the aperture of grid No. 1 is 0.035 in. in diameter, the accelerating voltage is 40 kv, and the beam current is  $1000\mu\text{a}$ . Because the gun structure has no ion trap, the cathode is subjected to heavy ion bombardment. After 1500 hr of operation under these conditions, the emission from the molded cathode was still satisfactory. A typical oxide cathode lasts only about 600 hr under such conditions.

### Acknowledgment

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## Equilibrium Reduction of Tungsten Dioxide by Hydrogen

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### ABSTRACT

A study has been made of the heterogeneous equilibrium involving  $\text{H}_2$ -W- $\text{WO}_2$ - $\text{H}_2\text{O}$  in the temperature range  $500^\circ$ - $1000^\circ\text{C}$ , using a static equilibrium-type of apparatus. The standard heat of formation and entropy of  $\text{WO}_2$ , as calculated from the equilibrium data, was found to be  $\Delta H^\circ = -135.0 \pm 0.3$  kcal and  $17.1 \pm 1.0$  e.u. The heats of formation of  $\text{WO}_2$  and the two higher suboxides were determined by direct combustion.  $\Delta H^\circ$  of  $\text{W}_{20}\text{O}_{40}$  ( $\text{WO}_{2.72}$ ) =  $-183 \pm 1$  kcal/mole W,  $\Delta H^\circ$  of  $\text{W}_{20}\text{O}_{38}$  ( $\text{WO}_{2.90}$ ) =  $-193 \pm 1$  kcal/mole W, and  $\Delta H^\circ$  of  $\text{WO}_2$  =  $-137 \pm 1$  kcal/mole W.

The oxide analyses of Glemser and Sauer (1) and the single crystal studies by Magneli, *et al.* (2) have established the existence of the following tungsten oxide phases which are stable at room temperature:

$\alpha$   $\text{WO}_3$ —yellow—triclinic pseudo-orthorhombic (stable below  $740^\circ\text{C}$ )

$\beta$   $\text{W}_{20}\text{O}_{38}$ —blue—( $\text{WO}_{2.90}$ ) monoclinic

$\gamma$   $\text{W}_{18}\text{O}_{40}$ —violet—( $\text{WO}_{2.72}$ ) monoclinic

$\delta$   $\text{WO}_2$ —brown—monoclinic

The homogeneity ranges of the above oxides are very narrow according to Magneli, *et al.* The exist-

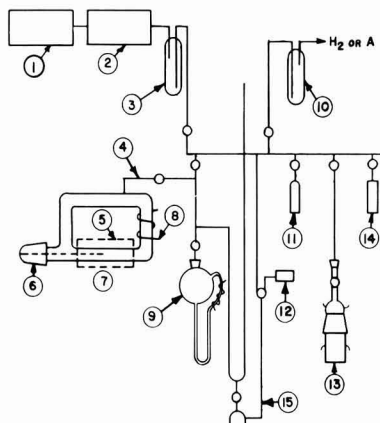


Fig. 1. Equilibrium Apparatus. 1, mechanical forepump; 2, diffusion pump; 3, liquid  $N_2$  trap; 4, quartz-Pyrex seal; 5, reaction furnace; 6, thermocouple well; 7, quartz reaction chamber; 8, auxiliary circulating heater; 9, condensing bulb; 10, liquid  $N_2$  trap; 11, vacuum gauge; 12, drier; 13,  $H_2O$  vessel; 14, drier; 15, constant volume manometer.

ence of a stable tetragonal form of  $WO_3$  above  $720^\circ$ - $740^\circ C$  has been reported (3-5). There is increasing evidence of an oxide phase  $W_5O$  (beta tungsten) (6-8). This point has been in dispute (9-11) and the question remains a point of controversy.

However, the thermodynamic data that are available for the tungsten oxides are based in most part on studies (12-17) made prior to these oxide phase investigations. In addition to the uncertainties concerning the oxide phases, it has been pointed out (18) that considerable errors, due to thermal diffusion effects, are encountered in the use of a Deville (19) type of apparatus such as was almost universally used in earlier studies. The purpose of the paper is to present a redetermination of the  $W-WO_3-H_2-H_2O$  equilibria as a first step in the study of the possible equilibria involved in the reduction of  $WO_3$  to  $W$  by  $H_2$ .

### Experimental

Figure 1 shows the experimental apparatus designed to avoid the separation of the equilibrium mixture of  $H_2$  and  $H_2O$  by thermal diffusion. The apparatus consists of a square doughnut-shaped 1 in. quartz tubing reaction chamber into which a small quartz boat, 4 cm long, 1 cm wide, and 0.8 cm high, containing the solid phases ( $W$  and  $WO_3$ ), is placed. The reaction chamber is sealed off from the atmosphere by a standard taper 24/40 joint containing the thermocouple well. The reaction furnace windings are spaced so that there is no appreciable radial temperature gradient, and the constant temperature ( $\pm 1^\circ C$ ) zone is approximately 3 cm long. All chromel-alumel thermocouples and lead extensions were calibrated, over the entire range, against a Bureau

of Standards Certified platinum-platinum 10% rhodium thermocouple to  $\pm 1^\circ C$ . Aluminum foil is used as a heat shield to help reduce the large end losses and to keep the entire reaction chamber at an elevated temperature to prevent condensation of water present in the reaction gases. The thermocouple serves both to control and indicate the temperature since the response of the detector to the addition or loss of heat is almost instantaneous due to the quartz construction. A small auxiliary heater on the vertical leg assures a circulation of the gases by convection currents. The chamber is connected by a quartz-Pyrex seal to the condensing bulb, constant volume mercury manometer, and vacuum manifold. The vacuum system includes a mechanical forepump, a two-stage mercury diffusion pump, liquid  $N_2$  trap, and thermocouple vacuum gauge. The condensing bulb includes a cold finger and circulating tube. The small heater in the circulating side arm causes the gas to rise and thus maintains a convection current which causes all of the  $H_2O$  vapor in the system to be frozen out in the cold portion immersed in liquid  $N_2$ . The manometer readings were made with a precision cathetometer to  $\pm 0.05$  mm. All manometer readings were corrected, when necessary, for the cooling effect of liquid  $N_2$ .

All equilibrium measurements were made by alternate reduction and oxidation of the samples. This alternating procedure yielded consistent values for  $K_p$  after 2 to 3 conditioning runs. The presence of both phases ( $W$  and  $WO_3$ ) enabled establishment of equilibrium in as short a time as possible which prevented surface depletion of either phase and sintering effects. This time varied from 2 hr for lower temperatures to less than  $\frac{1}{2}$  hr for higher temperatures. A 2-g sample was placed in the reaction chamber and the system evacuated to less than 0.1 micron for a period of 2 hr.  $H_2$  and/or  $H_2O$  vapor was introduced into the chamber which was then closed off from the rest of the system. The temperature of the chamber was raised to the desired point and the equilibrium run made while the condensing bulb and manometer were being pumped down. Upon completion of the run, the hot gases were expanded into the condensing bulb and manometer. The total pressure and the pressure after the  $H_2O$  was frozen out were then noted.

All reagents were prepared from purified  $WO_3$ , which was made by firing  $H_2WO_4$  at  $900^\circ C$  for  $1\frac{1}{2}$  hr. Spectrographic analysis of the  $WO_3$  is given in Table I.

The  $H_2$  gas was purified by passage through a Deoxo catalytic unit to remove  $O_2$ , and then through a liquid  $N_2$  trap to remove traces of  $H_2O$ . The  $H_2$  gas was obtained directly from manufacturing facil-

<sup>1</sup> Obtained from Chemical Products, General Electric Co., Cleveland, Ohio.

Table I. Analysis of  $WO_3$  starting material

	Al	Mo	Si	Ca	Metallic elements		Cu	Cr	Mr	Ti	Sn,Co,Pb
					Fe	Ni					
% by wt	0.002	0.002	0.020	0.001	0.001	0.001	0.001	0.001	0.001	trace	absent

ities providing a highly purified gas. Pure W metal was obtained by the reduction of  $WO_3$  with dry  $H_2$  (400 cc/min) at 650°C for a 24-hr period. Material balance and x-ray analysis showed the product to be  $\alpha$ -W. 100 grams of tungsten was made. There are two primary methods for producing  $WO_2$  and the other sub oxides (1, 2). Both yield the same product as evidenced by x-ray analysis. The bulk of the  $WO_2$  used for equilibrium samples was prepared by reduction of 15-g charges of  $WO_3$  at 700°C by  $H_2$  gas (200 cc/min), saturated with  $H_2O$  vapor at 45°C, for ½ hr. Approximately 160 g of  $WO_2$  was so prepared. 60 g each of  $W_{20}O_{38}$  ( $WO_{2.90}$ ) and  $W_{18}O_{30}$  ( $WO_{2.72}$ ) were prepared by heating stoichiometric quantities of W and  $WO_3$  in evacuated sealed quartz tubes as described by Magneli, *et al.* (2).

The standard heat of formation of  $WO_2$  was also determined (as well as values for  $WO_{2.90}$  and  $WO_{2.72}$ ) by combustion methods. The bomb assembly consisted of a single-valve Parr oxygen bomb and Series 1300 Plain Calorimeter. The bomb was flushed at 25 atm with  $O_2$  once to reduce the  $N_2$  content. The  $O_2$  contained 0.3% argon with about 0.001% hydrocarbon impurities. The calorimeter run was carried out according to the manufacturer's recommendations. Temperatures were measured with a Parr Calorimeter thermometer supplied with a test certificate which enabled scale correction to within  $\pm 0.005^\circ F$  to be made. The thermometer readings were made with a cathetometer to avoid parallax. No. 34 B & S gauge nickel-chromium alloy wire was used as a fuse. The combustion capsules were made of 25-20 stainless steel and were lined with a 10-g layer of  $WO_3$  for each run with the exception of the determination of the water equivalent by standardized benzoic acid. A correction was made for the difference in heat capacity. The samples were pressed into pellets 1 in. diam x ¼ in. thick. Tungsten was pressed at 12,000 psi while the other three oxides were pressed at 51,000 psi. The samples consisted of pieces of these broken pellets. Complete combustion was not obtained for samples of W and  $WO_3$ , but the higher oxides  $WO_{2.72}$  and  $WO_{2.90}$  reacted completely when mixed with W metal pellets. The residues of all runs were crushed and digested in 5% NaOH at 85°C for 24 hr, the hot solutions filtered and the metallic W weighed. X-ray examination of the treated residues showed only W present for the runs involving W,  $WO_{2.72}$ , and  $W_{20}O_{38}$ . Tungsten dioxide samples were reacted without any addition of W metal; residues were treated as above, and only  $WO_2$  was found after filtration. Other laboratory techniques showed that if 130 mg of  $WO_3$  is so treated, the recovery is close to 123 mg or better. This loss could be attributed to either the solution of the  $WO_2$  or, as has been reported (20), the reaction of the  $WO_2$  with  $(OH)^-$  to yield a higher oxide and metallic W. In either case the correction involved is less than the final estimated error. The combustion values for  $WO_{2.72}$  and  $WO_{2.90}$  have been corrected for the energy supplied by the combustion of the added W metal.

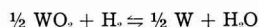
The  $\Delta E$  values from the combustion runs were corrected to unit fugacity of  $O_2$  by reference to the

work of Rossini and Frandsen (21). The conventional conversion of  $\Delta E$  to  $\Delta H$  was made and all results were calculated on the basis of 1 mole of W, for reasons of comparison.

### Results and Discussion

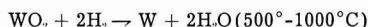
The experimental techniques described above were first used to determine the Fe- $H_2O$ - $H_2$ - $Fe_3O_4$  equilibrium over the temperature range 400°-550°C. The data of Emmett and Schultz (18) was used for comparison. Reagent grade  $Fe_2O_3$  (red) was used as a starting material. Twenty g of  $Fe_2O_3$  was prepared by reduction of  $Fe_2O_3$  at 700°C by wet  $H_2$  ( $H_2O/H_2$  ratio 1.8:1) for 1 hr: x-ray and material balance analysis indicated  $Fe_3O_4$ . Metallic Fe was prepared by reduction at 700°C with dry  $H_2$  for 3½ hr. Experimental results checked very favorably with the literature values.

The equilibrium values for the reaction:



in the temperature interval 500°-1000°C are given in Table II and Fig. 2.

$\Delta C_p$  for the reaction,



was calculated on the basis of literature values for  $H_2$ ,  $H_2O$ (22), W(23), and using  $C_p = 14.0 \text{ cal}^\circ/C$

Table II. Equilibrium data for the system  $WO_2$ - $H_2$ -W- $H_2O$

Run No.	Temp, C°	$K_p = P_{H_2O}/P_{H_2}$	Initial conditions
64A	500	0.112	reducing
68	500	0.118	reducing
82	500	0.120	oxidizing
83	500	0.121	oxidizing
88	500	0.120	reducing
83A	600	0.214	reducing
83B	600	0.212	reducing
83C	600	0.210	oxidizing
88A	600	0.208	reducing
88B	600	0.218	oxidizing
90	600	0.206	oxidizing
86A	700	0.356	oxidizing
86B	700	0.346	reducing
86C	700	0.348	oxidizing
87	700	0.340	oxidizing
91A	700	0.351	reducing
91B	700	0.355	reducing
88	800	0.507	reducing
90A	800	0.460	reducing
90B	800	0.460	oxidizing
90C	800	0.515	reducing
90D	800	0.520	oxidizing
90E	800	0.510	oxidizing
72A	900	0.694	oxidizing
72B	900	0.684	reducing
73	900	0.705	oxidizing
75A	900	0.690	reducing
75B	900	0.709	oxidizing
75C	900	0.695	reducing
94A	1000	0.931	reducing
94C	1000	0.935	reducing
94D	1000	0.935	oxidizing
95A	1000	0.945	oxidizing
95B	1000	0.937	oxidizing
95C	1000	0.934	reducing

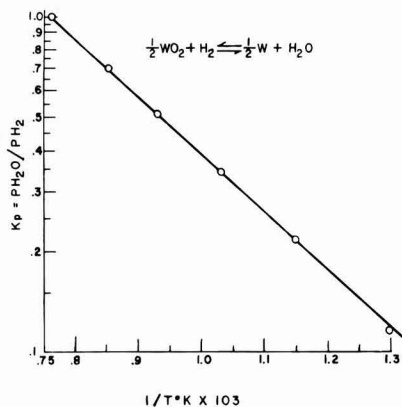


Fig. 2. Plot of  $\log K_p = \frac{P_{H_2O}}{P_{H_2}}$  vs.  $1/T^\circ K$  for the system  $WO_2-H_2-W-H_2O$ .

(Kopp's rule) for  $WO_3$  since no literature values are available.

$$\Delta C_p = 6.96 + 4.32 \times 10^{-3}T - 0.08 \times 10^{-5}T^2 \quad (I)$$

The equilibrium values in Table II were treated by means of Sigma functions and the method of least squares, using the value for  $\Delta C_p$ , to yield the following equations for this reaction:

$$\Delta H^\circ = 21,000 - 6.96T + \frac{4.32}{2} \times 10^{-3}T^2 + 0.08 \times 10^5 T^{-1} \quad (II)$$

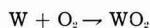
$$\Delta F^\circ = 21,000 + 6.96 T \ln T - \frac{4.32}{2} \times 10^{-3}T^2 + \frac{0.08}{2} \times 10^5 T^{-1} - 63.1T \quad (III)$$

From these were calculated,

$$\Delta H^\circ_{298} = +19.4 \pm 0.2 \text{ kcal/mole W}$$

$$\Delta F^\circ_{298} = +13.9 \pm 0.2 \text{ kcal/mole W}$$

Literature values of  $\Delta F^\circ_{298}$  and  $\Delta H^\circ_{298}$  (24) for the reaction  $2H_2 + O_2 \rightarrow 2H_2O$ , were used to calculate the following values of  $\Delta F^\circ_{298}$  and  $\Delta H^\circ_{298}$  for the reaction,



$$\Delta F^\circ_{298} = -123.1 \pm 0.3 \text{ kcal/mole W}$$

$$\Delta H^\circ_{298} = -135.0 \pm 0.3 \text{ kcal/mole W}$$

The standard entropy values for W and  $O_2$  (25) were used to calculate the standard entropy of  $WO_2$ .

$$S^\circ_{298} WO_2 = 17.1 \pm 1.0 \text{ e.u.}$$

Table III. Bomb calorimeter results

Reaction	$-\Delta H^\circ_{298}$ kcal/mole W
$W + 3/2 O_2 \rightarrow WO_3$	199.5
$W + 3/2 O_2 \rightarrow WO_3$	198.5
$W + 3/2 O_2 \rightarrow WO_3$	199.1
$WO_2 + 1/2 O_2 \rightarrow WO_3$	62.0
$WO_2 + 1/2 O_2 \rightarrow WO_3$	61.4
$WO_2 + 1/2 O_2 \rightarrow WO_3$	60.8
$WO_2 + 1/2 O_2 \rightarrow WO_3$	62.3
$WO_{2.72} + 0.28/2 O_2 \rightarrow WO_3$	15.0
$WO_{2.72} + 0.28/2 O_2 \rightarrow WO_3$	16.2
$WO_{2.72} + 0.28/2 O_2 \rightarrow WO_3$	17.1
$WO_{2.72} + 0.28/2 O_2 \rightarrow WO_3$	15.8
$WO_{2.90} + 0.10/2 O_2 \rightarrow WO_3$	4.7
$WO_{2.90} + 0.10/2 O_2 \rightarrow WO_3$	5.9
$WO_{2.90} + 0.10/2 O_2 \rightarrow WO_3$	6.2
$WO_{2.90} + 0.10/2 O_2 \rightarrow WO_3$	6.4

There is no literature value available for comparison, but it is reasonable since  $S^\circ_{298}$  of  $WO_3 = 19.9$  e.u. (26). The heat of formation of  $WO_2$  was also obtained by direct combustion technique. The results of the bomb calorimeter runs are tabulated in Table III.

The data in Table III can be used to determine the heats of formation of the oxides as summarized in Table IV.

### Summary

The equilibrium values obtained for the system  $W-WO_2-H_2O-H_2$  are slightly lower than the experimental data available in the literature for this system.  $\Delta H^\circ$  of  $WO_2 = -135.0 \pm 0.3$  kcal as calculated from these data and  $\Delta H^\circ$  of  $WO_2 = -137.0 \pm 1$  kcal as calculated from combustion experiments also reported here.  $S^\circ_{298}$  of  $WO_2 = 17.1 \pm 1.0$  e.u. (from equilibrium data).  $\Delta H^\circ WO_{2.72} (W_{18}O_{10}) = -183 \pm 1$  kcal and  $\Delta H^\circ WO_{2.90} (W_{20}O_{16}) = -193 \pm 1$  kcal. These values were obtained by combustion experiments and no literature values are available for comparison.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

Table IV. Heats of formation of tungsten oxides

Oxide	Heat of formation $\Delta H^\circ$ kcal/mole W	Method of determination	Literature value kcal/mole W
$WO_3$	$-199 \pm 1$	combustion	$-200.2 \pm 0.10$ (20)
$WO_2$	$-137 \pm 1$	combustion	$-135$ (27)
$WO_2$	$-135.0 \pm 0.3$	equilibrium	$-134 \pm 2$ (27)
$WO_{2.72} (W_{18}O_{10})$	$-183 \pm 1$	combustion	—
$WO_{2.90} (W_{20}O_{16})$	$-193 \pm 1$	combustion	—

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## Electropolishing Silicon in Hydrofluoric Acid Solutions

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### ABSTRACT

Silicon is electropolished in hydrofluoric acid solutions if a critical current density is exceeded. Below the critical c.d., silicon dissolution is largely divalent, and a thick solid layer forms. This film is unstable and reacts slowly with the electrolyte to form tetravalent silicon and hydrogen gas. In the electropolishing region, silicon dissolution is mainly tetravalent with the formation of a very thin high resistance type of film.

Experimental results on the effect of HF concentration, viscosity, and temperature indicate that electropolishing begins when the HF concentration at the silicon becomes limited by the rate of "mass transfer" of HF from the solution bulk to the surface.

Silicon is a semiconductor material used in making solid-state electronic devices. In their manufacture, it is necessary to employ chemical and electrochemical techniques to remove damaged surface material and/or shape the silicon to a particular geometry. The principle advantage of electrochemical over chemical methods of removing silicon is that the amount and the place where the material is to be removed can be controlled more easily. It is usually desirable that the surface of the silicon be polished after processing.

The technique of electropolishing involves making the metal to be polished anode in a suitable electrolyte at a current density sufficient to produce a thin continuous anode film on the surface. The anode film must be soluble in the electrolyte, but not too soluble or no appreciable electropolishing film will be built up at a reasonable current density. The electropolishing anode film is described by various workers as either a solid or highly viscous liquid layer. Polishing requires both brightening and smoothing. Hoar and Mowat (1) have proposed that the brightening effect is due to a random transfer of metal atoms into vacant cation sites in the anode film. Smoothing is due to preferential

dissolution of the film at high points on the surface.

Previous work on electropolishing silicon is almost nonexistent. Uhlir (2) was able to electropolish *p*-type silicon in a largely nonaqueous electrolyte of ethylene glycol containing some HF.

Electropolishing silicon appears practical only for *p*-type material at the present time since an internal voltage barrier is formed in *n*-type semiconductors (3) which causes excessive heating of the electrode before the required polishing current is attained. Methods of breaking down the voltage barrier by introducing hole-electron pairs with heat and/or light is effective with germanium, but this is difficult if not impossible with silicon because of its higher energy gap.

The experimental work was done in two parts. First, a number of exploratory experiments were performed to determine the best electrolyte and general conditions for electropolishing. This work was done with silicon electrodes held vertically in solution and without temperature control. The second part was done more carefully with the silicon positioned horizontally facing up and the temperature controlled.



### Preliminary Experiments

Most of the preliminary experiments were carried out with 1 ohm cm single-crystal *p*-type silicon electrodes. A number of electrolytes were investigated to determine one suitable for electropolishing silicon.

Strong alkaline solutions chemically attack silicon, forming a soluble silicate and hydrogen gas. The rate of reaction increases rapidly with temperature. If a piece of silicon is made anodic in hot 1*N* KOH, however, the chemical attack stops above a critical anode potential. The surface is passivated. Furthermore, after the cell current is interrupted, the hot alkaline solution requires several minutes to break through the passive layer and resume chemical attack of the silicon. A brief cathodic treatment reactivates the silicon immediately. Alkaline solutions do not appear promising for electropolishing silicon. The passivating anodic film formed, however, may be of value in stabilizing the surface electronically (4).

Electrolytes containing the fluoride ion were considered since they can be made to form soluble fluosilicate complexes with silicon. The most successful electrolyte found for electropolishing silicon was hydrofluoric acid. For a given set of conditions of HF concentration, temperature, viscosity, and stirring, there is a critical current density which must be exceeded before electropolishing can take place. Below this critical current density, a thick solid anode film forms on the silicon. For example, Uhler (2) reported that silicon does not electropolish in 24 to 48% HF solutions up to 0.5 amp/cm<sup>2</sup> because of a thick anode deposit. As will be seen later, higher current densities are required to electropolish silicon at these HF concentrations.

The HF concentration range in which a vertical *p*-type silicon electrode is electropolished at 400 ma/cm<sup>2</sup> current density is shown in Fig. 1. There was no temperature control in this experiment. The effective resistance of the electrolytic cell and the power dissipated in the cell were measured at the same time. These data are included only to show the qualitative effect of HF concentration on the cell resistance and power dissipation. At low HF concentrations the cell resistance is high, the power

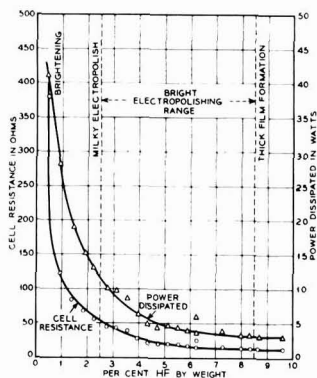


Fig. 1. Cell resistance and power dissipated in an electropolishing cell vs. HF concentration using a vertical *p*-type silicon anode at 400 ma/cm<sup>2</sup> density.

dissipated as heat is large, and the silicon is anodically etched but not electropolished. A clear polished silicon surface is not obtained until the HF concentration is at least 2.5%. More concentrated solutions of HF decrease the effective cell resistance and thus the power dissipated in the cell. The thick film begins to form at about 8.5% HF under the conditions of this experiment.<sup>1</sup> There is no discontinuity in the cell resistance with film formation which indicates that the thick film is probably porous.

Anode efficiency measurements were made during electropolishing in 5% HF using a vertical *p*-type silicon electrode. Since there was a tendency for the current to oscillate in the electropolishing range, it was necessary to employ a copper coulometer to integrate the current used. Assuming a silicon valence of 4, an anode efficiency of  $105 \pm 2\%$  was obtained which indicates that about 5% of the current formed divalent silicon. The anode efficiency appears to be independent of current density over the range studied between 110 and 850 ma/cm<sup>2</sup>. The rate of silicon dissolution by electropolishing in 5% HF calculated from the observed anode efficiency and the electrochemical equivalent for silicon is  $3.3 \times 10^{-5}$  cm<sup>2</sup>/coulomb. At 500 ma/cm<sup>2</sup>, the etching rate is  $1.7 \times 10^{-5}$  cm/sec (0.0004 in./min).

A silicon electrode held vertically in the solution without temperature control requires a relatively high minimum current density of about 300 ma/cm<sup>2</sup> to start electropolishing in 5% HF. A high current density promotes rapid electropolishing which is often desirable. However, the *I*<sup>2</sup>*R* heat generated in the silicon at these current densities can be excessive and cause the solution around the electrode to boil and even melt the soft solder connection made to a copper wire. It was of a practical interest, therefore, to investigate the various parameters of the silicon electropolishing process to determine how the minimum current density for electropolishing could be reduced.

### Experimental Arrangements Using a Horizontal Electrode

A cross-section view of the electrolytic cell designed for these experiments is shown in Fig. 2. The silicon electrode was mounted horizontally facing up

<sup>1</sup>Since this paper was submitted for publication, P. Wang, of Sylvania, in an oral presentation at the Buffalo Meeting of the Society reported that *p*-type silicon could be electropolished in 1-10% aqueous HF solutions.

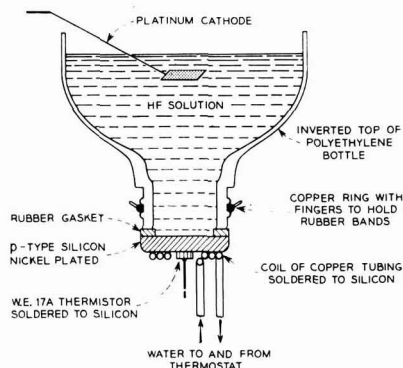


Fig. 2. Cross-section view of the electrolytic cell

to minimize stirring by convection. The arrangement also provides for a fairly uniform primary current distribution over the silicon and permits a visual examination of the surface at all times. A circular piece of single crystal  $3.5 \Omega \text{ cm}$  *p*-type silicon about 2.5 cm in diameter and 0.5 cm thick was used in most of the experiments. After the silicon was nickel plated by the "electroless" process (5), a coil of 3-mm diameter copper tubing was soft soldered to the back side. This served the dual purpose of forming an ohmic contact to the silicon and a convenient means of controlling the silicon temperature. The temperature of the silicon during an electropolishing experiment was usually controlled to  $\pm 0.3^\circ\text{C}$  by pumping water through the coil at the rate of about 400 cc/min from a 1-gal thermostat reservoir. A Western Electric thermistor type 17A was also soldered to the back side of the electrode to measure temperature. The thermistor was connected in series with a 5 ma milliammeter and a 1.5 v No. 6 dry cell and calibrated in terms of current as a function of temperature.

Prior to each experiment, the top surface of the silicon was lapped with No. 600 mesh silicon carbide. The electrode was held tightly against the rubber gasket by two rubber bands (not shown) attached to the fingers of the copper ring.

Also not shown is the polyethylene syphon used to make electrode potential measurements against a saturated calomel reference electrode. One end of the syphon was heated and drawn to a fine capillary tip. The syphon was filled with the HF solution and plugged at the large end with rolled-up filter paper. The plugged end of the syphon dipped into a saturated solution of KCl which contained the reference electrode, while the capillary tip end dipped into the electrolytic cell and was positioned so that only one corner touched the silicon. This arrangement produces a negligible amount of masking by the capillary tip and yet insures sufficient proximity to avoid including an appreciable solution *IR* drop in the potential measurement. An error of 10 or even 100 mv in the potential is not important in this study. Considerable difficulty was encountered in obtaining potential data when gas was being evolved at the electrode. Gas bubbles have a tendency to enter the capillary tip when close to a gassing electrode. This often produces an open circuit. The best procedure was to lower the tip to touch the silicon for each potential measurement and then withdraw it some distance away.

The cathode was a 1 cm square sheet of platinum welded to a platinum wire. All the HF solutions were made up using 48% by weight reagent grade hydrofluoric acid. About 100 cc of solution was used in each experiment as this was the cell capacity. The power supply consisted of one or two large 45-v dry batteries with two slide wire rheostats in series to adjust the current.

#### Anode Potential—Current Density Characteristic

A typical anode potential-current density curve for a horizontal *p*-type silicon electrode facing up is shown in Fig. 3. The curve was obtained by slowly decreasing the rheostat resistance while the anode

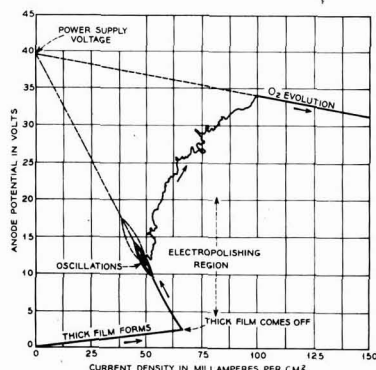


Fig. 3. Typical anode potential-current density curve for a horizontal *p*-type silicon anode facing up in 5% HF at  $25^\circ\text{C}$ .

potential and current were recorded on a L&N X-Y Recorder. In the initial portion of the curve, a thick film forms and there is considerable gassing. At a critical current density, the thick film suddenly starts coming off and floats to the surface. Gassing virtually ceases. If no change is made in the rheostat setting, the current slowly decreases while the anode potential increases. This is due to a high resistance film being formed on the silicon. The negative slope in the anode potential-current density curve above the critical c.d. is determined by the power supply voltage and the rheostat resistance. If the straight line sections are projected back to zero current, they intersect the potential axis at the power supply voltage as shown in Fig. 3. When the anode potential reaches about 10 v, oscillations in current and potential occur. It may take several minutes to reach this condition. The transition can be hastened by raising the voltage applied to the cell. If the transition stage in Fig. 3 had been allowed to continue, the current and potential would have changed further along the same straight line; however, the oscillations would have stopped at about 17 v. In one experiment, the transition stage was allowed to continue for about 1 hr and the anode potential rose to about 30 v while the current density dropped to 20 ma/cm. The anode potential-current density curve above the initial transition stage is erratic as seen in Fig. 3. It is interesting to note that above 20 v anode potential, if the current is interrupted, a burst of gas is given off the surface of the horizontal silicon electrode. At a second critical current density, continuous oxygen evolution begins and the anode potential decreases while the current increases in a runaway process.

The E-I curve for a vertical electrode (with convection stirring) differs from the curve shown in Fig. 3 in that there is no abrupt change in the current and potential when electropolishing starts. Perhaps this is due to electropolishing beginning at only some areas at first and gradually spreading to the entire surface with increasing current.

If a voltage is suddenly applied to the cell which is sufficient to pass more than the critical current density initially, the anode potential and current will pass quickly into the electropolishing region.

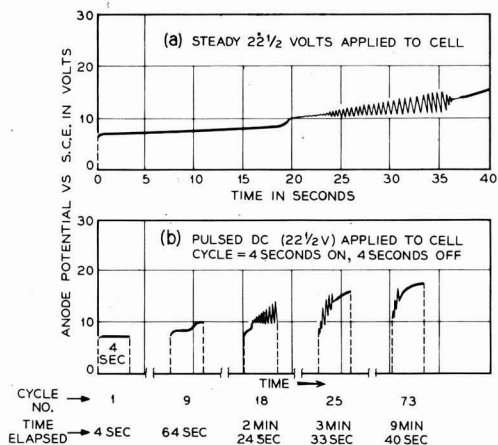


Fig. 4. Anode potential-time curves for p-type silicon in 5% HF at 30°C: (a) steady 22½ v applied to cell; (b) pulsed D.C. (22½ v) applied to cell cycle: 4 sec on, 4 sec off.

A short induction period is required before the transition takes place, however, as shown in Fig. 4a which is a record of the anode potential change with time. A 22½-v battery was connected directly across the cell with no external resistance. Electropolishing does not begin until after 20 sec, at which time there is a step in the curve. Oscillations also begin and tend to increase in amplitude with time. Eventually the oscillations stop and the anode potential rises to a fairly steady value approaching the supply voltage.

Another technique employed was to apply a pulsed d-c voltage to the cell. The anode potential-time curves obtained under these conditions are shown in Fig. 4b. A cycle of 4 sec on and 4 sec off was used. The first appearance of the step in potential comes during the ninth cycle or about 1 min after the start. In successive pulses, the E-t curve changes so that a greater portion of the pulse time is occupied in the electropolishing region.

The simplest means of electropolishing silicon in aqueous hydrofluoric acid solutions is to apply a constant voltage between 10 and 20 v directly across the cell. Initially the current is large and is limited mainly by the electrolyte resistance. As the high resistance electropolishing film forms, the current drops and an increasing amount of the applied voltage appears across the electropolishing film. The potential between the silicon and the electrolyte thus automatically stays in the electropolishing region.

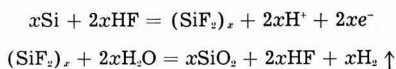
#### Nature of Thick Anode Film Prior to Electropolishing

The most reproducible and stable part of the E-I curve for silicon in HF solutions is the initial section where a thick, solid film forms. The film is removed easily for study by briefly raising the current above the critical value. It comes off in large flakes and floats to the surface. The film is a brown color when formed on a surface lapped with No. 600 mesh silicon carbide. If the silicon is electropolished beforehand, several orders of interference colors can be seen as the film thickens. Thick pieces grown on

an electropolished surface are an orange-red color and glassy in appearance. Electron and x-ray diffraction studies show the film to be amorphous. This is characteristic of anodically grown films. The film appears to be a good insulator since it holds a static charge well. Pieces of the film react with explosive violence when put in contact with a strong oxidizing agent such as nitric acid. This result and the fact that Uhlir (2) obtained an effective valence of about two for the dissolution of silicon with the thick anode film being formed means that the film contains divalent silicon. Brouillet and co-workers (6) also found that in perchloric acid solutions, if a metal has several valence states, the anodic dissolution process favors the lowest one. The gas evolved during the thick film formation is hydrogen (2). Hydrogen evolution at an anode is unusual. In this case it is due to the chemical reduction of hydrogen ions by divalent silicon in the anode film. Hydrogen has also been observed from anodized aluminum (7) and magnesium (8) as the result of a similar chemical reduction process.

Fluoride ion has also been detected in the thick anode film by means of a spot test. This could be due to some HF being trapped inside but it also could mean that the film is composed of silicon subfluoride. Subfluorides of silicon have been reported in the literature. Attempts by Ruff (9) to repeat this work were unsuccessful, nor could he obtain evidence of a subfluoride by means other than those previously tried. Recently, Schmeisser (10) has reported forming subfluorides of silicon by the reduction of  $\text{SiF}_2\text{Br}_2$  or  $\text{SiFBr}_3$  with magnesium in an ether solution.

On the basis of the experimental results it appears likely that some silicon subfluoride ( $\text{SiF}_2$ )<sub>x</sub> is formed anodically. This is unstable in water solutions and is oxidized to tetravalent silicon with hydrogen gas evolved as follows:



#### Critical Current Density for Electropolishing

In order to enter the current-potential region where the electropolishing of silicon takes place, a critical current density,  $i_c$ , must be reached. The effects of temperature, HF concentration, viscosity, and the concentration of the final anode product, fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), on  $i_c$  were determined. All of the data were obtained starting with a lapped surface.

*Effect of temperature.*—The E-I curve in Fig. 3 was obtained at 25°C. If the temperature of the silicon is varied, it is found that the critical current required to start electropolishing silicon also changes. The critical current density  $i_c$ , is defined as the current density at which the thick anode film starts coming off and the transition to the electropolishing region takes place. Higher temperatures require higher current densities. This is illustrated in Fig. 5. At a given current density, the anode potential decreases with increasing temperature. It can be seen from Fig. 5, however, that the anode potential at

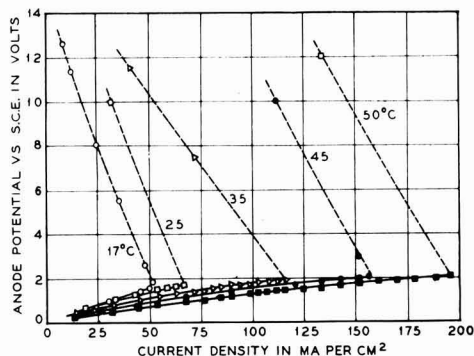


Fig. 5. Anode potential-current density curves for p-type silicon in 5% HF at various temperatures.

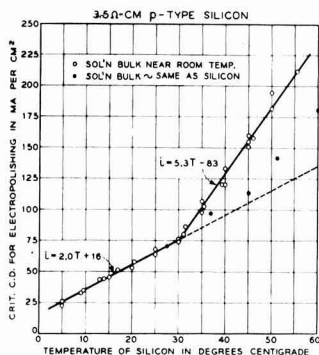


Fig. 6. Effect of temperature on the critical current density required to start electropolishing silicon in 5% HF.

which electropolishing starts, increases with temperature.

The critical current density required to start electropolishing silicon in 5% HF from 5° to 60°C is shown in Fig. 6. Most of the data were obtained with the bulk of the solution near room temperature. The points fall along two straight lines which intersect near room temperature. The critical current density is reproducible within  $\pm 2$  ma/cm<sup>2</sup> below 30°C. Above 30°C, the reproducibility decreased with an increasing temperature difference between the silicon and the solution bulk. A few additional points were obtained under conditions where the solution temperature was about the same as that of the silicon. These results will be discussed later.

**Effect of HF concentration.**—At a constant silicon temperature, the  $i_c$  is linearly related to the HF concentration. Data obtained at four temperatures, two below and two above 30°C, are shown in Fig. 7. The straight lines drawn are obtained from the empirical equations derived from the  $i_c$ - $T$  data in Fig. 6. These equations were modified to include the effect of HF concentration, assuming that  $i_c$  is directly proportional to the HF concentration. The data obtained in the two experiments agree rather well.

**Effect of viscosity.**—The viscosity of the solution is known to be a factor in electropolishing metals. To test the effect of viscosity alone, it is necessary that an inert material be used to change the viscosity. Glycerin is often used and was chosen for this

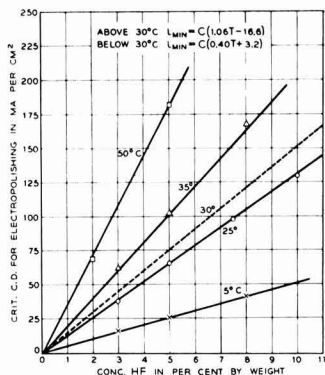


Fig. 7. Effect of HF concentration on the critical current density required to start electropolishing silicon at various temperatures.

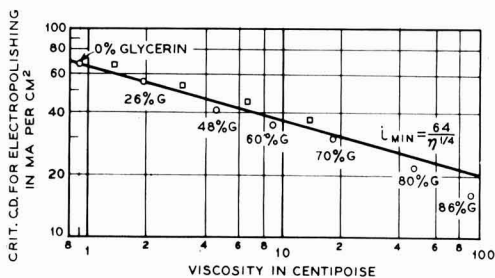


Fig. 8. Effect of viscosity on the critical current density required to start electropolishing silicon in 5% HF and glycerin at 25°C.

work. All solutions contained 5% by weight HF. Solution viscosities were obtained from published data on glycerin-water solutions (11). The data obtained in two series of experiments are presented on a log-log plot in Fig. 8. The straight line drawn for the empirical equation  $i_c = 64\eta^{1/4}$  is a reasonable fit to the data. It shows that  $i_c$  is inversely proportional to the fourth root of the viscosity. Large deviations from this relation occur only at high viscosities, i.e., solutions 80 and 86% by weight glycerin.

**Effect of  $H_2SiF_6$  concentration.**—Some workers (12) have found that the critical c.d. for electropolishing certain metals is decreased when the concentration of the metal in solution is increased. A series of six solutions were made up containing 5% HF and from 0 to 25% by wt fluosilicic acid ( $H_2SiF_6$ ). The critical current density required to start electropolishing silicon in aqueous HF was not affected by the addition of fluosilicic acid.

### Electropolishing n-Type Silicon

A few attempts were made to electropolish n-type silicon at 5°C where low polishing current densities can be used ( $\sim 25$  ma/cm<sup>2</sup>). The silicon was always pitted after the anodic treatment. This is due to the voltage barrier in the surface layer of the silicon which breaks down only at the points of pitting. It may be possible to obtain uniform breakdown of the voltage barrier by illuminating the silicon with a strong light. Even with a very strong light, however,

it will not be possible to electropolish *n*-type silicon rapidly since this requires a high current density.

### Discussion

The experimental results suggest that silicon begins to electropolish in hydrofluoric acid solutions when the HF concentration at the anode surface decreases to a critical value. Hydrofluoric acid is consumed in the anode process. The supply of HF at the anode surface is determined by its rate of "mass transfer," i.e., by diffusion, convection, and migration from the bulk to the electrode surface. The nature of "mass transfer" of the reacting species to a horizontal silicon anode in HF solutions prior to electropolishing is complicated by the fact that an anode film is formed and gas is evolved. The contribution due to ion migration probably can be neglected. There are, however, several sources for "free convection" at the surface as a result of density differences in the solution near the surface. The thick anode film that forms consumes HF which tends to make the solution layer at the surface less dense than the bulk. The anode film reacts slowly with the electrolyte, however, to form fluosilicic acid and hydrogen gas. Fluosilicic acid should tend to counter the decrease in density due to the consumption of HF. The hydrogen gas that comes off produces a stirring effect like that due to density differences in fluids. Bubble size is probably an important factor in determining the effectiveness of stirring due to gassing. Thermal gradients in solutions also produce convection stirring. If the horizontal silicon electrode is colder than the solution above it, the solution layer at the surface is more dense than the bulk and there is no tendency for convection stirring due to thermal effects. When the silicon electrode becomes warmer than the bulk solution, however, the surface layer becomes less dense than the bulk and convection stirring results. The break in the  $i_c - T$  curve in Fig. 6 shows this effect very clearly. Above 30°C the silicon is warmer than the bulk solution and the thermal gradient contributes to the "free convection." An attempt was made to thermostat the solution to the same temperature as the silicon. The few experimental points obtained under these conditions lie between an extension of the lower line and the upper line in Fig. 6. The results are in the right direction, but apparently thermal gradients have not been entirely eliminated.

If the reacting species reaches the electrode only by diffusion under steady-state conditions, the critical (or limiting) current density may be given by:

$$i_c = \frac{nFD C_b}{\delta} \quad (I)$$

where  $n$  = the number of electrons involved in the electrode reaction,  $F$  = Faraday's constant, amp sec/g equivalent,  $D$  = diffusion coefficient,  $C_b$  = bulk concentration of reacting species, and  $\delta$  = thickness of hypothetical diffusion layer. The diffusion layer thickness  $\delta$  is not a constant under conditions that are nonsteady state and where "free convection" contributes to the "mass transfer" of the

reacting species. Tobias, Eisenberg, and Wilke (13) have shown that the diffusion layer thickness depends on the electrolyte composition, viscosity, diffusion constant, density coefficient, electrode reaction, electrode height, shape, and orientation. With vertical electrodes under conditions of "free convection",

$$\delta = 1.91 \left[ \frac{x \eta D \rho_b}{g(\rho_b - \rho_s) \rho} \right]^{1/4} \quad (II)$$

where  $x$  = vertical height on electrode surface,  $\eta$  = viscosity,  $\rho_b$  = bulk solution density,  $\rho_s$  = solution density at the surface,  $\rho$  = average solution density, and  $g$  = acceleration due to gravity. It is convenient to relate the density difference to the concentration difference by a specific densification coefficient,  $\alpha$ , defined by:

$$\alpha = \frac{\rho_b - \rho_s}{\rho_b(C_b - C_s)} \quad (III)$$

where  $C_s$  is the reacting species concentration at the surface. At  $i_c$ ,  $C_s = 0$ , then from Eqs. (I)-(III)

$$i_c = 0.52 nFD^{3/4} C_b^{5/4} \left[ \frac{g \alpha \rho}{x \eta} \right]^{1/4} \quad (IV)$$

The general form of this equation has been verified experimentally by Wagner (14) and Wilke, *et al.* (15).

A similar mathematical analysis for horizontal electrodes has not been developed because of the complexity of the problem. However, empirical studies by Schmidt (16) on heat transfer and Fenech (17) on copper deposition under free convection conditions indicate that the critical or limiting current density on horizontal electrodes is proportional to the 4/3 power of the bulk concentration and is inversely related to the 1/3 power of the viscosity.

The critical current density at which electropolishing starts on a horizontal silicon electrode in HF solutions was found experimentally to vary linearly with HF concentration and temperature and inversely with the fourth root of viscosity. The diffusion constant and viscosity in Eq. (IV) are both temperature sensitive. Over a short range of temperatures,  $i_c$  should be approximately a linear function of temperature since  $D \propto T$  and  $\log \eta \propto 1/T$ . These effects of HF concentration, viscosity, and temperature are in the right order of magnitude to assume that the  $i_c$  for electropolishing silicon in HF solutions is controlled by the rate of "mass transfer" of HF from the bulk to the surface. The sudden change in the slope of the  $i_c - T$  curve in Fig. 6, signifying the start of convection stirring due to thermal effects, is also indicative that  $i_c$  is controlled by the "mass transfer" of HF to the silicon surface.

The mechanism for electropolishing silicon in HF solutions involves an understanding of the significance of the critical current density required to start electropolishing. Experimental results, while not extensive, do suggest that  $i_c$  is determined by the rate of "mass transfer" of HF from the bulk to the surface. As long as the HF concentration at the surface remains above a critical value, silicon dis-

solution is divalent and a solid anode film is formed, presumably  $(\text{SiF}_2)_x$ . At  $i_c$ , there is insufficient HF at the anode surface to continue this process and the next anode reaction begins. This involves dissolution of silicon in the tetravalent form. The anode product formed under these conditions produces the electropolishing film. The most likely assumption is that it is some form of  $\text{SiO}_2$ . Silicon dioxide is readily dissolved in HF which is consistent with the observation that the electropolishing film on silicon is always very thin—less than interference-color thickness.

#### Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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## Electrochemical Measurement of Oxide Formation

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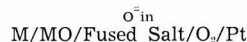
#### ABSTRACT

Measurements have been made of the potential developed between a metal wire covered with its oxide and a platinum wire over which air or oxygen was passed. The electrolyte was the eutectic mixture of  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , containing dissolved  $\text{CaO}$  and operated at various temperatures between  $550^\circ$  and  $750^\circ\text{C}$ . Heavy metal oxides are only very slightly soluble in this melt, so that the measured potential corresponds to the formation of metal oxide from the elements. Iron probably formed  $\text{FeO}$ , nickel formed  $\text{NiO}$  below  $658^\circ$  and probably a solid solution of  $\text{LiNiO}_2$  in  $\text{NiO}$  at higher temperatures, while copper formed  $\text{Cu}_2\text{O}$ . Gold showed only the thermoelectric potential expected. The values found are in agreement with the free energy of formation of the oxides as determined by other methods.

An electrode reversible to oxygen gas and oxygen ion is useful both for thermodynamic measurements involving oxide formation and for determining the oxide ion activity in reactions of metallurgical interest. Such an electrode has not been possible in water solution, but it was shown many years ago that molten metal in contact with oxygen gas appeared to serve as such an electrode in fused salts at high temperatures (1). More recently a study of solid metal electrodes with oxygen gas in fused salts has been published by Lux (2), whose work has been critically reviewed and extended by Flood, Forland, and Motzfeldt (3). These last workers showed that a platinum wire surrounded by oxygen and immersed in a fused salt gave reproducible potentials,

depending on the oxide ion concentration in the melt. The dependence of the potential on the concentration was discussed by Flood and Forland (4).

The authors combined this electrode with one made from a heavy metal covered with its oxide. The cell may be represented as



The metals studied form oxides which are only very slightly soluble in the molten salt, the melt giving no chemical test for the metal after use. The authors assume saturation with the metal oxide and, therefore, assume that the reaction measured is the formation of the metal oxide from its elements. In such a reaction, the oxide ion concentration should have no effect on the measured potential, which was found to be the case, save in one experiment to be

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discussed below. The only variable is the oxygen pressure, to which the measured potential showed the proper relation.

### Experimental

**Solvent.**—The fused salt solvent was the eutectic mixture of  $\text{Li}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , with 28.4%  $\text{K}_2\text{SO}_4$ . This has the high temperature stability of the other alkali sulfates, and the advantage of a lower melting point, 535°C. The lower melting point permitted study at temperatures at which corrosion by the oxide-containing melt was less severe, and lowered the vapor pressure of alkali oxides to a negligible value. Lux was forced to operate at 950°, where both problems were accentuated. The salts were reagent grade and were used without purification other than drying at 110°. Calcium oxide was added to establish the oxide ion concentration, which was varied from 0.1% to saturation. The latter is only approximately known, but is not far from 1%.

**Cell and furnace.**—The cell was heated in a Lindberg Pot Furnace with a controller operated by a thermocouple which measured air temperature in the furnace. This was constant only to  $\pm 4^\circ$ , but the large heat capacity of the cell itself reduced the variation as measured in the electrolyte to  $\pm 1^\circ$ , while installation of a stainless steel pot later reduced it to a few tenths of a degree.

A thick insulating top for the furnace was constructed of Marionite asbestos, which was covered on the bottom with a stainless steel sheet when the metal pot was used. The top was mounted on a Transite board with guides, support rods, and pulleys so that it could be raised and lowered while remaining aligned with the furnace. All electrodes and other fittings were mounted rigidly on the top, and raised and lowered into the melt by this means. Where the metal reflector was not used, the top was painted with water glass to prevent loose asbestos from falling into the melt.

The cell itself was a fused alumina crucible, Morganite, which was not attacked by the fused sulfates or even by moderate oxide concentrations. Tubing of this grade alumina was not available, so thermocouple well and gas inlet tubes were of less resistant alumina containing some silica. There is no evidence that a very small silica or alumina content in the fused salt was objectionable.

In the most successful cell the simplicity of the electrode system is noteworthy. The heavy metal electrode was a stout wire of the metal arranged to project into the melt when the top was lowered. An alundum shield was tried, but appeared to make no difference in the emf, and not as much as hoped in the corrosion. Preoxidation of the wire surface did not change the ultimate voltage but decreased the time required to reach equilibrium.

The most successful type of oxygen electrode was modelled on the Hildebrand hydrogen electrode long used in aqueous solution. An alundum tube 8 mm OD, 3 mm ID immersed 1 cm in the fused salt and extending through the top admitted the gas, either air or oxygen. A platinum wire was inserted through this tube and allowed to extend about 1 cm further into the liquid. Alundum appears to be a

good enough insulator up to our highest temperatures so that no electrical losses were observed.

**Gases.**—Air from a regulated pressure line or oxygen from a cylinder was dried with sulfuric acid and filtered through glass wool.

**Potential measurement.**—Potentials were measured on a L&N Student Potentiometer, which was sufficiently precise for the experiments where "equilibrium" potentials might vary by several millivolts. There was no correlation between the random variations in voltage and the temperature variations in the cell. This would be expected to be the case from the measured temperature effect in Table I.

### Results

The potentials observed when a metal wire and an oxygen electrode are inserted in a sulfate eutectic with dissolved oxide approach stable values at rates differing for the various metals. Iron at times was stable after 1 hr, although usually several hours were required. Copper required at least 24 hr, while nickel at the lowest temperature took even longer. Special care is needed to avoid a dependence on the rate of flow of the gas, whether air or oxygen, at the oxygen electrode. Flood, Forland, and Motzfeldt found that the rate of flow caused a change in measured potential when using oxygen electrodes in an oxide-ion concentration cell, but were able to eliminate it by insuring that the furnace atmosphere was identical to the entering gas. This source of error did not explain our variations when using air as the gas in a cell exposed to air, and investigation of each electrode was required.

The heavy metal-metal oxide electrodes change their potential when stirring takes place around them, the reason probably being the same as in the case of the poisoned oxygen electrode to be discussed below. However, it was possible to show by physically moving the electrode that, when located as much as 2 cm from the gas stream, no appreciable stirring took place. The emf reported is measured when the metal oxide is in a region essentially quiescent.

The potentials measured at these electrodes might be expected to be incorrect due to the occurrence of "mixed potentials." It was observed that the metal wires were heavily oxidized above the solution level by direct reaction with the gas present in the cell. In some cases the wire was led in through an alundum tube just dipping into the melt, which should much decrease the rate of chemical oxidation. The potentials were the same as with a bare wire exposed to the gas throughout, so the practice was discontinued in order to simplify the experimental arrangement. The fact that the potentials measured agree reasonably well with those calculated from the free energies of formation of the metal oxides appears to mean that mixed electrode conditions were not present. It is suggested that the solubility of oxygen in the melt is quite low, and that the diffusion of oxygen gas through a metal oxide layer is very slow. Under these circumstances, the conditions for mixed potential due to direct reaction would only be attained very close to the surface of the melt. The greater part of the wire be-

low the surface could react only in the electrochemical sense, so that the standard potential would be observed. It would seem to be of considerable interest that such simple experimental arrangements may be used without the appearance of mixed potentials.

At the oxygen electrode conditions are different since stirring occurs, and stirring caused potential changes in some cases. The observation that deposits were formed on the platinum wire of the oxygen electrode in all cells which showed a stirring potential at that electrode provided the explanation for it. The deposits gave an iron test on solution in HCl, so that iron compounds, presumably oxide, are the cause of the variability. Occasional cells in which no deposit formed were free of stirring potential. It proved very difficult to keep the iron content of the melt low enough to prevent formation of the deposit, since even reagent grade chemicals usually have a trace of iron. When an iron wire electrode was being measured, it was at first considered that stirring potentials were unavoidable. However, it was found that if the gas stream was shut off, the observed potential rose to a steady and reproducible value, and maintained it for many hours, finally falling off as the dissolved oxygen concentration in the cell decreased. Many observations were made with this technique, and some of the values given are open, therefore, to the objection that, although reproducible, they may not represent true equilibrium for the reaction postulated. These potentials are indicated as such.

Later in the work a method was developed which prevented the formation of the deposits on the platinum wire. Addition of active aluminum oxide or zirconium oxide, both of which have very low solubilities, to the cell contents before inserting the electrodes precipitates the small amount of dissolved iron (as a reddish brown solid on the powdered oxide), and prevents the deposition on the platinum of any which may be dissolved later, so that stable potentials are obtained, independent of stirring rate. With an iron electrode in the cell, a porous aluminum filter thimble surrounding the oxygen electrode serves to protect it from the very low iron concentration which is present in the melt. Many tests on used melts have shown that the equilibrium concentration of iron in the presence of dissolved CaO is too low for detection, but unless it is made still lower by a method like that indicated, deposits form on the oxygen electrode. It should also be mentioned that no substance has been found which is able to remove a deposit once formed. It is essential to keep the oxygen electrode free of iron at all times.

The poisoning observed for the Pt-O<sub>2</sub> electrode might be described equally well as a "mixed potential," as Wagner (5) has shown for similar poisoning at a Pt-H<sub>2</sub> electrode in aqueous solution. The aim in the present experiments has been to find a chemical explanation and means for preventing the deposit of poison.

The effect of iron oxide is to raise the apparent potential of the oxygen electrode, while stirring

Table I. Standard potentials for metal oxide formation

Metal	Temp, °C.	E <sub>0</sub> , v	E <sub>0</sub> (litt)	Ref.
Fe	584	1.111*		
	588	1.085	1.070 (FeO) 1.079 (Fe <sub>3</sub> O <sub>4</sub> )	(6)
	616	1.097*	1.058 (FeO) 1.062 (Fe <sub>3</sub> O <sub>4</sub> )	
	667	1.089*	1.043 (FeO) 1.043 (Fe <sub>3</sub> O <sub>4</sub> )	
Cu	714	0.520	0.540 (Cu <sub>2</sub> O)	(6)
Ni	658	0.788	0.792 (NiO)	(6-8)
	682	0.884*		
	692	0.932* higher	(black valence oxide)	
	708	1.032* nickel oxide		
Au	617	0.025-0.008		
	716	0.025-0.008		

\* Steady emf after turning off gas.

lowers it, makes it less positive. Sufficiently rapid stirring might bring the emf down to that of an unpoisoned wire, but an impractical rate would be required. Using two poisoned platinum wires and stirring with oxygen around one, it has been possible to measure a potential as much as 200 mv between them although no voltage is found for unstirred wires. We propose that an iron oxide deposit absorbs cations from the melt, thus raising its positive potential, and that stirring disrupts this layer, thus lowering the voltage.

The potentials measured with several metal/metal oxide electrodes against a Pt-O<sub>2</sub> electrode in Li<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub> eutectic containing CaO are given in Table I. Most of the measurements were made with air rather than oxygen, since corrosion of the metals was much reduced. Enough use was made of pure oxygen to show the expected obedience to the Nernst equation in terms of oxygen pressure. The values given are the standard potentials for the formation of solid metal oxide from the elements at 1 atm oxygen pressure. The literature values given for comparison are calculated from the standard free energies of formation of the oxides as determined from heat capacities or from equilibria such as the reduction of the oxide with CO. The potentials are reproducible to ±0.005 v, which would be considered very poor in aqueous solution. However, variations as large or larger than this are common and so far unexplained in all high temperature cells. Some discussion of the individual cells follows.

*Iron-oxygen cell.*—Equilibrium was rapidly established between either an initially bright iron wire or one superficially oxidized and an oxygen electrode, usually operated with air. Considerable oxidation of the wire occurred outside the liquid, shortening the life of a wire as the temperature was raised. Although iron reduces alkali sulfates at high temperatures, test of solids, melt, and exhaust gas showed that no reduction had occurred in an experiment.

The emf at 588° was obtained with an unpoisoned oxygen electrode protected with an aluminum filter thimble. The other values were all obtained earlier



with poisoned electrodes, and the steady voltage after turning off the air stream as recorded. These latter values are therefore too high.

Attempts were made to determine the formula of the oxide formed on the wire. The oxide was cracked off a wire after use in a cell, and the ratio of Fe(II) to Fe(III) determined by the method of Cheesbrough (9). The ratio varied from 2 to 5, averaging 3.2 over ten samples, and no correlation between length of time in the cell and oxide composition could be found. We believe that FeO is the oxide primarily formed, and that the higher oxides are formed by direct oxidation, which is not electrochemical in nature. In no case could any iron be found in the melt after a run.

**Copper-oxygen cell.**—At the one temperature studied this cell gave a potential for the formation of  $\text{Cu}_2\text{O}$ . Since at this temperature  $\text{CuO}$  is less stable by about 6 kcal, there seems little doubt that the reaction measured was the formation of the lower oxide. Both oxides were found on the wire, with the red adhering closely and the black on the outside as is often found in the air oxidation of copper. The reaction was not studied with pure oxygen, since the cell was much slower than the iron cell to reach equilibrium and destruction of the metal occurs with too long exposure. No copper was found in the used melt.

Stirring potentials were found in some, not all, cases in these cells, apparently caused by iron impurities. The cells quoted were free of stirring potentials, but the voltage was rather lower than calculated, so that it is possible that true equilibrium had not yet been attained. An attempt to prevent stirring potentials with alumina demonstrated that this was possible, but the cell failed to reach an equilibrium potential in 12 hr.

**Nickel-oxygen cell.**—At  $658^\circ$  this cell gave a potential agreeing very closely with that expected for NiO. The oxide was greenish in color and formed as a tight layer with an extremely high resistance. Presumably because of this property, it was not possible to reach equilibrium starting with a bright nickel wire. It was necessary to equilibrate at higher temperatures, forming "black oxide" (see below) and then to reduce the temperature. The compound then turned green rapidly, and the potential fell as rapidly to that given for NiO. The high electrical resistance of NiO layers has been noted by Verwey (10). Perhaps by accident, stirring potentials were not encountered in the measurements at  $658^\circ$  giving green oxide, and no deposits formed on the platinum wire. This was not the case with the higher temperature "black oxide" experiments.

At the higher temperatures a black material formed on the nickel wire. It was a good conductor, but still came to equilibrium very slowly. It gave a much higher potential than did green NiO and showed pronounced stirring potentials; the emf rose with the temperature. The substance appears to contain nickel in a higher valence state, since it was able to oxidize HCl to  $\text{Cl}_2$ , and, slowly, water to  $\text{O}_2$ . Verwey prepared a black material with a high oxidation potential and a low electrical resistance by

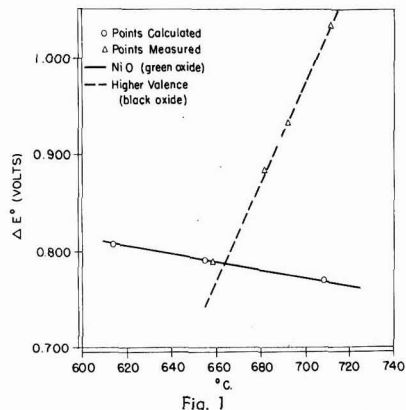


Fig. 1

the reaction of NiO with  $\text{Li}_2\text{O}$  at  $1200^\circ\text{C}$ . It is described as having the same crystal lattice as NiO, ( $\text{NaCl}$ ), but with a slightly smaller unit cell. In the crystal,  $\text{Li}^+$  ions fill some of the positions of  $\text{Ni}^{2+}$  ions at random and, for each lithium, one nickel must become trivalent to keep charge balance. This might be described as a solid solution of  $\text{LiNiO}_2$  in NiO.

Our experiments are consistent with the hypothesis that this solid solution is formed above  $663^\circ$  in contact with our sulfate eutectic containing  $\text{Li}^+$  and  $\text{O}^-$  ions. Below this temperature it decomposes to solid NiO, while  $\text{Li}_2\text{O}$  dissolves in the melt. If our measured  $E_0$  values are plotted against temperature, including the  $E_0$  values calculated for NiO from free energies, a transition at  $663^\circ$  seems to be indicated (see Fig. 1). The open circles are calculated from the thermal data (5).

We have attempted to obtain evidence for this transition by means of cooling curves. A mixture of Ni, NiO, sulfate eutectic and a small amount of CaO (dissolved) was heated at  $800^\circ$  until equilibrium was presumed to have been reached, and then allowed to cool slowly, following the temperature on a thermocouple recorder. Halts were not obtained in every trial, but they were found between  $660^\circ$  and  $663^\circ$  in a number of cases. Probably the transition is not fast enough for unambiguous thermal analysis, but the results lend confidence to the theory.

The "black oxide" was obtained with either air or oxygen at the oxygen electrode, and the potential followed the Nernst law, (observed increase in emf from air to oxygen, 31 mv, calc 33 mv). The potential in this case should also be dependent on the oxide ion concentration, but the changes in the latter were unfortunately not large enough to provide unambiguous evidence. In no case was nickel found in the melt, nor in the deposit on the platinum wire.

We therefore suggest that nickel in a fused sulfate bath containing both  $\text{Li}^+$  and  $\text{O}^-$  ions reacts with  $\text{O}_2$  below  $663^\circ$  to form NiO, while above this temperature the product is a solid solution of  $\text{LiNiO}_2$  in NiO. The possibility of similar reactions with other heavy metals and alkalis may depend on ionic diameters.

This explanation would imply that our emf values above the transition are not true  $E_0$  values, both be-

cause the oxide ion was not at unit activity and because a solid phase transition might require a very long time to reach equilibrium. Under these circumstances, the rise of apparent emf with temperature is not surprising.

**Gold-oxygen cell.**—Gold is not expected to form a stable oxide at the temperatures of our experiments. The only potential to be expected is the thermoelectric potential between Au and Pt, which should amount to about 10 mv. Although the potentials were erratic, those found were of the correct order of magnitude.

#### Acknowledgment

This work was supported in part by Research Contract AT-(40.1)-1526 between Duke University and the Atomic Energy Commission, whose assistance the authors thankfully acknowledge.

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## Equivalent Conductivities of $\text{AgNO}_3\text{-KNO}_3$ Mixtures

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The specific conductivities and the densities of  $\text{AgNO}_3\text{-KNO}_3$  mixtures have been determined by Polyakov (1). The densities have also been determined by Bloom and Rhodes (2). The density data of the two investigators agree within 1% where comparison is possible, except at the higher  $\text{AgNO}_3$  concentrations. Bloom and Rhodes agree with Spooner and Wetmore (3) on the density of pure  $\text{AgNO}_3$ . Thus, at higher  $\text{AgNO}_3$  concentrations, the data of Bloom and Rhodes were used. Polyakov's data on the specific conductivity of pure  $\text{AgNO}_3$  differ from those of Spooner and Wetmore. Thus, the present work is a redetermination of the specific conductivities of the mixtures, the values at high concentrations of  $\text{AgNO}_3$  being significantly different from those of Polyakov.

#### Experimental

The apparatus and techniques used were identical with those used by Duke and Fleming in a previous study (4). The thermocouple used for the measurement of the temperature of the cell was calibrated at the tin and lead freezing points, using especially purified samples of the metals.

The salts used were CP reagent grade, and the

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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mixtures were prepared by mixing carefully weighed amounts of each salt. In addition, the salt mixtures were partially analyzed, silver being determined by the Volhard method.

#### Results

Results are listed in Table I.

It is of interest to note that, when a plot of equivalent conductivity vs. composition is made, a very slight negative deviation from a straight line is observed at all temperatures. Thus,  $\text{AgNO}_3\text{-KNO}_3$  mixtures are, in this sense, "regular" solutions.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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Table I. Densities, specific and equivalent conductivities of  $\text{AgNO}_3\text{-KNO}_3$  mixtures at various temperatures

Mole fraction $\text{AgNO}_3$	350°C		325°C			300°C			275°C			250°C			
	$\rho$	$\lambda$	$\rho$	$\lambda$	$\rho$	$\rho$	$\lambda$	$\rho$	$\lambda$	$\rho$	$\lambda$	$\rho$	$\lambda$		
1.00	3.81	1.230	54.8	3.84	1.138	50.4	3.87	1.038	45.6	3.89	0.938	40.9	3.92	0.836	36.2
0.832	3.42	1.127	52.2	3.45	1.028	47.1	3.48	0.927	42.2	3.50	0.824	37.4	3.53	0.723	32.6
0.700	3.15	1.033	48.9	3.17	0.935	44.0	3.19	0.840	39.3	3.22	0.744	34.5	3.25	0.650	29.9
0.475	2.67	0.900	45.0	2.69	0.811	40.3	2.72	0.718	35.4	2.74	0.624	30.5	2.77	0.531	25.7
0.295	2.36	0.798	41.1	2.38	0.719	36.7	2.40	0.634	32.1	2.43	0.545	27.2	2.44	0.470	23.4
0.149	2.10	0.715	37.9	2.12	0.641	33.6	2.15	0.561	29.1	—	—	—	—	—	—
0.00	1.86	0.670	36.4	—	—	—	—	—	—	—	—	—	—	—	—

$\rho$  taken from Ref. (2) for pure  $\text{AgNO}_3$  and 0.832 mole fraction  $\text{AgNO}_3$ , and from Ref. (1) in the other cases.



## Electrolytic Iron Powders—Production and Properties

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A thorough discussion of all aspects of the production and use of electrolytic iron powder obviously would require more space than is available here. Consequently, after a brief historical review, we shall describe the production and properties of electrolytic iron powder as it is now prepared for the market by this corporation.

### Historical Background

The first recorded laboratory production of electrolytic iron in any form was by the French scientist, Becquerel, in 1831. The first practical use of electrolytic iron plating appears to have been in making iron electrolytes for printing bank notes by the Russian Mint in 1868 (1). This process, developed by Klein, used a cold ferrous sulfate bath at very low current densities. The process was quite successful and it was still in use at the time of the Russian Revolution in 1917.

Hot iron chloride baths were developed for commercial production of electrolytic iron sheet and tubes in France in 1910 (2). This French plant operated successfully for 15 to 20 years, after which it was forced to close because of economic reasons. Two ambitious, but unsuccessful, attempts were made in this country during 1920-1930 to electroform iron sheets and tubes, using hot chloride baths (3, 4). These attempts were made by the Milford and Niagara Electrolytic Iron Companies. An improved hot iron chloride bath was developed in 1930 by Thomas and Blum for the production of electrolytic iron printing plates by the U. S. Bureau of Engraving and Printing (5). So far as we know, this process is still in use. The first known commercial production of electrolytic iron powder was by the Western Electric Company in 1921. This was before the era of powder metallurgy as we now know it. A mixed ferrous sulfate, ferrous chloride, and ammonium sulfate bath was used, at a current density of 12 amp/ft<sup>2</sup>. A description of the process is found in the literature (6). The Western Electric plant had a capacity of 100,000 lb of iron powder per month. The powder was used by this firm chiefly in the construction of loading coils for telephone circuits. Electrolytic iron powder has since been replaced by Permalloy in this application because of its higher magnetic permeability. The era of modern iron

powder metallurgy began in the early 1930's. The new industry received much publicity and extravagant claims were made for it by enthusiastic sponsors. As frequently happens in such situations, more people were attracted to the industry than it could support. United States firms who have engaged in the commercial production of electrolytic iron powder since 1930 and the approximate periods of their activity follow:

Plastic Metals Division of The National-U. S. Radiator Corporation	— 1934 to Present
The National Lead Company	— 1940 to 1945
Bu-El Metals Company	— 1947 to 1949
Tacoma Powdered Metals Company	— 1948 to 1954

The only one of these firms in production today is The Plastic Metals Division of The National-U. S. Radiator Corporation. The main reason for this high mortality is probably failure of the demand for electrolytic iron powder to grow at the rate expected by many. There has been a steady growth in its applications, but it has met severe competition from nonelectrolytic iron powders which sell at 30 to 40% as much. At present, one domestic and two foreign firms are actively selling electrolytic iron powder in this country. The foreign firms are Husqvarna Vapenfabrik of Sweden and George Cohen Sons and Company, Ltd., of England.

Frequent inquiries are made about how our corporation, whose main products are boilers, radiators, and other heating equipment, became involved in the production of electrolytic iron powder. The story is as follows. The National Radiator Company, now the National-U. S. Radiator Corp., established a Fellowship at Mellon Institute in 1929, for the purpose of developing a process for electroforming iron radiators. It soon became evident that electroformed iron radiators could not compete in cost with conventional cast iron and nonferrous radiators and convectors. The production of electrolytic iron sheet was investigated, but also was abandoned for economic and technical reasons. At this time the new iron powder metallurgy appeared on the scene. Efforts were then directed toward salvag-



Fig. 1. Electrolytic iron cells

ing the knowledge and experience gained, in developing a process for the production of electrolytic iron powder.

### Production

The first pilot plant was built in Johnstown in 1934, and commercial shipments of electrolytic iron powder were made that year. Production and sale has increased manyfold in the years since then.

A description of the present process for producing electrolytic iron powder follows.

#### *Electrolytic Iron Deposition*

Cell dimensions, inside, 10 ft long x 2.5 ft wide x 2.5 ft deep; cell composition, Haveg No. 42; electrolyte, mixed ferrous and ammonium sulfates; pH of electrolyte, 5.0-6.0; anode material, Armco ingot iron plates; cathodes, 16 gauge Type 430 stainless steel; current density, 25 amp/ft<sup>2</sup>; number of anodes per cell, 17; number of cathodes per cell, 16; source of current, d-c motor-generators; temperature of electrolyte, 120°-140°F; plating time, 3½ days; plating thickness, 3/32 in. to ¼ in.; kilowatt hours/lb of iron produced, 1.50; quantity of iron produced per cell per day, 100 lb. View of the electrolytic iron cells with cathodes and anodes in position is shown in Fig. 1.

#### *Cell Operation*

The cathode efficiency of 95 to 99% is high, but not quite as high as the anode efficiency. This causes a gradual increase of iron in the cell, and there is some sludge formation. The sludge settles to the bottom of the cell and is removed about every 3 weeks.

Use of the usual low-carbon steel plates as anodes instead of Armco plates results in an increase of carbon, sulfur, and manganese in the deposits.

Some ferric iron is produced by the surface oxidation of the electrolyte and is helpful in producing brittle deposits.

Cell solutions are analyzed weekly and adjusted to specified levels of pH, NH<sub>3</sub>, and Fe<sup>++</sup>.

#### *Washing and Stripping*

The cathodes, with their deposits, are given cold and hot water rinses to remove as much of the electrolyte as possible. This washing is especially important in achieving low values of total sulfur. De-

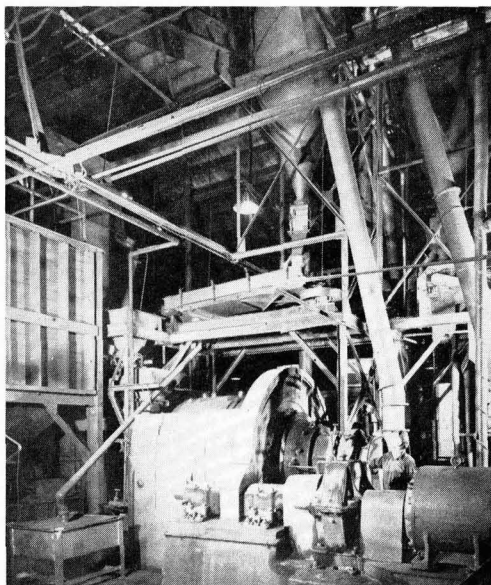


Fig. 2. Ball mill which grinds chips to powder of the desired mesh.

posits are allowed to dry and are removed from the cathodes by flexing and striking against a table top. Stripped cathodes are sanded, straightened when necessary, and returned to the cells.

#### *Crushing and Grinding of Deposits*

The stripped deposits, made brittle by their hydrogen content, are broken to approximately 1 in. chips in a spike roll crusher. Samples of the chips are analyzed for total sulfur, total carbon, and oxygen. Some iron is sold in this form as melting stock. Melting stock is analyzed further by chemical and spectrographic methods for total sulfur, carbon, oxygen, manganese, nickel, copper, silicon, and lead.

The chips are ground to powder of the desired mesh size in large ball mills such as shown in Fig. 2. The ball mills contain 11,000 lb of 2 in. steel balls and 3,000-4,000 lb of grinding stock at a time. Closed-type mills are used since it is generally necessary to use an inert atmosphere, such as nitrogen, to prevent firing and excessive oxidation.

Batch-type mills with 1 in. diameter steel balls are used in grinding powders to 200 mesh and finer. These mills must be kept tight during grinding, and precautions must be taken in discharging in order to prevent firing.

#### *Classification*

The next step after grinding the powder is to separate it into the desired mesh. This is done by both screens and air classifiers. In some cases the classifier is attached to the mill; this is preferred because of the obviously lower costs. This combination of mill and classifier is not always possible especially in producing finer mesh powders, because of fire hazards.

#### *Annealing*

The powder is hard, due to work hardening, and contained hydrogen as it leaves the ball mill or

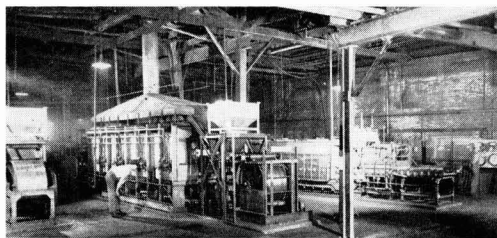


Fig. 3. Annealing furnaces

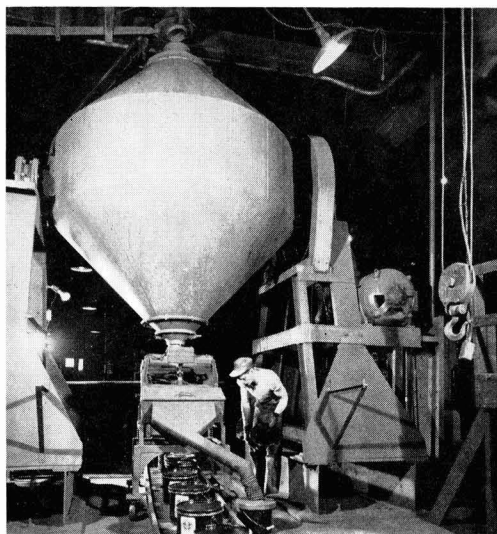


Fig. 4. 25,000 lb capacity mixers

classifier; it is dark in color because of surface oxidation. The powder can be used in this form for a few chemical and pharmaceutical applications. A combination annealing and reducing operation is required to soften it and remove the surface oxide for satisfactory use in powder metallurgy pressing and sintering operations. The annealed powder is soft and bright. Annealing is carried out at 1200°-1500°F for 30-45 min, in hydrogen or cracked ammonia, in furnaces such as the one shown in Fig. 3. The annealing temperature and time are adjusted to the mesh of the powder to prevent formation of an excessively hard sinter cake. Fine powders require lower temperatures than coarse powders. The sinter cake is given a light break-up in a crusher and reclassified.

#### Mixing and Packing

As a final step in processing, the powder is mixed to insure uniformity. The operation is carried out in mixers of 25,000-lb capacity as shown in Fig. 4. Samples of powder are taken during packing for chemical and physical tests and checking against specifications.

#### Properties of Electrolytic Iron Powder

The superior properties of electrolytic iron powder are due mainly to its high purity. Table I shows a comparison of the chemical analysis of Armco Ingot Iron with that of two grades of electrolytic

Table I. Typical chemical analyses of Armco ingot iron and electrolytic iron

Analysis, %	Armco ingot iron	Electrolytic iron	
		Grade A-101	Grade A-104
Carbon	0.03	0.015	0.004
Manganese	0.02	0.002	<0.001
Sulfur	0.025	0.004	0.003
Phosphorus	0.006	0.004	0.002
Silicon	0.020	0.005	0.001
Nickel	0.030	0.010	0.005
Cobalt	0.007	0.005	0.002
Chromium	0.005	0.002	<0.002
Lead	0.005	Nil	Nil
Arsenic	0.012	Nil	Nil
Boron	—	Nil	Nil
Copper	0.040	0.008	0.003
Total iron	—	99.840	99.900

iron grinding or melting stock. Grade A-101 is the usual, lower cost, grinding or melting stock. It is made by electrolytic refining of Armco Ingot Iron. Note the reduction of impurities. Grade A-104 was developed for those interested in unusually pure iron, who are willing to pay for it. This grade is made by further refining of Grade A-101.

Table II shows comparative data on typical 100 mesh electrolytic and nonelectrolytic commercial iron powders, excluding carbonyl powder. Note the superior purity of the electrolytic product. It is not, however, quite as pure as the grinding stock from which it is made because of impurities picked up in grinding and classifying.

Table III shows a comparison of the pressing and sintering properties of electrolytic and nonelectrolytic iron powders. Note especially the higher pressed densities and better sintering properties of the softer and purer electrolytic powder. This makes possible the production of "high density" sintered iron parts with good physical properties.

Table IV shows properties of electrolytic iron sinterings obtained under various processing conditions. Note especially the properties achieved at unusually high densities and with the use of carbon. The National Cash Register Company has been particularly successful in the production of high

Table II. Comparative data on typical 100 mesh electrolytic and nonelectrolytic iron powders

Property	Electrolytic	Nonelectrolytic
Chemical analysis, %		
Total Carbon	0.02	0.08
Sulfur	0.008	0.03
Silicon	0.01	0.15
Oxygen	0.40	0.60
Manganese	0.002	0.20
Phosphorus	0.005	0.03
All Others	0.03	0.25
Physical Properties		
Apparent density, g/cc	2.45	2.40
Flow (Hall)	35.00	30.00
Screen, %		
On 100 mesh	1.00	1.00
On 150 mesh	17.00	25.00
On 200 mesh	14.00	30.00
On 250 mesh	8.00	7.00
On 325 mesh	15.00	15.00
<325 mesh	45.00	22.00

Table III. Some comparative pressing and sintering properties of 100 mesh electrolytic and nonelectrolytic iron powders

Pressing properties	Electrolytic	Nonelectrolytic
At 30 tsi pressure:		
Pressed density, g/cc	6.70	6.25
Green strength of Transverse bar, psi	3000	2000
At 50 tsi pressure:		
Pressed density, g/cc	7.10	6.65
Green strength of Transverse bar, psi	5000	4000
Sintering properties		
At 30 tsi pressure:		
Ultimate tensile strength, psi	22,000	16,000
Elongation, %	7.00	4.00
Hardness, RH	55.00	70.00
At 50 tsi pressure:		
Ultimate tensile strength, psi	30,000	24,000
Elongation, %	12.00	6.00
Hardness, RH	60.00	75.00

Note: One per cent zinc stearate was mixed with powders as a lubricant for pressing and sintering was at 2050°F for 45 min in hydrogen. tsi equals tons per square inch.

density, high strength parts, with a resulting saving in costs.

As mentioned previously, the first commercial use for electrolytic iron powder was in a magnetic core application by Western Electric Company. Some

magnetic applications for cores, pole pieces, etc., still exist. Serious competition is met, however, from the ferrites, carbonyl iron powder, and Permalloy. Table V shows some of the magnetic properties of electrolytic iron in solid, powder, and flake form.

The use of electrolytic iron in flake form permits the achievement of higher magnetic permeabilities and lower core losses than when powder is used, because the flakes become somewhat oriented during pressing. Maximum permeability and minimum core losses are achieved when the long axes of the flakes are parallel to the magnetic flux.

### Concluding Remarks

It has been shown how electrolytic iron powder is produced and some of its properties have been discussed. Electrolytic iron powder is both superior in quality and higher in cost as compared with nonelectrolytic iron powders, excluding carbonyl iron. Its characteristics suit it to the production of high density sinterings with superior physical properties. These applications will increase in number and volume as the quality is increased and the relative cost is reduced.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

Table IV. Some properties of electrolytic iron sinterings obtained under various processing conditions

Processing conditions	Density	Ult. tensile strength, psi	Elongation in 2 in., %	Rockwell hardness	Source of information
1. Ingot iron — hot rolled rods or plates	7.87	42,000 to 48,000	22.00 to 28.00	39 to 55 RB	A.S.M. Handbook
2. Pressed at 50 tsi, sintered at 2050°F for 45 min	7.10	30,000	12.00	60 RH	P.M.*
3. Pressed at 50 tsi, sintered at 2050°F for 45 min, re-pressed at 50 tsi, re-sintered at 2050°F for 30 min	7.60	44,000	23.00	36 RB	P.M.
4. Pressed at 160 tsi, sintered at 2012°F, 1 hr	7.79	47,700	37.50	44 RB	(7)
5. Mixed with 0.8% C, pressed at 30 tsi, sintered 1 hr at 2050°F, quenched and tempered	6.65	105,000	—	88 RB	P.M.*
6. Mixed with 0.40% C, pressed at 50 tsi, sintered 1 hr at 2050°F	7.00	65,000	5.00	—	P.M.*
7. Pressed, sintered at 2070°F for 30 min, sized, carburized to depth of 0.05 to 0.06 in., quenched, and hardened	7.00	170,000	2.00	—	(8)

\* P.M.—Plastic Metals Div. Data.

Table V. Typical magnetic values

	Solid electrolytic iron	Armco iron	Sintered electrolytic iron	Cores from insulated electrolytic iron	
				16 Mesh flakes	100 Mesh powder
Maximum permeability (D.C.)	20,000 to 41,000*	7,250	1,200 to 15,000*	380	120
Initial permeability	410	250	450		
Saturation induction, gauss	23,050	22,000	—	18,000	—
Core loss ergs/cc/cycle	—	—	15,000	1,600	—

\* Value depends on purity, heat treatment, and density.

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## Electromagnetic Forces in Large Aluminum Furnaces

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The heavy direct currents used in large aluminum furnaces produce strong magnetic fields in the whole volume of the furnace. Of particular interest to the problem is the magnetic field produced in the volume of molten cryolite and aluminum, because these magnetic fields, by interaction with the electric currents present in this volume, produce electromagnetic forces acting on the two liquid layers. It has been observed that, under unfavorable conditions, the interface between cryolite and aluminum layers may be distorted. The anode-cathode distance may thus get out of control, which is harmful to the smooth operation of the furnace (1). In addition, the liquids may yield to the forces and flow, and the stirring action produced may influence the electrolysis adversely by mixing anolyte and catholyte and reduce the current efficiency.

A complete description of the system would require a tracing of the forces set up and an evaluation of the effects of these forces on the flow system. The hydraulic aspect of the problem need not be considered, however, except for the obvious effect that a reduction of the forces necessarily reduces the flow. The main purpose of the analysis is to demonstrate how the forces are set up, to indicate how they affect the interpolar distance, and to show the possible ways of reducing the harmful electromagnetic forces.

The distance between the anode and the metal layer acting as cathode is small compared with the size of the furnace, and the magnetic field in neighboring volumes of the two liquid layers may be considered to be equal, both in magnitude and in direction. An evaluation of the distribution of magnetic flux in the two liquid layers is the first part of the analysis. This distribution is strongly influenced by steel parts in the furnace structure and does not lend itself readily to any calculation. Therefore, scale models of the furnace have been used to determine the distribution of magnetic flux.

The forces are set up by interaction of magnetic fields with electric currents. The next part of the analysis, therefore, is the evaluation of electric current distribution in the two liquid layers. Measurements on furnaces in operation are extremely difficult or even impossible, so one must rely on calculations based on the design features and the assumed electric resistivities of the parts in question.

Such calculations show that the current distribution in the aluminum layer differs largely from that

in the cryolite layer. In the two liquid layers, therefore, quite different patterns of forces are set up. The difference in densities of the two liquids being small, the interface is unstable and any difference in forces acting on the two liquids may distort the interface and thus influence the anode-cathode distance.

The evaluation of electromagnetic forces is thus seen to be divided into three parts: (a) evaluating magnetic flux distribution; (b) evaluating electric current distribution in cryolite and aluminum layers; and (c) combining magnetic flux and electric current distributions to show the pattern of electromagnetic forces acting on the two liquid layers.

Aluminum furnaces differ largely in design and in the arrangement of the furnaces in pot lines. This work deals only with furnaces equipped with vertical contact stud Söderberg anodes with one central anode bus bar, the furnaces being arranged end to end in the pot line.

### *Magnetic Flux Distribution*

Without regard to the effect of steel parts, the distribution of magnetic flux may be calculated and some information obtained (2). However, models to a linear scale of 1:16 of a 100 ka furnace have been operated at room temperature to show the effect of steel parts on magnetic flux distribution (3). The models are designed to give close approximation to the anode and cathode bus bar current distribution of the prototype, and hence the magnetic field produced by these currents is closely reproduced in the models. To obtain the correct magnetic flux, the current of the model is made proportional to linear scale. This produces a high current density in the model, and water-cooled copper tubing is used for the conductors in the model. The magnetic flux density is measured at appropriate points with a ballistic galvanometer and a coil, the method of commutation being used.

It has been found that the current of the anode bus bar most significantly contributes to the dangerous magnetic field in the liquid layers. Two aspects of the furnace design have turned out to influence the magnitude of this magnetic field profoundly, viz., the method of feeding the current to the anode and the arrangement of steel parts in the vicinity of the anode bus bar, especially the vertical contact studs and the arrangement for suspending the anode.

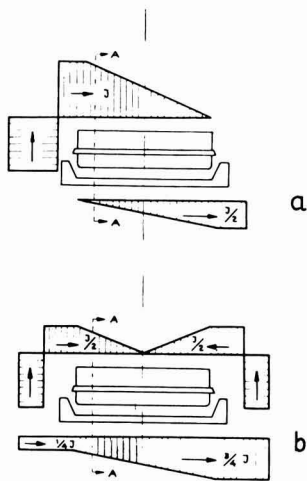


Fig. 1

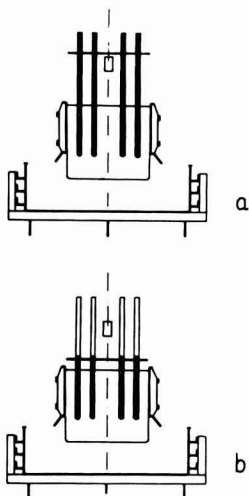


Fig. 2

Two methods of feeding the current to the anode, as illustrated in Fig. 1, have been tested: (a) total current fed to one end of the anode, and (b) half the total current fed to each end of the anode. As may be expected, the latter method gives a less intensive magnetic field. Several arrangements of steel parts have been tested; only two extreme cases will be reported, as illustrated in Fig. 2. The one arrangement (a) is found to be especially unfavorable as far as magnetic fields are considered, the other (b) especially favorable.

Figure 3 and 4 show magnetic field measurements on models of two extreme combinations: (a) a furnace designed unfavorably both with respect to method of feeding the current to the anode (Fig. 1a) and with respect to the arrangement of steel parts (Fig. 2a); (b) a furnace designed favorably in both respects (Fig. 1b and 2b). Magnetic flux den-

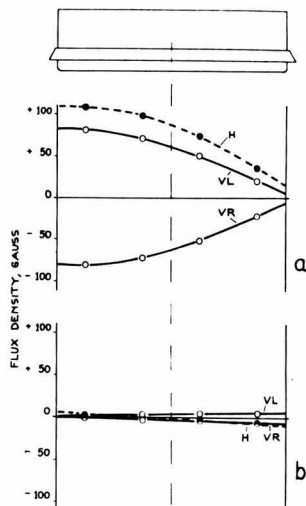


Fig. 3

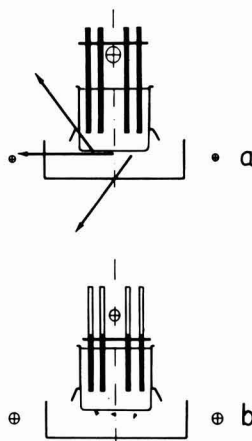


Fig. 4

sities are given in Fig. 3 for three lengthwise cuts of the anode. The horizontal transverse component (H) is given for a central cut, the vertical component in cuts on the left (VL) and right (VR) side of the anode. Transverse cuts A-A of Fig. 1 are shown in Fig. 4. The magnitude and direction of the magnetic flux density are shown in this figure by arrows.

It may be concluded that the magnetic flux density in the volume of interest is greatly influenced by the design of the furnace.

The importance of the arrangement of steel parts may be explained by some simple experiments. In Fig. 5 a conductor perpendicular to the plane of the paper carries a heavy direct current, and the magnetic flux density is measured at two diametrically opposed points. When the conductor is surrounded by a steel tube, no change in flux density is observed. When a part of the tube is cut away, leaving an air gap, the flux density is seen to be increased at



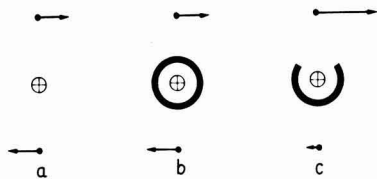


Fig. 5

the side of the air gap and reduced at the opposite side.

Thus it is not possible to reduce the total flux but, according to the design of the steel parts, the flux is pushed to one side or the other. In this way, the design given in Fig. 2a is seen to increase the flux density below the anode by setting up a magnetic circuit with steel parts on three sides and the air gap pointing downward. By arranging the steel structure for suspending the anode below the anode bus bar, a magnetic bridge is set up, short circuiting the air gap between the rows of vertical studs. By making the upper parts of the studs of nonmagnetic material an additional reduction in flux density below the anode is obtained.

#### Current Distribution

The electric current flows from the anode through the cryolite and aluminum layers to the carbon lining. The current is then collected by the steel collector bars and led to the cathode bus bars, by which the total current is passed to the next furnace.

The current thus flows in all three directions when passing from the anode bus bar of one furnace, through the furnace, and to the anode bus bar of the next furnace. In this flow several parallel circuits are set up. Compared with the other parts of the furnace, the aluminum layer is a good electric conductor and may carry large currents without appreciable voltage drop. In the transverse direction of the furnace, the aluminum layer is seen (Fig. 6) to be electrically connected in parallel to the collector bars, and in the lengthwise direction (Fig. 7) parallel to the cathode bus bars. Therefore, the aluminum layer may carry current in the horizontal direction, both transverse and lengthwise of the furnace. Calculations have been made on reasonable assumptions as to electric resistivities of the various parts of the furnace, and the horizontal currents have been found to be considerable under certain conditions.

In addition, when the normal operation of the furnace is disturbed, e.g., by a partly frozen bottom, the aluminum layer is bound to carry large currents in the horizontal direction.

In the cryolite layer no horizontal current will be set up because of the poor conductivity. In this way the current distribution in the two fluid layers differs significantly.

#### Pattern of Forces

The electromagnetic force acting on a volume element is equal to the vectorial product of the electric current and magnetic flux flowing through the element. If the volume element is taken to be a cube,

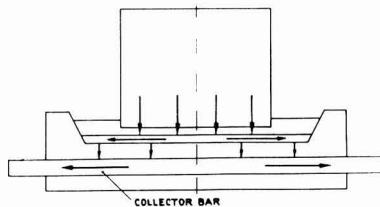


Fig. 6

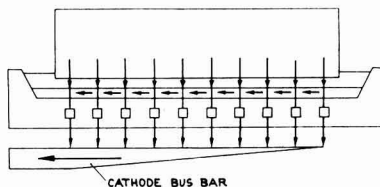


Fig. 7

the side being 1 cm, and if the directions of the electric current and magnetic flux are those of Fig. 8, the force will have the direction indicated on the figure and numerically, in dynes/cm<sup>2</sup>, will be equal to the product of current density in amp/cm<sup>2</sup> and flux density in gauss (and multiplied by 0.1). When the distributions of electric current and flux density have been determined, they may in this way be combined to give the pattern of forces.

In the volume of molten cryolite only horizontal forces are set up because the direction of the current is purely vertical. In the metal layer, forces may be set up in the vertical as well as in the horizontal direction. The horizontal forces, however, are considered more important because their action is cumulative in the direction of the forces. No doubt the vertical forces play a part, but as a test of the quality of a design only the pattern of horizontal forces need be considered.

The unfavorable furnace design which has given the strong magnetic field of Fig. 3a and 4a, combined with a reasonable distribution of electric current in the aluminum layer, will turn out to give the pattern of forces of Fig. 9a in this layer. In the cryolite layer, however, much weaker forces are set up, as shown by Fig. 9b.

The much weaker magnetic field, shown in Fig. 3b and 4b, produced in a well designed furnace, gives rise to electromagnetic forces so small that they would need another scale of plotting to be readable.

#### Methods of Reducing the Electromagnetic Forces

In principle, the electromagnetic forces may be reduced by lowering the electric current density or the magnetic flux density, or by reducing both of them. Reduction of current density is considered first.

The vertical current through the cryolite layer is the electrolyzing current, the density of which is determined by other considerations. The horizontal currents in the aluminum layer, however, may be influenced by the furnace design. These currents, being in parallel to the currents of collector bars

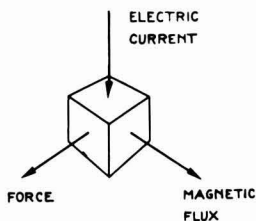


Fig. 8

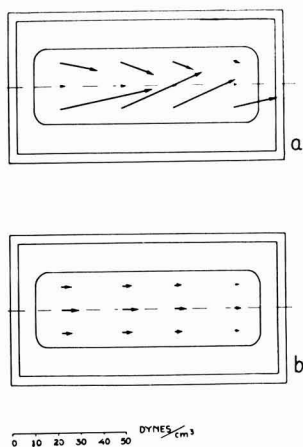


Fig. 9

and cathode bus bars, in the transverse and longitudinal directions, respectively, may be reduced by using heavy cross-sectional areas of these bars. More generally, a design of collector bar and bus

bar arrangements that insures that no large potential drop is set up along the bars will give only small horizontal currents in the aluminum layer.

The forces set up in the aluminum layer may be reduced most significantly by increasing the thickness of this layer. In this way the density of horizontal currents in the aluminum layer may be kept at a low level—when the furnace is in good operation. Any disturbance of the good operation, e.g., a partly frozen bottom, will cause heavy horizontal currents to be set up in the aluminum layer. Such disturbances normally occur in the operation of a pot line, and unpredictable wild currents in the aluminum layer must be taken as a more or less normal condition.

This fact makes it the more important to reduce the magnetic flux density as far as possible. As has been seen, the magnitude of the flux density may be influenced largely by furnace design. By feeding half the total current to each end of the anode the flux density is reduced. When, in addition, the steel structure is designed to produce a screening effect, a further reduction in flux density is obtained. Figure 2a and b may be taken as examples of poor and good designs, respectively, as far as the screening effect of steel parts is concerned.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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## Fundamentals of the Theory of Electrodes and Galvanic Cells

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Present day electrochemistry is in a rather peculiar state. On the one hand there have been, particularly during the last two decades, important theoretical developments based on fundamental principles of thermodynamics and kinetics, as well as considerable progress on the experimental side on account of the availability of many new and ingenious methods and devices. On the other hand there is repeated evidence in textbooks and in research publications of a continued confusion with regard to fundamental concepts, definitions, matters of nomenclature, etc., which had originated in the early stages of the development of electrochemistry, but for the persistence of which there is no valid reason. The conflict between the so-called American

and the so-called European signs for electrode tensions is but one example of this situation. Constantly recurring discussions of this particular problem have not settled it yet [see, for instance, the recent articles of deBéthune (1), Ramsey (2), Licht and deBéthune (3)].

In this connection, the recommendation made at Stockholm in 1953 by the International Union of Pure and Applied Chemistry (IUPAC) and formulated by Christiansen and Pourbaix (4) constituted a first step toward the removal of these unnecessary difficulties. This recommendation was in favor of the European signs and, in spite of a presentation judged unsatisfactory even by some of the Commission members involved in its preparation, it is to

be hoped that universal adoption of the recommendation itself will take place. The problem, however, requires a more fundamental approach and a better formal presentation of its solution. This has been done over a period of eight years in the successive editions of the report on Electrochemical Nomenclature and Definitions of the International Committee of Electrochemical Thermodynamics and Kinetics (CITCE), now an affiliated IUPAC Commission (5).

The purpose of the present communication is to outline the fundamental ideas which have been serving as guides for the work of CITCE's Commission of Electrochemical Nomenclature and Definitions (identical with the Sub-Commission of Electrochemical Symbols and Terminology of IUPAC's Commission of Electrochemistry). In addition the authors present some points beyond the contents of the latest CITCE report but within its spirit, details about these being available elsewhere (6-11).

The authors had the benefit of oral or written discussions with many electrochemists in the United States, with their CITCE colleagues, and with numerous other electrochemists in Europe. They feel that large areas of agreement have thus been established. It is their hope that the outline offered here will help in bridging certain gaps between points of view and methods of reasoning and in promoting greater interest toward the elaboration of a better presentation of electrochemical fundamentals.

The outline starts with some essential points concerning single electrodes and continues, practically and intentionally in the same language, with the corresponding aspects of the theory of galvanic cells. Some expressions used in this paper will be new for most readers. This will be the case in particular with the various uses of the word *tension* which we are adopting as the exact equivalent of the French "tension" and of the German "Spannung" and which we are recommending for general adoption. So far there has been no "official" IUPAC recommendation for the use of "tension" in English and our use of it here must be regarded as a suggestion. This is also the case with the various symbols, since no list of electrochemical notations has so far been recommended officially.

### Electrochemical Two-Phase Systems—Single Electrodes

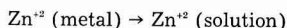
[2.1] The phases of an *electrode* are numbered in the sequence I, II in the following manner. Taking as a typical example a zinc-zinc ion solution electrode, we may represent it by the diagram Zn/Zn<sup>+2</sup>, which we shall designate as x, phase I being Zn and phase II being Zn<sup>+2</sup>; or we may represent it by the diagram Zn<sup>+2</sup>/Zn, which we shall designate as y, phase I being now Zn<sup>+2</sup> and phase II being Zn.

The direction in which the phases are counted and in which they are read from the diagram will normally be from left to right, independently of whether or not a current is flowing through the electrode and, in the case of current flow, independently of the direction of this current. A current flowing in the direction of the counting, i.e., from phase I to phase II, will be regarded as posi-

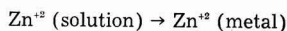
tive, while a current flowing in the opposite direction, i.e., from II to I, will be regarded as negative.

[2.2] An *electrode reaction* is a heterogeneous chemical reaction involving thermodynamically defined reagents and products (ions, electrons, atoms, and molecules) in the two phases of the electrode and transferring a corresponding electrical charge from one phase to the other.

The electrode reaction is completely represented, with respect to both extent and direction, by writing, in the case of our example, either electrode reaction  $\alpha$ :



or its reverse, electrode reaction  $\beta$ :



The electrode reaction is written in a direction independent from that of the counting of the phases because, according to the direction of the current, we shall have either reaction  $\alpha$  or reaction  $\beta$  occurring at either electrode x or at electrode y.

[2.3] The *chemical affinity* A of the electrode reaction and its *free enthalpy change*  $\Delta G$  ( $G = G. N. Lewis'$  "free energy" F) are related to the chemical potentials  $\mu_i$  of the reactants and products and to their stoichiometric coefficients  $\nu_i$  as follows:

$$\text{for } \alpha: A_\alpha = -\Delta G_\alpha = -\sum \nu_{i,\alpha} \cdot \mu_i$$

$$\text{for } \beta: A_\beta = -\Delta G_\beta = -\sum \nu_{i,\beta} \cdot \mu_i = -A_\alpha = +\Delta G_\alpha$$

If chemical forces were alone effective (i.e., in the absence of electrostatic forces) a positive  $A_\alpha$  would indicate that the corresponding reaction is spontaneous, a negative  $A_\alpha$  that it is nonspontaneous.

[2.4] The *reaction charge*  $z \cdot F$  or the *number of charges transported*  $z$  corresponds to one occurrence of the electrode reaction, F representing one equivalent of positive charge or one Faraday. If the charge transported across the interphase in the direction of the counting, i.e., from I to II, is positive,  $z$  is positive; if a positive charge is transported against the direction of the counting, i.e., from II to I,  $z$  is negative.

Since the electrode reaction can be either  $\alpha$  or  $\beta$  and the electrode can be either x or y, we have the following four possibilities and the corresponding values of  $z$ :

	Electrode reaction $\alpha$	Electrode reaction $\beta$
Electrode x, Zn/Zn <sup>+2</sup>	$z_{\alpha,x} = +2$	$z_{\beta,x} = -2$
Electrode y, Zn <sup>+2</sup> /Zn	$z_{\alpha,y} = -2$	$z_{\beta,y} = +2$

A number of charges such as  $z_{\alpha,x}$  is related to the stoichiometric coefficients  $\nu_{i,\alpha}$  of the reactants  $i$  of reaction  $\alpha$  located in phase I and to their charge numbers  $z_i$  as follows:

$$z_{\alpha,x} = -\sum \nu_{i,\alpha} \cdot z_i$$

It is similarly related to the stoichiometric coefficients  $\nu_{i,\alpha}$  of the products  $i$  of reaction  $\alpha$  located

in phase II and to their charge numbers  $z_i$  as follows:

$$Z_{a,x} = + \sum \nu_{i,a,II} \cdot Z_i$$

[2.5] The *chemical tension*<sup>1</sup>  $\epsilon = A/(z \cdot F)$  of an electrode represents, in magnitude and in sign, the force with which the electrode reaction tends to move *positive* charges through the interphase in the direction of the counting of the phases on account of *chemical* (or, more generally, nonelectrostatic) causes, *no other forces being effective*.

Applying the general relation  $\epsilon = A/(z \cdot F)$  to electrodes  $x$  and  $y$  and to reactions  $\alpha$  and  $\beta$ , we have:

$$\epsilon_x = \tilde{A}_\alpha / (z_{\alpha,x} \cdot F) = A_\beta / (z_{\beta,x} \cdot F)$$

$$\epsilon_y = \tilde{A}_\alpha / (z_{\alpha,y} \cdot F) = A_\beta / (z_{\beta,y} \cdot F) = -\epsilon_x$$

The practical unit of tension is the volt.

[2.6] The *Galvani tension* or *inner electric tension* of an electrode is defined as being equal to the inner electric potential  $\phi_i$  of phase I minus the inner electric potential  $\phi_{II}$  of phase II. It represents, in magnitude and in sign, the force with which the electrode reaction tends to move *positive* charges through the interphase in the direction of the counting of the phases on account of purely *electric* causes, i.e., on account of the electrostatic distribution of space charges, *no forces other than the electrostatic ones being effective*.

We shall designate these nonmeasurable Galvani tensions by  $g$ :

$$g_{i,II} = \phi_i - \phi_{II}$$

At electrode  $x$  we have  $g_x$  and at electrode  $y$  we have  $g_y$ .

[2.7] The *electrochemical affinity* of an electrode reaction  $\alpha$  or  $\beta$  (as defined in [2.2]) at an electrode with a Galvani tension  $g$  (defined in [2.6]) is given as follows:

$$\text{for } \alpha : \tilde{A}_\alpha = A_\alpha + z_{\alpha,x} \cdot F \cdot g_x \quad \text{at electrode } x$$

$$= A_\alpha + z_{\alpha,y} \cdot F \cdot g_y \quad \text{at electrode } y$$

$$\text{for } \beta : \tilde{A}_\beta = A_\beta + z_{\beta,x} \cdot F \cdot g_x \quad \text{at electrode } x$$

$$= A_\beta + z_{\beta,y} \cdot F \cdot g_y = -\tilde{A}_\alpha \quad \text{at electrode } y$$

If  $\tilde{A}_\alpha$  is positive, reaction  $\alpha$  is spontaneous under the influence of the existing chemical and electric forces. If  $\tilde{A}_\alpha$  is negative, reaction  $\alpha$  is nonspontaneous.

[2.8] The *electrochemical tension*  $\tilde{\epsilon}$  of an electrode I/II is defined as follows:

$$\tilde{\epsilon}_x = \tilde{A}_\alpha / (z_{\alpha,x} \cdot F) = \tilde{A}_\beta / (z_{\beta,x} \cdot F) \quad \text{for electrode } x$$

$$\tilde{\epsilon}_y = \tilde{A}_\alpha / (z_{\alpha,y} \cdot F) = \tilde{A}_\beta / (z_{\beta,y} \cdot F) = -\tilde{\epsilon}_x \quad \text{for electrode } y$$

[2.9] When reaction  $\alpha$  or  $\beta$  at electrode  $x$  or  $y$  is at *electrochemical equilibrium*, i.e., when no cur-

rent is flowing through the electrode, the electrochemical affinities are equal to zero:

$$\tilde{A}_\alpha = 0 \quad \text{and} \quad \tilde{A}_\beta = 0$$

and the electrochemical tensions are likewise equal to zero:

$$\tilde{\epsilon}_x = 0 \quad \text{and} \quad \tilde{\epsilon}_y = 0$$

This state of equilibrium can be regarded as resulting from the compensation exerted by a "reversible" Galvani tension  $g$  acting as a counterforce against a chemical tension  $\epsilon$ :

for electrode  $x$  :

$$g_{x,\alpha} = -A_\alpha / (z_{\alpha,x} \cdot F) = g_{x,\beta} = -A_\beta / (z_{\beta,x} \cdot F) = -\epsilon_x$$

for electrode  $y$  :

$$g_{y,\alpha} = -A_\alpha / (z_{\alpha,y} \cdot F) = g_{y,\beta} = -A_\beta / (z_{\beta,y} \cdot F) = -\epsilon_y$$

The reversible Galvani tension of a given electrode  $x$  is the same whether the electrode reaction is regarded as being  $\alpha$  or  $\beta$ , but it is equal to minus the reversible Galvani tension of the "reverse" electrode  $y$ :

$$g_{x,\alpha} = g_{x,\beta} = -g_{y,\alpha} = -g_{y,\beta}$$

The sign of the corresponding chemical tension  $\epsilon$  of the electrode depends on the chosen direction of the counting of the phases, but it does not depend on whether reaction  $\alpha$  or  $\beta$  is used for the calculation of  $\epsilon$ .

In the case of the Zn/Zn<sup>2+</sup> electrode at equilibrium the electrochemical potentials of the Zn<sup>2+</sup> ion have the same value in two phases:

$$\tilde{\mu}_{Zn^{2+},I} = \tilde{\mu}_{Zn^{2+},II}$$

[2.10] At a Galvani tension  $g_x$  different from the reversible value  $g_{x,\alpha} = g_{x,\beta}$  (defined in [2.9]) the measurable *overtension* (or overvoltage)  $\Delta g$  of electrode  $x$  has the same value whether reaction  $\alpha$  or reaction  $\beta$  is being considered:

$$\Delta g_{x,\alpha} = g_x - g_{x,\alpha} = \Delta g_{x,\beta} = g_x - g_{x,\beta}$$

When  $g_x > g_{x,\alpha}$ , we have  $\Delta g_{x,\alpha} = \Delta g_{x,\beta} > 0$ , and when  $g_x < g_{x,\alpha}$ , we have  $\Delta g_{x,\alpha} = \Delta g_{x,\beta} < 0$ .

The over tensions at electrode  $x$  under the actual tension  $g_x$  are related to the corresponding electrochemical affinities of electrode reactions  $\alpha$  and  $\beta$  as follows:

$$\tilde{A}_\alpha = z_{\alpha,x} \cdot F \cdot \Delta g_{x,\alpha} \quad \text{and} \quad \tilde{A}_\beta = z_{\beta,x} \cdot F \cdot \Delta g_{x,\beta} = -\tilde{A}_\alpha$$

They are related to the electrochemical tension  $\tilde{\epsilon}_x$  of electrode  $x$  as follows:

$$\tilde{\epsilon}_x = \tilde{A}_\alpha / (z_{\alpha,x} \cdot F) = \Delta g_{x,\alpha} = \tilde{A}_\beta / (z_{\beta,x} \cdot F) = \Delta g_{x,\beta}$$

[2.11] With current flowing through the electrode the *face* of the metallic phase of an electrochemical two-phase system into which the positive current *enters* from the adjacent nonmetallic phase (a solution, for instance) is called a *cathode*. If the positive current *leaves* the face of the metallic phase toward the adjacent nonmetallic phase, this face is called an *anode*.

<sup>1</sup> A "tension" ("tension" in French, "Spannung" in German) between the initial point I and the final point II of an interval is a force tending to move positive charges from I to II, regardless of the particular nature of the tension and of the signs of the ions or electrons actually set in motion. The expression "electric tension" is synonymous with such expressions as "voltage," "potential drop," and sometimes "potential difference."

[2.12] An electrode reaction taking place at a cathode, with electrons and metallic ions moving in the appropriate directions defined in [2.11], is sometimes called a *reduction*. An electrode reaction taking place at an *anode* is sometimes called an *oxidation*.

[2.13] The minimum Galvani tension  $g$  (more positive than the reversible value  $g_a$  or  $g_p$ ) of an electrode metal I / nonmetal II able to produce an arbitrarily fixed minimum velocity of the electrode reaction in the direction of oxidation may be called *oxidation tension*, while the maximum Galvani tension  $g$  (more negative than the reversible value  $g_a$  or  $g_p$ ) of the same electrode able to produce an arbitrarily fixed minimum velocity of the electrode reaction in the direction of reduction may be called *reduction tension*.

[2.14] Let us consider electrode  $x$  and reaction  $\alpha$ , with the stationary current  $J$  flowing through the electrode during time  $t$ . The change  $\Delta n_{i,II}$  in the number of moles of ion  $i$  (*electrolytic change of mole number*) in the end portion of phase II in contact with phase I and affected by the electrode reaction and by migration is given by the following equation (10):

$$\Delta n_{i,II} = \left( \frac{\nu_{i,II}}{z_a} - \frac{\delta_{i,II}}{z_i} \right) \cdot \frac{J \cdot t}{F}$$

in which  $\nu_{i,II}$  is the stoichiometric coefficient of  $i$  in II,  $z_a$  is the number of charges transported,  $\delta_{i,II}$  is the transference number of  $i$  in II,  $z_i$  is the charge number of  $i$ .

Similarly, for the change  $\Delta n_{i,I}$  in the end portion of phase I in contact with phase II we have:

$$\Delta n_{i,I} = \left( \frac{\nu_{i,I}}{z_a} + \frac{\delta_{i,I}}{z_i} \right) \cdot \frac{J \cdot t}{F}$$

[2.15] The *Volta tension* or *outer electric tension* of an electrode is defined as being equal to the outer electric potential  $\psi_I$  of phase I minus the outer electric potential  $\psi_{II}$  of phase II.

The inner and outer electric potentials of a phase,  $I$  for instance, are related by the formula

$$\phi_I = \psi_I + \chi_I$$

in which  $\chi_I$  is the surface electric tension of the phase.

### Overtensions at Electrodes with Diffusion Layers (II)

[3.1] The concepts and definitions developed above for single electrodes metal I / nonmetal II or nonmetal I / metal II do not take into account the possible presence of diffusion layers. We shall now give some additional definitions applying to cases in which a diffusion layer occupies the end portion of the nonmetal phase (usually a solution) and is being taken into account. Such a situation in general will be the result of the passage of current through single or multiple electrodes (i.e., electrodes at which, respectively, one or several reactions may occur), but it may also be the result of corrosion processes at multiple electrodes with zero net current.

[3.2] Moving from the bulk of the solution toward the outer surface of the metal phase we find the *diffusion layer* starting at some last *homogeneous layer*  $c$  and finishing at the *end layer*  $b$  of solution in contact with the metal. Between positions  $b$  and  $c$  the chemical potentials of the constituents of the solution may differ from their values in the bulk of the solution, but the standard chemical potentials in  $b$ - $c$  are the same as those in the bulk of the solution.

[3.3] All intensive quantities and concepts already considered as pertaining to the bulk solution can be regarded as pertaining also to the homogeneous layer  $c$ . We may designate them as *bulk quantities* or *bulk concepts* and represent them by the bulk symbols without any  $c$  specification:

the *bulk* chemical potential  $\mu_i$ ,  
the *bulk* inner electric potential  $\phi_{II}$ ,  
the *bulk* electrochemical potential

$$\tilde{\mu}_i = \mu_i + z_i \cdot F \cdot \phi_{II},$$

the *bulk* electrode reaction  $\alpha$ ,  
the chemical affinity of the *bulk* electrode reaction

$$A_a = -\sum \nu_i \cdot \mu_i,$$

the *bulk* chemical tension  $\epsilon = A_a / (z_a \cdot F)$ ,

the *bulk* Galvani tension  $g = \phi_I - \phi_{II}$ ,

the *bulk* reversible Galvani tension

$$g_a = -A_a / (z_a \cdot F),$$

the *bulk* overpotential  $\Delta g_a = g - g_a$ ,

the electrochemical affinity of the *bulk* electrode

$$\text{reaction } \tilde{A}_a = -\sum \nu_i \cdot \tilde{\mu}_i =$$

$$A_a + z_a \cdot F \cdot g = z_a \cdot F \cdot \Delta g_a,$$

the *bulk* electrochemical tension

$$\tilde{\epsilon} = \tilde{A}_a / (z_a \cdot F) = \Delta g_a,$$

the *bulk* electrode polarization  $\Delta g = g_{J \neq 0} - g_{J=0}$ ;  
at simple electrodes  $\Delta g = \Delta g_a$ .

[3.4] Some quantities and concepts pertaining to the end layer  $b$  may be designated as *end quantities* or *end concepts* and represented by symbols with, for instance, an asterisk (\*) as a specification:

the *end* chemical potential  $\mu_i^*$ ,

the *end* inner electric potential  $\phi_{II}^*$ ,

the *end* electrochemical potential

$$\mu_i^* = \mu_i + z_i \cdot F \cdot \phi_{II}^*,$$

the *end* electrode reaction  $\alpha^*$ ,

the chemical affinity of the *end* electrode reaction

$$A_a^* = -\sum \nu_i \cdot \mu_i^*,$$

the *end* chemical tension  $\epsilon^* = A_a^* / (z_a \cdot F)$ ,

the *end* Galvani tension  $g^* = \phi_I - \phi_{II}^*$ ,

the *end* reversible Galvani tension

$$g_a^* = -A_a^* / (z_a \cdot F),$$

the activation overpotential of the *end* electrode reaction

$$\Delta g_a^* = g^* - g_a^*,$$

the electrochemical affinity of the *end* electrode

$$\text{reaction } \tilde{A}_a^* = -\sum \nu_i \cdot \tilde{\mu}_i^* \text{ (including } \tilde{\mu}_{i,1}) =$$

$$A_a^* + z_a \cdot F \cdot g^* = z_a \cdot F \cdot \Delta g_a^*,$$

the *end* electrochemical tension

$$\tilde{\epsilon}^* = \tilde{A}_a^* / (z_a \cdot F) = \Delta g_a^*,$$

the *end* electrode polarization  $\Delta g^* = g_{J \neq 0}^* - g_{J=0}^*$ ;  
at mono or single electrodes  $\Delta g^* = \Delta g_a^*$ .

[3.5] We now have to consider several important *bulk-end concepts* and *bulk-end relations* involving simultaneously properties of the bulk layer *c* and of the end layer *b*:

the diffusion tension in the diffusion layer

$$g_{diff.} = \phi_{11}^* - \phi_{11} = g - g^*,$$

the concentration overvoltage

$$\Delta g_{ak} = g_a^* - g_a = - (A_a^* - A_a) / (z_a \cdot F),$$

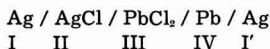
the following *general* relation between the various overvoltages at single electrodes:

$$\Delta g = \Delta g_a = \Delta g_{ak} + \Delta g_a^* + g_{diff.}, \text{ which can be simplified to the following relations under special conditions: } \Delta g = \Delta g_a = \Delta g_{ak} + g_{diff.}, \text{ if } \Delta g_a^* = 0, \Delta g = \Delta g_a = \Delta g_{ak} + \Delta g_a^*, \text{ if } g_{diff.} = 0, \text{ for instance in the presence of an excess of foreign electrolyte in the solution,}$$

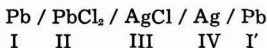
$$\Delta g = \Delta g_a = \Delta g_{ak}, \text{ if } \Delta g_a^* = 0 \text{ and } g_{diff.} = 0.$$

### Ideal Galvanic Cells

[4.1] A typical *ideal galvanic cell* is that represented by the following diagram in which the successive phases are counted from left to right as indicated, and in which eventual irreversible diffusion phenomena (for instance at the II/III interphase) are neglected:



which we shall designate as galvanic cell *v*, or by the following diagram:



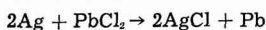
which we shall designate as galvanic cell *w*.

In both cases the chemically identical terminal phases I and I' are the *ideal poles* or *terminals* of the *open* cell. In accordance with current practice we may also designate the chemically different metallic phases I and IV as the *real poles* of the cell. Besides the open galvanic cell it is useful, for many practical purposes, to consider the corresponding *closed* cell which, in addition to phases I and I', also includes a metallic connection between poles I and I' (see [4.14] below).

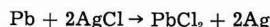
The mode of representation of the cell and the order of the counting of the phases must be independent of whether a current is flowing or not and, in the case of current flow, of whether this current flows in the direction of the counting or against this direction. The current *J* is positive in the former case and negative in the latter, whether the actual reaction is known or not known.

[4.2] The *cell reaction* is a heterogeneous chemical reaction between *thermodynamically defined* reagents and products (ions, electrons, atoms, or molecules) present in the homogeneous interiors of the phases of the cell, while a simultaneous transfer of a corresponding electrical charge takes place through the cell.

The cell reaction is completely represented, with respect to both extent and direction, by writing, in the case of our example, either cell reaction  $\gamma$ :



or the reverse cell reaction  $\delta$ :



Depending on the direction of the current, reaction  $\gamma$  or reaction  $\delta$  will occur in cell *v* or in cell *w*.

There must be independence of the direction of the cell reaction from the fixed direction of the counting of the phases.

[4.3] If we wish to consider the corresponding transfer of electrons through the external metallic connection between I and I', we may designate this transfer as the *pole reaction*. Adding this pole reaction to the *open cell reaction* in the *open galvanic cell* we obtain the *closed cell reaction* in the *closed cell*. It thus becomes clear that no essential difference needs to be introduced between the treatments of open and closed cells and cell reactions (see [4.14] below).

[4.4] The *chemical affinity* *A* of the cell reaction and its *free enthalpy change*  $\Delta G$  are related to the chemical potentials  $\mu_i$  of the reactants and products and to their stoichiometric coefficients  $\nu_i$  as follows:

$$\text{for reaction } \gamma: A_\gamma = -\Delta G_\gamma = -\sum \nu_{i,\gamma} \cdot \mu_i$$

$$\text{for reaction } \delta: A_\delta = -\Delta G_\delta = -\sum \nu_{i,\delta} \cdot \mu_i = -A_\gamma$$

According to whether cell reaction  $\gamma$  is chemically spontaneous or nonspontaneous its chemical affinity is positive or negative.

[4.5] The *reaction charge*  $z \cdot F$  and the *number of charges transported*  $z$  correspond to one occurrence of the cell reaction. If the charge transported through the cell in the direction of the counting, i.e., from I to I' is positive,  $z$  is positive; if a positive charge is transported against the direction of the counting, i.e., from I' to I,  $z$  is negative.

Since the cell reaction can be either  $\gamma$  or  $\delta$  and the cell can be either *v* or *w*, we have the following four possibilities and corresponding values of  $z$ :

	Cell reaction $\gamma$	Cell reaction $\delta$
Galvanic cell <i>v</i> :	$z_{\gamma,v} = +2$	$z_{\delta,v} = -2$
Galvanic cell <i>w</i> :	$z_{\gamma,w} = -2$	$z_{\delta,w} = +2$

[4.6] The open cell reaction, the pole reaction, and the closed cell reaction, when written in terms of the same stoichiometry, have the *same* number of charges transported  $z$ .

[4.7] The *chemical tension* or *electromotive force*  $E = A / (z \cdot F)$  of a galvanic cell represents, in magnitude and in sign, the force with which the cell reaction tends to move *positive* charges through the cell in the direction of the counting of the phases on account of *chemical* (or, more generally, nonelectrostatic) causes, *no other forces being effective*. The chemical tension *E* is given in units of tension, for instance in volts.

Applying the general relation  $E = A / (z \cdot F)$  to galvanic cells *v* and *w* and to cell reactions  $\gamma$  and  $\delta$ , we have:

$$E_v = A_\gamma / (z_{\gamma,v} \cdot F) = A_\delta / (z_{\delta,v} \cdot F)$$

$$E_w = A_\gamma / (z_{\gamma,w} \cdot F) = A_\delta / (z_{\delta,w} \cdot F) = -E_v$$

[4.8] The *cell tension*  $U = \phi_i - \phi_{i'}$ , sometimes called "cell voltage," of an open galvanic cell (with

a chosen direction I to I' for the counting of the phases) is defined as being equal to the inner electric potential of pole I minus the inner electric potential of pole I'. This quantity is *measurable*. It represents, in magnitude and in sign, the force with which the cell reaction tends to move *positive* charges through the cell in the direction of the counting of the phases on account of purely *electric* causes, i.e., on account of the electrostatic distribution of space charges, no other forces being effective.

This definition of the cell tension is in agreement with the general definition of a tension:  $U = \phi_{in} - \phi_{r,in}$ , between the initial and the final points of an interval, while the "electric potential difference" is, on the other hand, defined as  $\Delta\phi = \phi_{r,in} - \phi_{in}$ . It follows therefore that, in general,

*electric tension* = - *electric potential difference*

The expression "cell potential" is sometimes used in place of "cell tension," but this easily leads to confusion with other kinds of potentials (chemical, electrochemical, surface, outer electric, etc.) and cannot be recommended.

[4.9] The *electrochemical affinity* of the cell reaction  $\gamma$  or  $\delta$  of an open cell with a cell tension  $U_v$  or  $U_w$  is given as follows:

$$\tilde{A}_\gamma = A_\gamma + z_{\gamma,v} \cdot F \cdot U_v = A_\gamma + z_{\gamma,w} \cdot F \cdot U_w$$

$$\tilde{A}_\delta = A_\delta + z_{\delta,v} \cdot F \cdot U_v = A_\delta + z_{\delta,w} \cdot F \cdot U_w = -\tilde{A}_\gamma$$

[4.10] The *electrochemical tension*  $\tilde{E}_v$  or  $\tilde{E}_w$  of an open galvanic cell v or w is defined as follows:

$$\tilde{E}_v = \tilde{A}_\gamma / (z_{\gamma,v} \cdot F) = \tilde{A}_\delta / (z_{\delta,v} \cdot F)$$

$$\tilde{E}_w = A_\gamma / (z_{\gamma,w} \cdot F) = \tilde{A}_\delta / (z_{\delta,w} \cdot F) = -\tilde{E}_v$$

[4.11] When reaction  $\gamma$  or  $\delta$  of an open cell v or w is at *electrochemical equilibrium*, i.e., when no current is flowing through the cell, the electrochemical affinities are equal to zero:

$$\tilde{A}_\gamma = 0 \quad \text{and} \quad \tilde{A}_\delta = 0$$

and the electrochemical tensions are likewise equal to zero:

$$\tilde{E}_v = 0 \quad \text{and} \quad \tilde{E}_w = 0$$

This state of equilibrium can be regarded as resulting from the compensation exerted by the "reversible" cell tension U acting as a counterforce against the chemical tension (or electromotive force) E:

$$\text{for cell v: } U_{v,\gamma} = -A_\gamma / (z_{\gamma,v} \cdot F) = \\ U_{v,\delta} = -A_\delta / (z_{\delta,v} \cdot F) = -E_v$$

$$\text{for cell w: } U_{w,\gamma} = -A_\gamma / (z_{\gamma,w} \cdot F) =$$

$$U_{w,\delta} = -A_\delta / (z_{\delta,w} \cdot F) = -E_w$$

$$\text{with: } U_{v,\gamma} = -U_{w,\gamma}; U_{v,\delta} = -U_{w,\delta}; E_v = -E_w$$

The sign of the reversible cell tension U, as well as that of the corresponding chemical tension (or electromotive force) E, depends on the chosen direction of the counting of the phases of the cell, but

it does not depend on whether reaction  $\gamma$  or  $\delta$  is used for the calculation of U and E.

It is most important to make a sharp distinction, both as to denomination and as to symbol, between U and E, their respective electrostatic and chemical natures being emphasized by the fact that they have opposite signs.

Even when the cell reaction, its affinity, and the number of charges transported are unknown, we always have  $U = -E$ . On account of the definition  $U = \phi_I - \phi_{I'}$ , it follows mathematically, but not by definition, that  $E = \phi_{I'} - \phi_I$ .

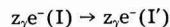
[4.12] The reversible cell tension of an open ideal galvanic cell I/II/III/IV/I' is the resultant of the reversible Galvani tensions at the successive interphases:

$$U_v = \phi_I - \phi_{I'} = g_{I,II} + g_{II,III} + g_{III,IV} + g_{IV,I'}$$

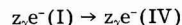
It is clear that the Galvani tension between the two metallic phases IV and I' must fully be taken into account (12).

[4.13] For some practical purposes, especially if the sign of the cell tension is not ambiguous, or if it happens to be of no importance, one may, as a simplification, use the absolute value of the reversible cell tension or that of its chemical tension (or electromotive force). However, for purposes of tabulation and calculation, the signs are essential.

[4.14] Let us consider a certain *cell reaction*  $\gamma$  in an *open* galvanic cell v. The corresponding *pole reaction*  $\pi$  with the same number of charges transported,  $z_\pi = z_\gamma$ , consists of the transfer of electrons from pole I to pole I' through an external metallic connection (see [4.3]):



By adding  $\pi$  to  $\gamma$  we transform the open cell reaction  $\gamma$  into the *closed cell reaction*  $\lambda$  of the *closed* cell I/II/III/IV/I'/I (the phases being counted by rotation from I back to I). We can also consider a *real pole reaction*  $\rho$  with the same number of charges transported as  $\gamma$  or  $\pi$ ,  $z_\rho = z_\gamma$ , consisting of the transfer of electrons from pole I to phase IV through the external metallic connection and pole I':



The quantities  $z$ , A, E, U,  $\tilde{A}$  and  $\tilde{E}$  for reactions  $\gamma$ ,  $\pi$ ,  $\lambda = \gamma + \pi$  and  $\rho$  at electrochemical equilibrium may be tabulated as follows:

$\gamma$	$\pi$	$\lambda = \gamma + \pi$	$\rho$
$z_\gamma$	$z_\pi = z_\gamma$	$z_\lambda = z_\gamma$	$z_\rho = z_\gamma$
$A_\gamma$	$A_\pi = 0$	$A_\lambda = A_\gamma + A_\pi = A_\gamma$	
$E_\gamma = A_\gamma / (z_\gamma \cdot F)$	$E_\pi = 0$	$E_\lambda = E_\gamma + E_\pi = E_\gamma$	
$U_\gamma = \phi_I - \phi_{I'} = -E_\gamma$	$U_\pi = -U_\gamma$	$U_\lambda = U_\gamma + U_\pi = 0$	
$\tilde{A}_\gamma = A_\gamma + z_\gamma \cdot F \cdot U_\gamma = 0$	$\tilde{A}_\pi = z_\gamma \cdot F \cdot U_\pi$	$\tilde{A}_\lambda = \tilde{A}_\gamma + \tilde{A}_\pi = \tilde{A}_\pi$	$\tilde{A}_\rho = \tilde{A}_\lambda = \tilde{A}_\pi$
$\tilde{E}_\gamma = \tilde{A}_\gamma / (z_\gamma \cdot F) = 0$	$\tilde{E}_\pi = -U_\gamma = E_\gamma$	$\tilde{E}_\lambda = \tilde{E}_\gamma + \tilde{E}_\pi = -U_\gamma$	$\tilde{E}_\rho = \tilde{E}_\lambda = -U_\gamma$

It is practically important that the electrochemical tension  $\tilde{E}_\pi$  between I' and I, as well as the electrochemical tension  $\tilde{E}_\rho$  between IV and I, are equal but (on account of the counting of the phases by rotation) of opposite sign to the cell tension  $U_\gamma$ .

[4.15] At a cell tension U, different from the reversible value  $U_{v,\gamma} = U_{v,\delta}$ , the measurable *cell po-*

larization of cell  $v$ , with cell reaction  $\gamma$  or  $\delta$ , is given by

$$\Delta U_{v,\gamma} = U_v - U_{v,\gamma} = \Delta U_{v,\delta} = U_v - U_{v,\delta}$$

This polarization of the cell, under the cell tension  $U_v$ , results in general from the passage of current and is related to the corresponding electrochemical affinities of cell reactions  $\gamma$  and  $\delta$  as follows:

$$\tilde{A}_\gamma = z_{\gamma,v} \cdot F \cdot \Delta U_{v,\gamma} \quad \text{and} \quad \tilde{A}_\delta = z_{\delta,v} \cdot F \cdot \Delta U_{v,\delta} = -\tilde{A}_\gamma$$

and to the electrochemical tension  $\tilde{E}_v$  of cell  $v$  resulting from cell reaction  $\gamma$  or  $\delta$  as follows:

$$\tilde{E}_v = \tilde{A}_\gamma / (z_{\gamma,v} \cdot F) = \Delta U_{v,\gamma} = \tilde{A}_\delta / (z_{\delta,v} \cdot F) = \Delta U_{v,\delta}$$

[4.16] If the actual Galvani tensions  $g$  and the actual cell tension  $U$  differ only on account of the passage of current from the reversible values of the  $g$ 's and of  $U$  in the same cell at zero current, the polarization values being then such that

$$\Delta g = g_{J \neq 0} - g_{J=0} \quad \text{and} \quad \Delta U = U_{J \neq 0} - U_{J=0}$$

and if ohmic tensions  $U_\Omega$  occur in each homogeneous phase, we have the general relation

$$\Delta U = \Sigma \Delta g + \Sigma U_\Omega$$

In other words, the cell polarization  $\Delta U$  is the algebraic sum of the electrode polarizations  $\Delta g$  and of the ohmic tensions  $U_\Omega$  within the phases.

[4.17] A distinction is often made, particularly in the Anglo-American electrochemical literature, between a "galvanic cell" able to produce a spontaneous current (for which  $J < 0$  corresponds to  $U > 0$  and  $J > 0$  to  $U < 0$ ) and an "electrolytic cell" in which the cell reaction results from a nonspontaneous current (for which  $J > 0$  corresponds to  $U > 0$  and  $J < 0$  to  $U < 0$ ).

The recommendations put forward in the CITCE report on Electrochemical Nomenclature and Definitions (5) do not make such a distinction, the single expression *galvanic cell* being used for both types of cases, whether or not a current is flowing and, in the event of current flow, whether its direction is spontaneous or nonspontaneous.

[4.18] Let us consider a galvanic cell in which a constant current  $J$  flows between time  $t_0$  and time  $t_1$ . The cell tension  $U_r = \phi_1 - \phi_2$  will in general vary with time during the interval  $t_1 - t_0$ . The outside circuit, under the tension  $U'_r = \phi_2 - \phi_1 = -U_r$ , receives, in this *primary* performance of the cell, the quantity of electric work [see (10)]:

$$W_{0,1} = \int_{t_0}^{t_1} U'_r \cdot J \cdot dt = - \int_0^{\Delta q} U_r \cdot dq$$

with  $\Delta q = J \cdot (t_1 - t_0)$ . If, from time  $t_1$  to time  $t_2$ , with  $t_2 - t_1 = t_1 - t_0$ , the constant current  $J_r = -J$  is made to flow through the cell in the direction opposite to that of  $J$ , the total charge transported by this reverse current will be  $\Delta q_r = J_r \cdot (t_2 - t_1) = -J \cdot (t_1 - t_0) = -\Delta q$ , and the outside circuit, under the tension  $U'_{r,r} = -U_{r,r}$ , will receive, in this *secondary*

performance of the cell, the quantity of electric work

$$W_{1,2} = \int_{t_1}^{t_2} U'_{r,r} \cdot J_r \cdot dt = \int_0^{\Delta q} U_r \cdot dq$$

The material changes produced in the cell during the primary performance are exactly compensated by those produced during the secondary performance. At given temperature and pressure the cell may thus be regarded as having accomplished a cyclic process and the total external work done by the cell must, in accordance with thermodynamic principles, be either negative or equal to zero:

$$W = W_{0,1} + W_{1,2} = - \int_0^{\Delta q} U_r \cdot dq + \int_0^{\Delta q} U_r \cdot dq \leq 0$$

In the case of over-all *irreversible* performance there is a dissipation of external work,  $W < 0$  (as in the case of a resistance), while in the limiting case of *reversible* performance we have  $W = 0$  (as in the case of a condenser).

[4.19] When, at each instant between  $t_0$  and  $t_2$ , the galvanic cell can be regarded as having a *tension at rest*  $U_r$  which is a determinable function of the charge  $q$  transported up to that instant and which remains unchanged at each value of  $q$  to which the cell will return after further performance and current reversal, we may add to, and subtract from the foregoing equation the integral

$$\int_0^{\Delta q} U_r \cdot dq$$

Introducing the polarizations

$$\Delta U = U_r - U_r \quad \text{and} \quad \Delta U_r = U_r - U_r$$

we then obtain:

$$W = - \int_0^{\Delta q} \Delta U \cdot dq + \int_0^{\Delta q} \Delta U_r \cdot dq \leq 0$$

The primary performance may be *spontaneous*, in which case we have:

$$U_r > 0 \quad \text{with} \quad U_r < U_r, \quad \Delta U < 0, \quad \text{and} \quad J < 0;$$

$$\text{or} \quad U_r < 0 \quad \text{with} \quad U_r > U_r, \quad \Delta U > 0, \quad \text{and} \quad J > 0,$$

or it may be *nonspontaneous*, in which case we have:

$$U_r > 0 \quad \text{with} \quad U_r > U_r, \quad \Delta U > 0, \quad \text{and} \quad J > 0;$$

$$\text{or} \quad U_r < 0 \quad \text{with} \quad U_r < U_r, \quad \Delta U < 0, \quad \text{and} \quad J < 0.$$

At vanishing polarization, i.e., as  $\Delta U$  tends toward zero, the performance of the cell becomes *reversible*.

#### Real Galvanic Cells—Reference Cells

[5.1] Real galvanic cells differ from ideal ones on account of the fact that the former exhibit certain irreversible chemical changes even when no current is flowing. Typical cases of this sort are those of galvanic cells in which phases II and III are solutions of electrolytes between which irreversible diffusion processes occur. An example is the real galvanic cell  $v$ :



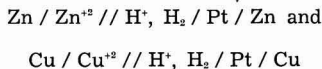


In this case there is, strictly, a small diffusion tension  $g_{II,III}$  between the two electrolyte solutions II and III. If we neglect it, the relation given in [4.12] can be simplified to

$$U_v = \phi_I - \phi_{I'} = g_{I,II} + g_{II,IV} + g_{IV,I'} \\ = g_{I,II} - g_{IV,III} + g_{IV,I'}$$

We see that  $U_v$  does not represent only the difference of the two Galvani tensions  $g_{I,II}$  and  $g_{IV,III}$ , but that it also includes the Galvani tension  $g_{IV,I'} = g_{Cu,Zn}$  which specifically depends on the properties of the two metals in contact.

[5.2] We designate as *reference cells* such real galvanic cells as



In each one of these cells the electrode on the right is the reference electrode  $Pt / H^+, H_2$  taken at standard conditions. It is thermodynamically and experimentally established that the *reference cell tensions*  $U_{h,Zn}$  and  $U_{h,Cu}$  are related to the cell tension  $U_v$  of the cell considered above as follows:

$$U_v = U_{h,Zn} - U_{h,Cu}$$

These reference cell tensions  $U_h$ , listed according to their increasing or decreasing values, constitute the so-called electrochemical series.

[5.3] An incorrect interpretation of the foregoing important difference relations originates in the erroneous assumption that, in the exact relations for the cell tension given in [5.1], i.e.,

$$U_{h,Zn} = g_{Zn/Zn^{+2}} - g_{Pt/H^+,H_2} + g_{Pt/Zn} \\ U_{h,Cu} = g_{Cu/Cu^{+2}} - g_{Pt/H^+,H_2} + g_{Pt/Cu} \\ U_v = g_{Zn/Zn^{+2}} - g_{Cu/Cu^{+2}} + g_{Cu/Zn}$$

the individual Galvani tensions between the corresponding two metals,  $g_{Pt/Zn}$ ,  $g_{Pt/Cu}$  and  $g_{Cu/Zn}$  can be neglected. Indeed, in this manner, we would obtain the formally simpler but incorrect relations:

$$U_{h,Zn} = g_{Zn/Zn^{+2}} - g_{Pt/H^+,H_2} \\ U_{h,Cu} = g_{Cu/Cu^{+2}} - g_{Pt/H^+,H_2} \\ U_v = g_{Zn/Zn^{+2}} - g_{Cu/Cu^{+2}}$$

[5.4] A further incorrect step consists of putting  $g_{Pt/H^+,H_2} = 0$ , with the deceptively simple but again incorrect result:

$$U_{h,Zn} = g_{Zn/Zn^{+2}} \quad \text{and} \quad U_{h,Cu} = g_{Cu/Cu^{+2}}$$

We find here the reason for the denomination "electrode potentials" which is sometimes used to designate the reference cell tensions  $U_h$ . Even among those who know the arbitrariness of this last hypothesis, there are many who overlook the error made in neglecting the individual Galvani tensions between metals in contact (12) when they consider that the sequence of the  $U_h$  values as given by the electrochemical series is also the sequence of the corresponding Galvani tensions such as  $g_{Zn/Zn^{+2}}$ .

### Some Remarks Concerning Multiple Electrodes

[6.1] The foregoing fundamental considerations apply to simple (or mono-) electrodes and to galvanic cells constituted of such electrodes. It is important to add some remarks concerning *multiple* (or *poly-*) electrodes, which are frequently encountered in real galvanic cells.

[6.2] A *bi-electrode* is the seat of two different electrode reactions. A *poly-electrode* is the seat of several different electrode reactions.

[6.3] Among the bi-electrodes we further distinguish two important types of cases: (i) The 2-2 electrodes whose metallic phases I contribute one ionic species to one of the electrode reactions and another ionic species to the other electrode reaction. For instance, the metallic ion  $Me^+$  in I is involved in reaction 1 and the electron  $e^-$  in I is involved in reaction 2. (ii) The 1-2 electrodes whose metallic phases I contribute the same ionic species, for instance  $Me^+$  or  $e^-$ , to both reactions.

[6.4] A frequent complication with bi-electrodes is the occurrence of an inner reaction in the solution phase II between the reactants or products of the two electrode processes without the formation of a new solid phase. Certain additional material changes will then superpose themselves to the diffusion phenomena in the diffusion layer, concentrations and overpotentials being thus markedly affected.

A further complication resulting from an inner reaction is the formation of one or several new solid phases. In addition to material disturbances within the diffusion layer the electrode end reactions will now be affected and their respective barriers modified.

[6.5] Some particular concepts, magnitudes and relations applying to a bi- or to a poly-electrode result directly from those pertaining to each of the two or of the several separate electrode reactions and which have been examined in the foregoing treatment of mono-electrodes. For instance, the total current is the sum of the partial currents:  $J = J_1 + J_2$ .

[6.6] A simple case is that of the *double electrochemical equilibrium* in which the equilibrium Galvani tensions of the two electrode reactions of a bi-electrode are equal to each other:  $g_1 = g_2$ .

[6.7] A more complicated case is that of a *mixed electrode* for which the equilibrium Galvani tensions of the several reactions are different from one another: for instance,  $g_1 \neq g_2$  for a bi-electrode.

At zero net current we then have a *mixed Galvani tension*  $g_{J=0}$  and a *local current*  $J_1 = -J_2$ , concepts applying for instance both to *corrosion* and to *passivity*.

With a net current different from zero we have a *mixed Galvani tension*  $g_{J \neq 0}$ , a *polarization*  $\Delta g_J = g_{J \neq 0} - g_{J=0}$ , and such phenomena as *difference effects* in the material changes at phase ends and *changes in the signs of the polarizations* of the separate electrode reactions, all of these resulting from the shapes and relative positions of the polarization curves of these separate reactions.

### Concluding Remarks

In view of the rapid development of electrochemistry in recent times, only a rational system of concepts, definitions, symbols, etc., can provide a firm basis for further research and for teaching. The carefully worked out recommendations contained in the yearly reports of CITCE's Commission No. 2 on Electrochemical Nomenclature and Definitions (5) should go a long way toward the fulfillment of this goal.

It is to be hoped that all electrochemists interested in the fundamentals of their subject, and especially the younger students in the field, will display the same spirit of cooperation and mutual understanding which has presided over the work of the international CITCE group and that considerable benefits for the future of electrochemistry will thereby ensue.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

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## The Fuel Cell Round Table

A Report by Ralph Roberts

Office of Naval Research, Washington, D. C.

A round-table discussion of fuel cells was held on October 10, 1957, as part of the Battery Division program of the 112th Meeting of The Electrochemical Society in Buffalo, N. Y. The discussion was organized by George Heise, National Carbon Laboratories (retired), who also acted as panel chairman. Other members of the panel were: Ernest Yeager, Western Reserve University; George E. Evans, National Carbon Research Laboratories; Howard L. Recht, Pittsburgh Consolidation Coal Co.; and Ralph Roberts, Office of Naval Research. The attendance at the discussion was approximately 175.

In his opening remarks Mr. Heise indicated that the objectives of the panel were to review the status of fuel cell development and the potentialities of fuel cells as a power source. He read a letter from Professor Farrington Daniel, University of Wisconsin, who indicated that a solution to the solar energy problem might be a combination of the fuel cell with the photochemical decomposition of water. It was further suggested that the storage of hydrogen might be accomplished by adsorbing it at one temperature and releasing it at a higher one.

Dr. Yeager reviewed some of the theoretical considerations regarding fuel cells, which he defined as electrochemical systems in which the direct or indirect oxidation of conventional fuels occurs. In the comparison of the fuel cell with methods of power generation based on the Carnot cycle, one should account for any energy losses due to reactions in preparing the fuel for utilization in the cell. The heat of reaction in the cell itself is given by:

$$Q_{\text{cell}} = nF(E_{\text{rev}} - E_{\text{cell}}) + T\Delta S \quad (1)$$

where the terms all have their usual significance.

In most fuel cells the gas-consuming electrodes are semihydrophobic. The reactant diffuses through the electrode pores to the electrode-electrolyte interface. The life-time of the electrode depends on its rate of wetting by the electrolyte or, for high-temperature cells, on the deterioration of the porous plate. The internal losses due to the resistance of the cell are related to the bulk properties of the materials within the cell and their method of assembly. To overcome activation polarization Dr. Yeager suggested the use of large effective areas of electrode, catalysts, and increasing the temperature of cell operation. For example in the Bacon cell, which utilizes a nickel electrode at 200°-250°C, the activation polarization is an important factor. In the high-temperature fuel cells, i.e., those operating above 500°C, there is very little activation polarization. Mass or concentration polarization can be reduced by increasing the porosity of the electrode through which the gas reactants diffuse. The reactants should not diffuse into the electrolyte, as this not only leads to poor efficiency in their utilization,

but can lead to dangerous mixtures of fuel and oxidant.

Available evidence indicates that the oxygen electrode, on an active carbon surface in alkaline media and at temperatures below 100°C, is reversible with respect to the hydroperoxide ion,  $\text{HO}_2^-$ :



However, it is possible to obtain a four-electron process in terms of coulomb efficiency, utilizing both atoms of oxygen in the oxygen molecule by the incorporation of a good catalyst for the decomposition of the hydroperoxide ion in the carbon electrode. Thus, the loss of oxygen by the diffusion of the hydroperoxide ion away from the electrode is prevented. Silver has been found to be a very effective catalyst for this purpose, but the addition of the catalyst does not assure a four-electron process in terms of free energy or voltage. In the use of metal electrodes with oxygen it is necessary to have the interaction between the metal and oxygen and the electron transfer process highly reversible if the potential of the oxygen electrode is to be realized.

In low-temperature cells utilizing hydrogen at the anode, the addition of metals, especially platinized platinum, to the carbon electrode helps overcome the activation polarization. In the high-temperature fused electrolyte fuel cells, utilizing hydrocarbons, it appears that the hydrocarbon is cracked to carbon and hydrogen and the latter reacts at the electrode.

Dr. Yeager referred to the possibility of closed cycle battery systems. In such a system the reactants are regenerated from the products formed during the discharge of the cell. In a semi-closed system only one of the reactants would be regenerated from the cell products. The following methods of reactant regeneration were suggested: (a) chemical; (b) photochemical; (c) radiochemical; (d) thermal; (e) electrolytic. The process involved in the case of thermal regeneration is shown in Fig. 1 and the maximum efficiency is given by the Carnot cycle. In the case of electrolytic regeneration, the regenerating cell would be operated at a temperature higher than the energy-producing one. The efficiency of such a system is given by:

$$\frac{nF(E_{T_1} - E_{T_2})}{Q_{T_1}} = \frac{T_1 - T_2}{T_1} \quad (\text{III})$$

where  $T_1$  is the higher temperature and  $T_2$  the lower one.

Dr. Evans defined the fuel cell as "an electrochemical system in which the oxidant and reductant

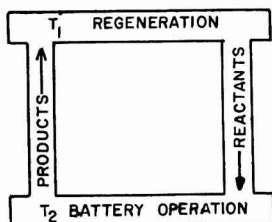


Fig. 1. Closed cycle system

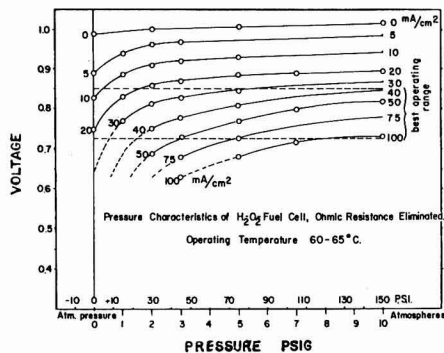


Fig. 2. Pressure characteristics of hydrogen-oxygen fuel cell

are introduced continuously and the products withdrawn continuously, with the composition of the system remaining invariant during the generation of electricity."

Research at the National Carbon Research Laboratories is concerned with the low-temperature hydrogen-oxygen cell, below 100°C. The electrodes are specially prepared carbon and the electrolyte is potassium hydroxide solution. The water formed due to the electrochemical reactions is evaporated at the same rate that it is produced. The low operating temperature makes the use of air more practical than in the high-temperature systems as heat loss to the nitrogen is negligible. Because of the polarization of the cathode in the presence of air such a cell is limited to low power densities. For high power outputs it is necessary to increase air pressure above atmospheric or to use oxygen. The effect of oxygen pressure on cell performance is shown in Fig. 2. When the pressure is above three atmospheres the curves become nearly linear. No real difficulty is presented until the pressure exceeds five atmospheres; up to this pressure conventional construction can be used.

The anode utilizes commercial tank hydrogen. It is insensitive to sulfur-containing impurities, carbon monoxide and other impurities, and has operated on natural gas and then returned to hydrogen without loss in its operating characteristics. Because of the storage problem, an inexpensive source of hydrogen would be advantageous. The actual source and method of storage would be determined in part by the use conditions. Research is being continued to obtain more information regarding the optimization of the cell parameters and the effect of temperature and pressure on its operation. The low operating temperature permits greater flexibility in the selection of materials of construction and leads to low maintenance cost. Battery lifetime depends largely on the rate at which the electrode is wetted. To date the National Carbon Company has operated the same electrodes for 300 days, drawing current during the day and allowing the system to stand on open circuit overnight. This cell is still in operation.

The present status of the Bacon cell, a hydrogen-oxygen fuel cell which operates at elevated pressure and temperatures above 200°C, was reviewed by Dr. Roberts. This was based on published informa-

Table I. Operating data for the Bacon cell

Temp, 200°C Voltage	Pressure 600 lb/in <sup>2</sup> Amp/ft <sup>2</sup>
1.10	open circuit
0.89	90
0.83	180
0.72	360
0.62	540

tion (1). The electrodes are of porous nickel about 4 mm thick, and have a pore size of about 30 microns on the gas side, and a thin layer with much smaller pores on the liquid side. The oxygen electrode, which initially controlled the cell lifetime, has been improved by a preoxidation treatment. Lithium atoms are incorporated into the crystal lattice of the nickel oxide, thus converting the ordinary green nickel oxide into a black double oxide of nickel and lithium, which is a good semiconductor. Using this method of preparation, oxygen electrodes have now been in operation for up to 1500 hr at 200°C. Specimens of the preoxidized nickel have been exposed to oxygen and caustic potash, the electrolyte, at 200°C for more than 8000 hr without visible deterioration. Each cell in this battery is approximately ½ in. thick. Because of the vapor pressure of water over the caustic potash solution at 200°C, it is essential to operate this system at elevated pressure. Table I presents characteristic operating data.

The system requires high purity hydrogen, being more sensitive to contaminants in the anode feed gas than reported above for the National Carbon low-temperature battery. It presents similar problems regarding hydrogen sources, with the additional high purity requirement.

Bacon has suggested that the high-pressure hydrogen-oxygen cell would be primarily used as a storage battery. In this case, the gases for use in the cell would be generated electrochemically from water. The use of hydrogen obtained from the reaction between water and coal and with oxygen obtained from air also has been mentioned. An application noted by Bacon is in the field of railway traction, particularly for rail cars, on lines where it is uneconomic to electrify completely with overhead wires or a third rail. This type of operation, with storage batteries, is in use in the German state railway.

Dr. Recht discussed the high-temperature fuel cell. The primary reason for development of such a system is the wider range of fuels that it can accommodate. The low-temperature cells which have been studied to date can utilize only hydrogen. The high cost of this gas and the difficulties associated with its transport rule out its economic application except in highly specialized situations. The high-temperature cell can accommodate gases containing mixtures of hydrogen, carbon monoxide, and carbon dioxide which can be generated directly from coal, natural gas, and petroleum. It is even likely that hydrocarbon fuels could be used either directly or indirectly in these cells. The integration of the high-

temperature fuel cell with a coal gasification unit is possible. The high-temperature cells also offer the possibility of higher output at comparable gas pressures due to the reduced electrode polarization and higher diffusion rates in the electrolyte.

One of the major drawbacks in the high-temperature cell is the severely corrosive conditions encountered. This affects not only the containing structure of the cell, but also the materials of which the cell itself is constructed. Another problem is the maintenance of cell stability i.e., the prevention of loss of electrolyte through seepage from the cell, attack on the electrodes or the matrix by the electrolyte, and the accumulation of corrosion products within the electrolyte.

The discussion of Dr. Recht was on the work of the Pittsburgh Consolidation Coal Co., which is under the sponsorship of the Army Signal Corps. The electrolyte section of the cell consists of a porous magnesium oxide matrix containing the molten electrolyte and an equi-molar mixture of sodium and lithium carbonates. It has been found necessary to use an extremely pure grade of magnesium oxide for the matrix. For the fuel electrode a porous nickel metal sheet has been found to be satisfactory. The air electrode has presented a more difficult problem. The most promising result to date has been obtained with the use of nickel oxide with additives to produce a semiconducting material. Carbon dioxide is added to the air supply to reduce concentration polarization and maintain a stable system.

The work at Pittsburgh Consolidation Coal Company has been in the temperature range of 500°-800°C, mainly to simplify solution of the problem of materials of construction. Due to the disproportionation of carbon monoxide at the lower end of this temperature range, fuels containing carbon monoxide are difficult to use. Therefore, hydrogen has been used in the low-temperature range. At the higher temperatures, in the order of 800°C, carbon monoxide and mixtures of carbon monoxide and hydrogen can be used without carbon deposition. The open-circuit voltages obtained, of the order of one volt, are usually within 50 mv of the theoretical value, and often closer. A power output of 30 w/ft<sup>2</sup> of electrode has been achieved. With proper cell assembly, the open-circuit voltage and the performance level do not change appreciably over a period of several days with the cell maintained at operating temperatures. The ultimate operating life of the unit has not been determined.

In addition to the chemical nature of the cell components, the physical form has a great effect on the performance obtained. Good contact between the electrodes and the electrolyte, as well as good electrical contact from the electrodes to the external circuit are not always easy to obtain. These problems, and that of retaining the molten electrolyte within the cell, will prove major problems for the engineer, if a commercial high-temperature fuel cell is to be developed. In addition, the operating life of a commercially satisfactory fuel cell must be of the order of several years because of the expected high capital cost.

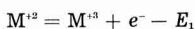
Dr. Recht noted the lack of knowledge of the mechanism of the electrode reactions occurring in the high-temperature fuel cell. He indicated that the understanding of the fundamental mechanism of the fuel cell reactions is extremely important to the attainment of the practical goals.

The work in Great Britain on the Redox fuel cell was reported by Dr. Roberts. The information was based on a report which was made available through the courtesy of the United Kingdom Electricity Council (2). The work was under the general direction of Sir Eric Rideal at Kings College, London.

This type of cell is one in which the electrode reactants are regenerated outside the cell, but the net reaction is equivalent to that of fuel combustion. This is illustrated in the following summary:

Negative electrode:

Internal to cell

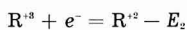


External to cell

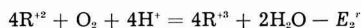


Positive electrode:

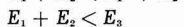
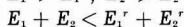
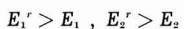
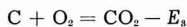
Internal to cell



External to cell



Net reaction:



The electromotive force of the cells studied by this group is limited by the free energy of the carbon, oxygen reaction or approximately 1.02 v. It is further reduced because each regeneration reaction must have a negative free energy, thus giving a net effective voltage, as noted above, less than that of the carbon-oxygen cell. The thermodynamic efficiency of this system is given by Eq. (IV):

$$\text{Eff} = \frac{E_1 + E_2}{E_3} \times 100\% \quad (\text{IV})$$

$E_1$ -anode potential;  $E_2$ -cathode potential;  $E_3$ -carbon-oxygen cell potential.

Two general types of redox fuel cells have been studied. In the first, the same element in different oxidation states is used as the anode and cathode reactants. An example of this is the ferrous-ferric couple. This, as expected by the Nernst equation, is limited to low voltages ( $\sim 0.25$  v). In the second type, different elements are used in the anode and cathode compartments.

The best of the anodic materials studied to date has been stannic chloride in a hydrochloric acid solution. However, it has not been found possible to regenerate this from the cell product by use of coal. Even at temperatures of  $100^\circ$ - $180^\circ\text{C}$ , in an autoclave, only a small amount of reduction of the stan-

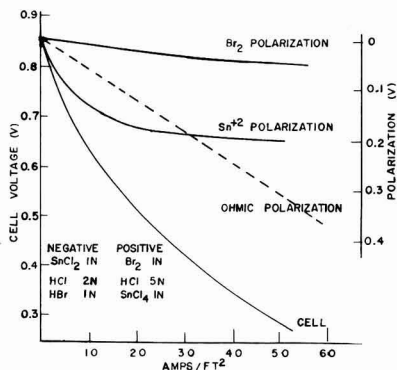


Fig. 3. Operating characteristics of stannous ion-bromine cell

nic ion occurs. The sulfur dioxide-sulfate ion couple is more rapidly regenerated; however, few cell performance data were reported for this couple. As much as 30% of the coal has been utilized for the reduction of the sulfate ion and the results have given interesting information on coal chemistry. More success has been obtained with the positive electrode. Using bromine in a solution of hydrobromic acid as the cathodic material, it has been found possible to regenerate the bromine at room temperature using oxygen in the presence of nitrogen dioxide as a catalyst. The group has reported on the kinetics of this reaction (3).

The operating characteristics of the stannous ion, bromine cell are shown in Fig. 3.

The concept of the redox fuel cell is a very interesting one, but a complete working system has not been developed. The regeneration problem, especially of the negative reactant with coal, has only been attained with low coal utilization efficiency. The investigators are of the opinion that the material efficiencies that can reasonably be expected, on the basis of the present stage of development, are about 70% for fuel consumption, 90% for the cell, and 60% over-all.

During the discussion Dr. George J. Young, Pennsylvania State University, reviewed some of the recent work in his laboratory on electrodes related to fuel cells. In the metal-oxygen electrode system he indicated the importance of the equilibrium between the chemically adsorbed state and the solution, the potential of the oxygen electrode depending on the nature of the chemisorbed state. The ultimate limitation in current density is the chemical kinetics of the system, which includes the activated adsorption of reactants, activated desorption of products, and the activation energy for surface mobility. He also reviewed some work on the relationship between the heat of chemisorption of hydrogen on metals as related to the d-band vacancies of the latter. The chemical adsorption energies are greatest where there is binding between the bonding orbital of the metal and the adsorbed substance. He has concluded that the best catalysts for the hydrogen anode are the metals of Group 8b.

Although there was considerable discussion of potential applications very few specific ones were

noted. Dr. Evans pointed out that the portability and availability of power on demand from fuel cells make them of interest in nonmilitary parts of the economy. However, it appears that certain military applications are more immediate. Dr. R. C. Shair and Dr. H. L. Foote of the Bell Telephone Laboratories indicated that there may be a possible application of the fuel cell in the telephone system. With the decrease in the nominal power required for telephone operation through the greater use of transistors, a small reliable power generator of 1-100 w may be required. Such power generators are either not available or are inefficient and uneconomic. A reliable fuel cell that could be operated in remote areas as required would therefore be of interest to this telephone application.

It was the general consensus that a fuel cell symposium should be held within two to three years.

The writer wishes to acknowledge the assistance of the members of the panel and Mr. U. B. Thomas.

Manuscript received Feb. 12, 1958.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

#### REFERENCES

1. F. T. Bacon, *The Times Science Review Quarterly*, No. 20, p. 6, *The Times*, London, England (Summer 1956).
2. A. L. Benjamin, B. E. M. Bingham, and A. M. Posner, "On the Production of Electrical Energy From Redox Processes", Final Report to the Central Electricity Authority, United Kingdom, dated Nov. 25, 1955.
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## Brief Communication



### ZnS:Sn,Li Phosphor

A. Wachtel

Research Department, Westinghouse Electric Corporation, Bloomfield, New Jersey

Garlick and Mason (1) have described the use of Sn as an activator in ZnS, resulting in a red photoluminescence peaked at 6450Å. During the course of some investigations of this system, it was noted that the use of Li salts (and to a lesser degree, Na salts) results in the formation of a yellow-emitting photo- and cathodoluminescent phosphor. The best results were obtained by the use of Li halides, of which only very small concentrations (of the order of 100 ppm) are necessary to effect the conversion to this system, although about 4 mole % were found practical so as to obtain additional fluxing action.

Figures 1 and 2 show the excitation and emission spectra at room temperature of a typical hexagonal ZnS:Sn,Li phosphor prepared with 1 mole % Sn and 4 mole % LiBr. It can be seen that, in this case, the emission at 4380Å of Li in ZnS as reported by Kröger (2) for cubic ZnS is not apparent. The excitation spectrum, especially that of ZnS:Sn (not shown here), has the appearance of being due to Cu (presumably present as a contaminating impurity) so that even in this case an energy transfer could be visualized (3).

It has been suggested (4) that Sn, replacing Zn, can act as a double donor center. In the red-emitting ZnS:Sn phosphor, the Sn may be neutralized by a Zn-vacancy. On the other hand, charge compensation by monovalent cations such as Li would require two such atoms for each atom of Sn present. If the energy levels of these are not equivalent to each other, then the presence of the double peak in the emission spectrum of ZnS:Sn,Li may thus be explainable.

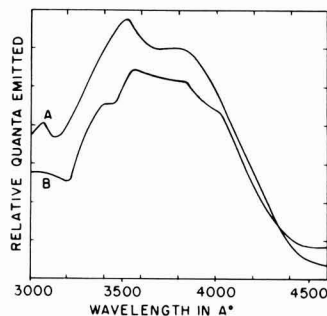


Fig. 1. Excitation spectra of ZnS:Sn,Li. Curve A, 5800Å peak, not corrected for overlap; curve B, assumed peak at 6300Å, corrected for assumed 5800Å overlap.

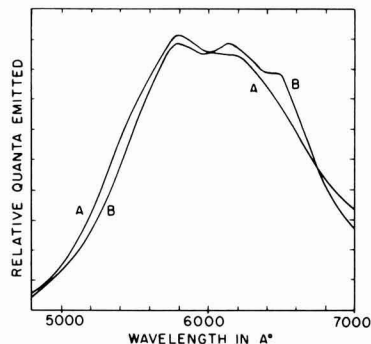


Fig. 2. Emission spectra of ZnS:Sn,Li. Curve A, 3650Å excitation; curve B, 4048Å excitation.

During the course of these investigations, it has been noted that even brief reheating to 800°-900°C completely destroys the red emission of hexagonal ZnS:Sn or the yellow emission of hexagonal ZnS:Sn,Li, respectively, although this was not accompanied by formation of a detectable concentration of cubic ZnS. It was noted similarly that rapidly quenched small samples were invariably more successful. Also, the amount of Sn used was found to be critical and optimum ZnS:Sn phosphor fired at 1150°C with 1 mole % SnS and 5% S addition in 10-g lots in capped silica tubes showed an emission peak at 6800Å and no evidence of the blue "self-activated" band reported by Garlick and Mason. However, the addition of Li salts appears to increase the amount of Sn which can be added without formation of a discolored product and appreciable decrease in fluorescence. In spite of considerable difficulties, some analytical estimates were made by chemical and spectrographic procedures on phosphors fired as described above, with and without the addition of 4 mole % LiBr. According to these, the amount of Sn incorporated in the presence of LiBr appeared to be about 10 times larger and of the order of 0.1 to 0.2%, while the Li content was in

the neighborhood of 50-80 ppm. However, it has not been determined as yet whether this large amount of Sn represents an optimum concentration for this system.

The unusual behavior of the ZnS:Sn and ZnS:Sn,Li systems suggests the need for considerably more extensive investigations. These are contemplated, particularly with reference to the effect of definite concentrations of Cu.

#### Acknowledgment

The writer is particularly indebted to Dr. N. T. Melamed for his numerous measurements of excitation and emission spectra, only a portion of which are shown here, as well as for his valuable suggestions for future efforts in this direction.

Manuscript received April 21, 1958.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1959 JOURNAL.

#### REFERENCES

1. G. F. J. Garlick and D. E. Mason, *Proc. Phys. Soc. (London)*, **62**, 817 (1949).
2. F. A. Kröger, *J. Opt. Soc. Amer.*, **39**, 670 (1949).
3. N. T. Melamed, Private communication.
4. E. Banks, Private communication.

## Correction

In the paper "Impedance and Polarization Measurements in Fused Lithium Chloride-Potassium Chloride" by H. A. Laitinen and H. C. Gaur which appeared on pp. 730-737 in the December 1957 JOURNAL, Vol. 104, No. 12, on p. 734, Eq. (I) and (II) apply to the case of both reactants in solution [see H. A. Laitinen and R. A. Osteryoung, *This Journal*, **102**, 598 (1955)], rather than the metal-metal ion electrode. Equation (III) should read

$$\Delta = \frac{RT}{n^2 F^2 A C^{1-\alpha} k} = \frac{RT}{n F} \cdot \frac{1}{i_0} \quad (\text{III})$$

where  $i_0$  is the exchange current. Since  $\alpha$  is not known, the calculation of  $k$  should be omitted, and

a direct comparison should be made between  $i_0$  as measured by the impedance method and estimated from polarization curves.

For Cd<sup>2+</sup>,  $C = 5.95 \times 10^{-3}$  moles cm<sup>-3</sup>,  $A = 1.3 \times 10^{-3}$  cm<sup>2</sup>,  $i_0 = 1.0 \times 10^{-2}$  amp from impedance measurements and  $1.2 \times 10^{-5}$  amp from polarization curves.

For Zn<sup>2+</sup>,  $C = 7.16 \times 10^{-3}$  moles cm<sup>-3</sup>,  $A = 1.3 \times 10^{-3}$  cm<sup>2</sup>,  $i_0 = 2.4 \times 10^{-3}$  amp from impedance measurements and  $4 \times 10^{-6}$  amp from polarization curves.

The final conclusion (p. 736) regarding incompatibility of the two sets of values is still valid.

In Fig. 14, the potential scale should read +0.1 to -0.1 v, instead of +1.0 to -1.0 v.

# FUTURE MEETINGS OF The Electrochemical Society



**Ottawa, Canada, September 28, 29, 30, October 1, and 2, 1958**

Headquarters at the Chateau Laurier

Sessions will be scheduled on

Batteries, Corrosion, Electrodeposition (including symposia on "Electrodeposition  
on Uncommon Metals" and "Electrodeposition from Fused Salts")

Electronics (Semiconductors),

Electrothermics and Metallurgy,

and a symposium on "Films Formed in Contact with Liquids"

sponsored by Theoretical Electrochemistry, Battery, and Corrosion Divisions

★ ★ ★

**Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959**

Headquarters at the Sheraton Hotel

Sessions probably will be scheduled on

Electric Insulation, Electronics (including Luminescence  
and Semiconductors), Electrothermics and Metallurgy,

Industrial Electrolytics, and Theoretical Electrochemistry

★ ★ ★

**Columbus, Ohio, October 18, 19, 20, 21, and 22, 1959**

Headquarters at the Deshler-Hilton Hotel

★ ★ ★

**Chicago, Ill., May 1, 2, 3, 4, and 5, 1960**

Headquarters at the Lasalle Hotel

★ ★ ★

**Houston, Texas, October 9, 10, 11, 12, and 13, 1960**

Headquarters at the Shamrock Hotel

★ ★ ★

Papers are now being solicited for the meeting to be held in Philadelphia, Pa., May 3-7, 1959. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at Society Headquarters, 1860 Broadway, New York 23, N. Y., *not later than January 2, 1959* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled, and underline the name of the author who will present the paper.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at 1860 Broadway, New York, 23, N. Y.





## On Research—Its Care and Nourishment

### Presidential Address\*

Norman Hackerman

This is the close of the 56th tenure of the office of President of The Electrochemical Society, and it brings to an end what appears to have been a quite satisfactory year in the history of our Society. It is clear that this could not have been the result of the operation during any one year but, instead, is the result of an accumulation of the efforts of many people over a long period of time. Certainly, it is not feasible to name all of those to whom the Society owes a debt of gratitude. I shall mention only two groups. Both have had a great deal to do with providing for the Society the necessary financial stability so that it could go about its main business of helping to advance the science and the technology in its several areas of interest. One group is the Investment Advisory Panel (G. W. Heise, A. K. Graham, Hans Thurnauer, M. J. Udy, C. E. Williams) and the other is the Committee on Sustaining Membership (F. A. LaQue; Hans Thurnauer). In addition, all of the office staff and many of the members have contributed mightily, and, to all, my sincere appreciation. At this juncture, I wish also to tell you that I enjoyed the opportunity of serving the Society in this capacity and that I shall certainly be willing to serve in any way possible if called on to do so in the future.

The Society is very kind to its retiring Presidents in that it provides them this period in which to talk about anything they wish. This could be an evaluation of the Society's position, or a tabulation of its accomplishments, or an exposition on some topic perhaps of interest only to the speaker. As some here can tell you, I am not favorably inclined to editorials written just because there is a place for them. By the same token, the verbal editorial prepared because there is time-space allotted to it can be deadly. Naturally, this gave me quite a problem and I debated with myself for quite a while as to what might be appropriate. A conversation I had with a scientist, now in research administration, who had recently attended one of the numerous executive development courses, gave me a lead. All of the participants at this course, except the person in question, were involved in administration of production facilities, or business functions, or operating departments. The point was made that these people had quite a different point of view than do those who are more closely associated with research and development. This appears to stem largely from a difference in conception of what might be called time-yield. That is, the production head expects to see evidence of a fruitful idea appear in the order of hours or days, and also has come to expect serious problems to appear with relatively high frequency. On the other hand, the research administrator recognizes that, in much of the work over which he has cognizance, time does not appear to be of the essence, and that the likelihood is good that much of the work under-

way will not be fruitful in the usual sense. The difference has been ascribed variously to "drive," "eggheadedness," "impracticality," etc. However, it actually seems to be largely a matter of a balance of the several ingredients which make up the incentive to go into one kind of endeavor as opposed to another. At any rate, this brought to mind the many informal discussions on the sometimes sacred and sometimes infamous sounding word "Research," and this became the topic for the rest of this address. I shall take this up in four briefly titled parts: Yield, Incentive, Supply, and Support.

#### Yield

The yield of research includes the great new concepts which open vast areas for further search; the smaller ideas which, when gathered together by a superior intellect at the proper time, produce the great concepts; the use of each type of advance in application to new research procedures; and, finally, the application of all three to generally useful purposes. Two examples from fields of research to which this Society is closely tied are the fairly well-known development of cells for converting chemical to electrical energy and the somewhat less well-known area involving concentration polarization, polarography, and, recently, solions.

In the first case, the art was known in ancient times, and the quantitative relationships which permitted predictability of limits were developed over a period starting more than 100 years ago. The use of cells under thermodynamic conditions was applied in the numerous and important studies of solutions of electrolytes with little or no thought of practical application. The use of working cells for practical purposes is well known and has been a large factor in present-day civilization. Considerable advances in the kinetic aspects of electrode reactions in the last decade or two must inevitably result in improved packages of chemical energy. This will also lead to the production of useful fuel cells and to the development of new and exotic types of cells.

In the second case, the problem of concentration polarization at working electrodes was recognized during the last century. The quantitative relationships between current and concentration are somewhat more recent in origin. Heyrovsky was one leader in developing these relationships and in showing the way to the analytical application we now know as polarography. In spite of the extensive use of this tool, there still remains considerable mystery, and a great deal of *purely inquisitive research* goes on in this field. Only recently, the same phenomenon of concentration polarization has been put to use in a more general way. Not too many years ago, it was proposed that a concentration polarized cell and an acoustic impulse could be combined in such a way as to provide amplification. This was a concept that did not prove especially fruitful at first but, later,

\* Delivered at the New York Meeting, April 29, 1958.

its development surged forward under the impetus supplied by the ingenuity of a few interested researchers. Quite a few electrochemical devices now have been produced, opening a whole new aspect in the field of electrochemistry. Many of the phenomena of working electrodes and cells are now being scrutinized from this fresh point of view. Quite a few difficulties have been encountered which stem from a lack of basic information. In fact, in both of these cases as in innumerable others, the same conclusion is reached, namely, that there remains much, much more to learn in the field of electrochemistry than is now known.

### Incentive

The incentive for research almost certainly includes any one, or any combination, of the following: gain, fame, satisfaction. It is easy to recognize that these are the same ingredients for incentive in any field. It is likely, however, that, in the case of those who decide to be trained to carry on independent research, there is a greater bias toward the last item—satisfaction. Indeed, if any one of the three were to be the sole incentive for research, it would very likely be that of satisfaction. Of course, there are vanishingly few who fit into such a framework, since just about all who are in the field use their training to earn a living. Perhaps Count de Broglie, whose concept of the dualism of wave and particulate character of material particles added so much to theoretical chemistry and physics, was such a person.

There are many persons trained for research who make use of their training to become associated with a company or corporation at a reasonably high level in a research laboratory, and then waste little time in striking out for an administrative position in research and development or in operating functions of the company. Even these people must have the satisfaction incentive to some degree since there are certainly other, and perhaps better, avenues to high administrative responsibility. The same reasoning must be even more applicable to those who seek fame (either along with gain or in lieu of gain), since the laboratory discovery or the theoretical development is not likely to receive plaudits from any but other scientists. Even there, it is likely to be grudgingly given, since absolute proof is generally not possible.

Granted that the individual has as an incentive for research which is to a greater or lesser degree the satisfaction of unraveling a knot (small or large), can it be said that the same applies to industrial research laboratories and to educational institutions which support research? As far as company or corporation research is concerned, there is only one good incentive, namely, gain. Although a case might be made for fame as an incentive, it is not difficult to see that this is little more than a feedback to the gain incentive. The only way in which satisfaction can enter is vicariously through the company's employed scientists. The educational institution appears to have as its major incentive for research the fame which accrues to outstanding work. This may seem to be a harsh judgment since such institutions should nurture scholarly activity for its own sake. The fact remains, however, that to obtain money to provide the facilities to attract good researchers, the institution must have a reputation as a source of first-class original work.

### Supply

The supply of new people to carry on research at an ever-increasing rate and scope constitutes a difficult

problem. There does not appear to be any need for the hysteria which enveloped the country a few months ago, particularly since mere shouting that more scientists and engineers are needed cannot build into the school child a true bias toward research. As a former President of this Society, Dr. J. C. Warner, pointed out not long ago, if the percentage of all students in school who go into the technical areas remained constant, the number of people so trained would also increase. This must follow, since there are ever-larger numbers entering the schools. This and other points of that speech were commented on very favorably by the lead editorial in the *Chicago Herald Tribune* of April 6 of this year.

The serious problem which remains, however, is whether the percentage of all students going to college who go into scientific or technical fields is remaining constant. A recent survey [*Science*, **127**, 682 (1958)] of Ph.D. degrees granted over the past ten years shows a leveling off and a decrease in the natural and biological sciences, and an increase in the humanities, social sciences, psychology, and education. This is very likely because of lack of proper contact with mathematics in the grade schools, and with higher mathematics and natural sciences in the high schools. Although time is spent in these areas in the grade and high schools, it is generally wasted because the spectacular is emphasized and the sound basic concepts are not properly transmitted. This is so largely because they are imperfectly understood by the teachers themselves. It is important to realize that this is only in part attributable to the present-day popular scapegoat, the professional educator. We, the science professionals, have been strangely lax in not perceiving the danger earlier or in not making vigorous enough protestations (it took Russian scientists and engineers to do this inadvertently). We are especially blameworthy in fostering a kind of snobbery that says, for example, that any well-trained scientist would not waste his time teaching in high school. The indictment can be made even worse; we stood aside and let the professional educator cut out the roots which were our only source of supply. Parenthetically, the drastic reduction in real substance in mathematics and science was contagious and the same thing happened in other fundamental material, for example in the study of the mother tongue. Thus, this led to the single most disastrous change, namely, an approach to learning which deleted all semblance of the development of the habits of work.

The problems at the college and university level are different but nonetheless present. This is because of the low level of training of incoming college students. For those who intend to pursue studies in a technical area, the whole Mathematics, English, and Language curriculum is displaced forward in time by a year or more. This means that prerequisites are not available soon enough, and many courses which should be taken in the second year in residence are held off until the third or fourth. In turn, this means that those who go into graduate work generally take at least two and sometimes three years of course work as graduate students instead of putting the major portion of their time into undertaking original work. Thus, there have come to be turned out many who know the jargon and can cite the works but who have not had the research experience which the advance degree says is theirs.

### Support

The support of research is tied closely to the incentives for research. Funds are rather readily available for development purposes and for some researches which are perhaps only a step or so away from applica-

tion. The great weakness now is that the unspectacular work and the work with very little prospect of early application get short shrift in terms of financial support. Project research, proposal research, and development research may gain, but at the expense of the seemingly insignificant items which must be added to the literature continuously to keep it well nourished. Educational institutions must find the means for supporting the research in their laboratories in a completely free and unfettered fashion.

Another problem which we face is the insufficiency of good, critically obtained data. As many of you know, an Office of Critical Data has been formed under the supervision of NAS-NRC, and The Electrochemical Society will participate in that wholly worthy work. However, a problem which will be faced at once is that there are few in research who choose to put their time into exhaustive data taking. This has an onus which simply drives workers away from it. Such work should be supported, and there is one way in which it might be done. The NSF is certain to receive a greatly

increased budget this year and they could make good use of some of the funds to support such work. For instance, it should be possible to arrange for installation of duplicate equipment at, let us say, three liberal arts colleges where there are capable staff members. Each could make measurements which would be checked against one another. Provided the people are capable and the program is well planned, much useful information can be made available. Such a plan would permit able people to carry on useful work in addition to their teaching. Furthermore, it can be used for introducing interested students to research before they leave college.

In looking back over the four segments discussed, I became convinced that the most difficult one to deal with was that of yield. It is made up in large part of intangibles and its assessment, therefore, is a highly subjective matter. It would help greatly to consider the yield of research in conjunction with culture. This is not as far fetched as some believe if we agree that culture is the ability to live properly in one's own time, to appreciate the past, and to anticipate the future.



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## Annual Report of the Board of Directors, January 1, 1957–March 31, 1958

It has been decided that the Report of the Board of Directors and the Report of the Secretary should coincide with our fiscal year. This period more nearly coincides with the term of office of the national elected officers, and also results in the various reports being up to date at the time of the annual meeting. Therefore, this report covers a 15-month period, from January 1, 1957 to March 31, 1958.

During this period, the following awards were made.

**Palladium Medal Award**—Dr. K. F. Bonhoeffer (awarded posthumously; accepted by Professor Paul Harteck, Dept. of Physical Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.).

**Young Author's Prize**—Dr. Paul Ruetschi, Research Dept., Electric Storage Battery Co., P.O. Box 5723, Philadelphia 20, Pa., for his paper: "The Galvani Electrode Potential" (March 1957 issue).

**Francis Mills Turner Memorial Award** (Sponsored by the Reinhold Publishing Corp.)—Dr. A. C. Makrides, Dept. of Chemistry, University of Texas, Austin, Texas, for his paper: "Stoichiometric Numbers and Hydrogen Overpotential" (November 1957 issue).

**Honorable Mention**—Milton Stern, for his papers: "Anodic Behavior of Iron in Acid Solutions" (June 1957 issue), "The Relation between Pitting Corrosion and the Ferrous-Ferric Oxidation-Reduction Kinetics on Passive Surfaces" (October 1957 issue), "Electrochemical Polarization, III. Further Aspects of the Shape of Polarization Curves" (November 1957 issue); and K. M. Carlsson for his paper: "Mechanisms of Aqueous Corrosion of Aluminum at 100°C" (March 1957 issue).

The revised Constitution has been approved, along with compatible By-laws, to become effective at the Spring 1958 Meeting. With the new Constitution, the Office of the Secretary has been completely reorganized. Our former Assistant Secretary will become the Executive Secretary as of May 1, 1958. The Secretary of the Society again will be elected by a popular vote of the membership and will serve as a member of the Board of Directors. It is envisioned that the Secretary's duties will be primarily that of acting as a member of the Board with responsibility for the operation of the national office, rather than responsibility for any details of operation.

There were no monographs published during this period.

The Indianapolis Section was chartered at the Spring 1957 Meeting in Washington with the following officers: *Chairman*—L. L. Deer, *Vice-Chairman*—A. E. Middleton, *Secretary-Treasurer*—T. C. O'Nan.

The Mohawk-Hudson Section was chartered at the Spring 1957 Meeting in Washington with the following officers: *Chairman*—H. R. Schmidt, *Vice-Chairman*—J. H. Westbrook, *Secretary-Treasurer*—A. L. Jenny.

The Columbus Section was chartered at the Spring 1957 Meeting in Washington with the following officers: *Chairman*—C. L. Faust, *Vice-Chairman*—Luther Vaaler, *Secretary-Treasurer*—E. F. Stephan.

This makes a total of 18 Local Sections of The Electrochemical Society.

During the year, the Board agreed that members of the Faraday Society and Deutsche Bunsen Gesellschaft will, upon subscription to the

JOURNAL, automatically become Active Members of our Society. It is the feeling of our Board that, if the individual is properly qualified to be a member of either of these two organizations, he is properly qualified for membership in our Society. This arrangement applies only to individuals residing outside of North America.

During the year 1957, the Board deemed it advisable to change the printer of the JOURNAL. Waverly Press, Inc., of Baltimore, Md., published the JOURNAL from its inception in 1948. The Board expressed regrets at having to make this shift, since the working arrangements with Waverly Press were very satisfactory. However, labor costs in the Baltimore area forced their prices out of reach of our budget. Therefore, starting with the April 1957 issue of the JOURNAL, Lew A. Cummings Co., Inc., of Manchester, N. H., has been doing the printing.

Mr. Jack Bain, our advertising representative, terminated his contract six weeks before it was due to end. He felt that he was not producing for the Society and, therefore, requested that the contract be terminated.

On June 1, 1957, the National Office moved from 216 West 102 St. to 1860 Broadway (at 61st St.), Rm. 512-514. The new quarters are not adequate for holding Board meetings and, therefore, our winter Board meeting was held on January 24 at the Statler Hotel in New York. A three-year lease was signed on this property, since the Board has gone on record as favoring space in the new Engineering Societies Building which is due to be completed in the fall of 1960.

Norman Hackerman, *Chairman*

# Financial Statement of The Electrochemical Society, Inc.

## Statement of Income and Expenses,

April 1, 1957—March 31, 1958

	Budget 12 months	General Fund	Society Reserve Fund
<b>Income</b>			
All Membership Dues .....	\$39,200	\$39,265.45	
Patron and Sustaining			
Memberships .....	16,000	18,500.00	
Reprints .....	4,700	7,824.09	
Nonmember Journal Sub- scriptions .....	22,000	27,387.59	
Office Sale Journal and Publications .....	500	590.82	
Advertising .....	12,500	11,947.89	
Bound Volumes .....	2,500	2,692.55	
Conventions .....	5,300	7,826.87	
"Cathodic Protection"			
Sales .....		125.00	
Interest Earned on General Funds .....		330.32	
	<u>\$102,700</u>	<u>\$116,490.58</u>	
Nonmember Journal Sub- scriptions .....	4,200		\$ 5,279.06
Nonmember Convention Registrations .....	2,520	2,493.00	
Monograph Royalties .....	6,000	3,218.21	
Income from Investments .....	1,800	2,482.36	
	<u>\$ 14,520</u>		<u>\$13,472.63</u>
	<u>\$117,220</u>		
<b>Expenses</b>			
Print and Mail Journal .....	\$40,000	\$35,705.70	
Reprints .....	2,500	5,215.08	
Publication Committee .....	350		
Advertising Commissions .....	5,200	4,456.60	
Salaries .....	44,500	43,514.73	
Rent .....	4,000	4,000.00	
Postage, Supplies, Miscellaneous .....	6,200	6,517.24	
Local Sections and Divi- sions .....	1,000	1,120.06	
Young Author's Prize .....	100	100.00	
New Capital Equipment .....	585		
Bound Volumes .....	3,000	2,504.60	
Non-Budgeted Moving Expense .....		260.50	
Conventions:			
Program Booklets .....	1,580	1,716.03	
Travel New York Per- sonnel .....	1,400	1,245.68	
Materials and Supplies .....	320	348.67	
Postage and Express .....	500	295.06	
	<u>\$111,235</u>	<u>\$106,999.95</u>	
Contingency— 1% Estimated Income .....	1,027		
	<u>\$112,262</u>		

Excess Income over Ex- penses—General Fund .....	-9,562	9,490.63
Income Credited to Society Reserve Fund .....	+14,520	13,472.63
Total Excess Income over Expenses .....	<u>+ 4,958</u>	<u>\$ 22,963.26</u>

## Balance Sheet, April 1, 1957—March 31, 1958

### Statement of Assets

<b>Cash</b>			
<i>Chemical Corn Exchange Bank</i>			
Electronics Division .....	\$ 71.34		
Corrosion Division Monograph Fund .....		2,054.83	
Electrodeposition Division Monograph Fund .....		928.02	
Electrothermics & Metallurgy Division Monograph Fund .....		1,035.35	
Theoretical Division Monograph Fund .....		441.13	
New Capital Equipment .....		1,121.95	
Society Reserve Fund .....		4,031.56	
General Fund .....		12,371.56	
		<u>\$22,055.74</u>	
Petty Cash .....		175.77	
<i>Excelsior Savings Bank</i>			
General Fund .....		10,273.45	
<i>Greenwich Savings Bank</i>			
General Fund .....		10,056.87	
<i>Chase Manhattan Bank Savings Account</i>			
General Fund .....		10,000.00	\$ 52,561.83
<i>Hanover Bank</i>			
Edward Weston Fellowship Fund .....			130.35
			<u>\$ 52,692.18</u>
<b>Investments</b>			
<i>Edward Goodrich Acheson Fund</i>			
Stocks and Bonds .....	\$33,126.50		
Chemical Corn Ex- change Savings Account .....	2,780.75	\$35,907.25	
<i>F. M. Becket Memo- rial Award Fund</i>			
Common Stocks and Bonds .....	9,680.38		
Chemical Corn Ex- change Savings Account .....	506.66	10,187.04	
<i>Consolidated Fellowship Fund</i>			
Fundamental In- vestors, Inc. ....	11,912.68		
Wellington Fund, Inc. ....	10,468.97		
Incorporated Investors .....	1,722.17	24,103.82	

<i>Joseph W. Richards Memorial Fund</i>			
Central Savings Bank .....	848.08		
<i>Edward Weston Fellowship Fund</i>			
Hanover Trust Fund A .....	13,942.18		
<i>General Portfolio of Investments</i>			
Corrosion Division Monograph Fund	18,195.88		
Electrodeposition Division Monograph Fund .....	1,000.00		
Electrothermics & Metallurgy Monograph Fund .....	3,000.00		
Society Reserve Fund .....	48,469.12	70,665.00	155,653.37
<b>Other Assets</b>			
Convention Advance Furniture and Fixtures .....	5,748.89	500.00	
Less Reserve for Depreciation .....	1,914.91	3,833.98	
Inventory .....	9,595.75	13,929.73	
			<u>\$222,275.28</u>

**Statement of Liabilities and Surpluses**

<b>Liabilities</b>			
Deferred Income India Section .....	\$ 12.96		
Overseas Subscriptions Payable (Faraday and DBG)	1,554.44		
Life Memberships .....	1,668.27		
Prepaid Sustaining Memberships .....	100.00		
Federal and State Taxes Withheld .....	630.11	\$ 3,965.78	

**Surpluses**

<b>Special Funds</b>			
Edward Goodrich Acheson Fund ....	\$35,907.25		
F. M. Becket Memorial Award Fund .....	10,187.04		
Consolidated Fellowship Fund .....	24,103.82		
Joseph W. Richards Memorial Fund ..	848.08		
Edward Weston Fellowship Fund	14,072.53	85,118.72	
<b>Division Monograph Funds</b>			
Corrosion Division	20,250.71		
Electrodeposition Division .....	1,928.02		
Electrothermics & Metallurgy Division .....	4,035.35		
Theoretical Division .....	441.13		
Electronics Division .....	71.34	26,726.55	

<b>Society Reserve Fund</b>				
Surplus ..	\$40,155.84			
Income				
Received	13,472.63	53,628.47		
<b>Less Advances</b>				
Electro-Organic Chemistry	500.00			
10-Year Index (1952-1961)	627.79	1,127.79	52,500.68	
<b>General Fund</b>				
Surplus ..	\$43,350.97			
New Capital Equipment	1,121.95	44,472.92		
<b>Excess Income over Expenses</b>		9,490.63	53,963.55	218,309.50
				<u>\$222,275.28</u>

**General Portfolio of Investments**

Value of Securities 3/31/57 .....	\$49,113.48		
<b>Additional Investments:</b>			
Electrothermics & Metallurgy Division .....	\$3,000.00		
Corrosion Division .....	1,000.00		
<b>Society Reserve Fund:</b>			
Interest and Dividends	\$1,071.99		
New Purchases .....	17,210.07	18,282.06	
			\$22,282.06
<b>Less Return Columbus Convention Fund .....</b>	400.00	21,882.06	
			\$70,995.54
<b>Less Adjustment in Value of Securities Based on Closing Prices 3/31/58 .....</b>			330.54
<b>TOTAL VALUE FUND 3/31/58 .....</b>			<u>\$70,665.00</u>

**Society Reserve Fund**

Equity in General Portfolio of Investments .....	\$30,517.60		
*Savings Account Interest and Dividend Shares in Mutual Funds Reinvested .....	1,071.99		
New Securities Purchased .....	17,210.07	\$48,799.66	
<b>*Less Adjustment in Security Values 3/31/58 ..</b>			330.54
<b>Equity Value in General Portfolio 3/31/58 ..</b>			<u>\$48,469.12</u>
Monograph Advances 3/31/57 .....	638.15		
Monograph Advances 3/31/58 .....	489.64	1,127.79	
<b>Bank Credit Balance 3/31/57 .....</b>	\$9,000.09		
*Cash Dividends .....	\$1,740.91		
*Monograph Royalties .....	3,218.21		
*Convention Registration Fees .....	2,493.00		
*Nonmember Journal Subscriptions .....	5,279.06	12,731.18	
			<u>\$21,731.27</u>

New Securities Purchased .....	17,210.07	
Additional Monograph Advances .....	489.64	17,699.71
Bank Credit Balance 3/31/58 .....		4,031.56
<b>TOTAL VALUE FUND 3/31/58 .....</b>		<b>\$53,628.47</b>

\*Total Net Income from Sources Indicated \$13,472.63

### Division Monograph Funds

#### Corrosion Division

Equity in General Portfolio .....	\$17,195.88	
Additional Investments .....	1,000.00	\$18,195.88
Bank Credit Balance 3/31/57 .....	\$2,454.68	
Monograph Royalties .....	2,294.55	4,749.23
Corrosion Research Council .....	1,000.00	
Contribution Passivity Conference .....	500.00	
Palladium Medal Award .....	194.40	
New Securities Purchased .....	1,000.00	2,694.40
Bank Credit Balance 3/31/58 .....		2,054.83
<b>TOTAL VALUE 3/31/58 .....</b>		<b>\$20,250.71</b>

#### Electrothermics and Metallurgy Division

Equity in General Portfolio 3/31/58 .....	\$3,000.00	
Bank Credit Balance 3/31/57 .....	\$2,855.45	
Monograph Royalties .....	1,179.90	4,035.35
Investment in General Portfolio .....	3,000.00	
Bank Credit Balance 3/31/58 .....		1,035.35
<b>TOTAL VALUE 3/31/58 .....</b>		<b>\$4,035.35</b>

#### Electrodeposition Division

Equity in General Portfolio 3/31/58 .....	\$1,000.00	
Bank Credit Balance 3/31/57 .....	\$484.47	
Monograph Royalties .....	443.55	
Bank Credit Balance 3/31/58 .....		928.02
<b>TOTAL VALUE 3/31/58 .....</b>		<b>\$1,928.02</b>

#### Theoretical Electrochemistry Division

Bank Credit Balance 3/31/57 .....	\$328.39	
Monograph Royalties .....	112.74	
Bank Credit Balance 3/31/58 .....		\$441.13

#### Electronics Division

Bank Credit Balance 3/31/58 .....	\$71.34
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### Special Funds

#### Edward Goodrich Acheson Fund

Value of Securities 3/31/57 .....	\$32,926.25	
New Securities Purchased .....	400.00	
		\$33,326.25
Less Adjustment in Security Value 3/31/58 .....		199.75
Value of Securities 3/31/58 .....	\$33,126.50	
Bank Balance 3/31/57 .....	\$1,781.81	
Dividends from Investments \$1,381.28		
Savings Bank Interest .....	17.66	1,398.94
		3,180.75
Purchase of New Securities .....	400.00	
Savings Account Bank Balance 3/31/58 .....		2,780.75
<b>TOTAL FUND VALUE 3/31/58 .....</b>		<b>\$35,907.25</b>

#### Consolidated Fellowship Fund

##### Fundamental Investors, Inc.

Total Shares 3/31/57 (Value \$12,641.77) .....	806.750	
Shares Accumulated to 3/31/58 .....	45.983	
Total Shares 3/31/58 .....	852.733	
Share Value 3/31/58 .....	13.97	\$11,912.68

##### Wellington Fund, Inc.

Total Shares 3/31/57 (Value \$10,387.44) .....	811.519	
Shares Accumulated to 3/31/58 .....	61.623	
Total Shares 3/31/58 .....	873.142	
Share Value 3/31/58 .....	11.99	10,468.97

##### Incorporated Investors

Total Shares 3/31/57 (Value \$1,548.80) .....	176.0000	
Shares Accumulated to 3/31/58 (Including 47.8055 purchased by Weston Fund) .....	72.1517	
Total Shares 3/31/58 .....	248.1517	
Share Value 3/31/58 .....	6.94	1,722.17

**TOTAL FUND VALUE 3/31/58 .....** **\$24,103.82**

#### Joseph W. Richards Memorial Fund

Central Savings Bank Balance 3/31/57 .....	\$821.62	
Interest Income 3/31/58 .....	26.46	
<b>TOTAL FUND VALUE 3/31/58 .....</b>		<b>\$848.08</b>



**F. M. Becket Memorial Award Fund**

Value of Securities 3/31/57.....	\$9,674.00	
New Securities Purchased.....	503.16	\$10,177.16
Less Adjustment in Value 3/31/58.....		496.78
Value of Securities 3/31/58.....		\$ 9,680.38
Bank Balance 3/31/57.....	\$539.02	
Interest on Savings Account.....	\$13.60	
Cash Dividends.....	457.20	470.80
		1,009.82
New Securities Purchased.....	503.16	
Bank Balance 3/31/58.....		506.66
TOTAL FUND VALUE 3/31/58.....		\$10,187.04

**Edward Weston Fellowship Fund**

Value of Shares in Hanover Bank Trust Fund A 3/31/58 (Value 3/31/57 \$13,715.03).....	\$13,858.52	
Principal Account Balance 3/31/58.....	83.66	\$13,942.18
Checking Account Balance 3/31/57.....	9.31	
Income from Investments.....	462.89	
		\$472.20

Purchase of Shares of Incorporated Investors for Consolidated Fellowship Fund.....	341.85	
Checking Account Balance 3/31/58.....		130.35
TOTAL FUND VALUE 3/31/58.....		\$14,072.53

**Certificate of Audit**

I have examined the balance sheet of The Electrochemical Society, Incorporated, as of March 31, 1958, and the related statement of income and expenses for the period from April 1, 1957 to March 31, 1958. My examination was made in accordance with generally accepted auditing standards and, accordingly, included such tests of the accounting records and such other auditing procedures as I considered necessary in the circumstances.

In my opinion, the balance sheet and statement of income and expenses present fairly the financial position of The Electrochemical Society, Incorporated, at March 31, 1958, and its income and expenses for the 12-month period then ended.

(Signed) H. K. Leicht, Auditor

## Annual Report of the Secretary, January 1, 1957–March 31, 1958

The membership count is reported each quarter in the JOURNAL. As of March 31, 1958, the count—including all categories of membership—was 2,838.

During the period January 1, 1957 to March 31, 1958, the following companies took out Patron Memberships:

1. Westinghouse Electric Corp.
2. Olin Mathieson Chemical Corp.

Total Patron Members as of March 31, 1958: 5.

The following new Sustaining Members were obtained during this period:

1. General Electric Co.
2. Kaiser Aluminum & Chemical Corp.
3. Sprague Electric Co.
4. Superior Tube Co.
5. Texas Instruments, Inc.
6. P. R. Mallory & Co.
7. Minnesota Mining & Manufacturing Co.
8. Federal Telecommunication Labs.
9. International Business Machines Corp.
10. C & D Batteries, Inc.
11. Raytheon Manufacturing Co.

12. Motorola, Inc.
13. Sumner Chemical Co. (Div. of Miles Labs., Inc.)
14. K. W. Battery Co.
15. Libbey-Owens-Ford Glass Co.
16. Basic, Inc.
17. Pittsburgh Metallurgical Co., Inc.
18. Upjohn Co.
19. Columbian Carbon Co.
20. Catalyst Research Corp.
21. Hughes Aircraft Co.
22. Cooper Metallurgical Associates
23. Continental Can Co., Inc.
24. Eastman Kodak Co.
25. Keokuk Electro-Metals Co.
26. Reynolds Metals Co.

We lost four Sustaining Members during this period, one of which transferred to Patron Membership. Total Sustaining Members as of March 31, 1958: 140.

**Report of Tellers of Election**

*Constitutional Revision:* Yes, 925; No, 15; Not voting, 199.

*For President:* Sherlock Swann, Jr., 1106; Write-ins, 10.

*For Vice-President:* H. B. Linford, 749; H. M. Scholberg, 102; Ernest

Yeager, 260; No candidate, 8; Void, 13; Write-ins, 7.

*For Treasurer:* L. I. Gilbertson, 1108; No candidate, 28; Write-ins, 3.

Three ballots were declared invalid (1, illegible; 1, signed; 1, a 1956 ballot), leaving 1139 ballots.

Total ballots received as of December 15, 1957, the deadline for casting ballots, was 1142.

The ballot tabulations have been placed in a sealed envelope in the charge of the Assistant Secretary at The Electrochemical Society office.

(Signed) G. A. Lux, Chairman,  
Tellers' Committee  
F. A. Lowenheim  
E. B. Saubestre

The Tellers' Report was unanimously accepted by the Board of Directors, and a motion was made declaring the candidates, Sherlock Swann, Jr. (President), H. B. Linford (Vice-President), and L. I. Gilbertson (Treasurer), duly elected.

Henry B. Linford, Secretary

## Looking Back at New York



**A**—H. N. Hammer, K. B. McCain, and R. J. McKay; **B**—Abner Brenner, delivering the Richards Memorial Lecture; **C**—M. F. Quaelly and C. A. Hampel; **D**—H. T. Francis, W. M. Hetherington, and G. W. Bodamer; **E**—Dr. and Mrs. Norman Hackerman, H. H. Uhlig, and W. C. Gardiner; **F**—Dr. and Mrs. L. I. Gilbertson; **G**—Mr. and Mrs. C. J. Lang, F. P. Peters, and E. K. Camp; **H**—Mrs. H. R. Copson, Dr. Copson, and A. J. de Bethune; **I**—N. C. Cahoon, L. M. Litz, and Morris Eisenberg; **J**—F. C. Mathers, Mrs. Lottie Fink, and R. M. Hunter; **K**—F. A. Lowenheim, Earl Howells, and G. W. Heise; **L**—Dr. and Mrs. L. O. Case; **M**—C. V. King, Paul Delahay, and E. B. Yeager; **N**—R. R. Rogers, I. E. Campbell, R. M. Hunter, H. B. Linford, and C. E. Thorp; **O**—C. L. Faust, R. F. Bechtold, F. W. Koerker, and C. W. Tobias; **P**—H. C. Miller and M. S. Kircher; **Q**—C. A. Snavelly, Mrs. R. K. Shannon, and Mr. Shannon; **R**—Mrs. J. T. Owen and Mrs. F. A. Lowenheim.

## News Items

### R. B. MacMullin Awarded 1958 Schoellkopf Medal

The 1958 Jacob F. Schoellkopf Medal of the Western New York Section of the American Chemical Society was awarded to Robert Burns MacMullin, senior partner of R. B. MacMullin Associates, Consulting Engineers of Niagara Falls, N. Y. He was honored "for his original contributions to the science of chemical engineering, and for his achievements at home and abroad, as a consulting engineer, particularly in the field of industrial electrolytic processes." The medal was awarded at the annual Schoellkopf Award Dinner Meeting at the Hotel Niagara, Tuesday, May 20, 1958, at 8:00 P.M.

Mr. MacMullin was born in Philadelphia in 1898, attended Bowdoin College, and was graduated in chemical engineering from Massachusetts Institute of Technology in 1919. During the First World War, prior to graduation, he served in France with the Chemical Warfare Service. Up until the close of World War II, he was employed by the Mathieson Alkali Works, Inc. (now Olin-Mathieson Chemical Corp.). At that time, he again served his country



R. B. MacMullin

as a member of a technical team (FIAT-TIIC) sent to Europe to study the state of their chemical industry. During the War he was instrumental in developing a new process for making metallic magnesium for a full-scale plant built at Lake Charles, La. Since 1946, his consulting practice has carried him

to the four corners of the world. His firm has established international recognition in process engineering, particularly in the design of chlor-alkali plants and other electrolytic processes. The most recent plant designed by his firm was completed in 1956 for the Weyerhaeuser Timber Co., and is the largest captive chlorine plant in the pulp and paper industry.

Mr. MacMullin has been active in the affairs of the numerous professional and scientific societies of which he is a member, especially the American Chemical Society, the American Institute of Chemical Engineers, and The Electrochemical Society. He was chairman of the Western New York Section of the American Chemical Society in 1930. He is founder of the *Double Bond*, the section's monthly bulletin. He was a charter member of the local section of the A.I.Ch.E., chairman in 1939, and recipient of the Professional Achievement Award of the section in 1955. He was chairman of the Niagara Falls Section of The Electrochemical Society in 1956, and General Chairman of the Society's Buffalo Meeting in October 1957. He has contributed to the sciences of chemistry and chemical engineering through numerous technical publications, books, and patents.

### Allen G. Gray New Editor of "Metal Progress"

Allen G. Gray, formerly technical editor of *Steel*, became editor of ASM's *Metal Progress* in February of this year. Ernest E. Thum, who had been editor since the publication's inception in 1930, has assumed the title of editor-in-chief.

Dr. Gray was born on July 28, 1915 in Birmingham, Ala. He received his B.S. degree in chemistry and his M.S. in metallurgy from Vanderbilt University in Tennessee, and his Ph.D. degree in chemistry from the University of Wisconsin in 1940. His postgraduate work was on molybdenum steels and tungsten alloys.

He was consulting editor and a frequent contributor to *Steel* from 1942, becoming technical editor in 1952. Between graduation and his association with *Steel*, Dr. Gray worked for E. I. du Pont de Nemours & Co. on various of the manifold problems of metal processing, principally the chemical aspects. He was active in the development of the fast electroplating process to

conserve scarce tin, in the perfection of bearings for aircraft engines, and in the electropolishing of stainless steels. He was largely responsible for the commercial electropolishing process now widely used. During the later war years in the 1940's, he was loaned to the University of Chicago's Metallurgical Lab. as a member of the team which solved the critical problem of canning the uranium slugs for the Hanford atomic piles. For part of 1951-1952 he was connected with du Pont's Atomic Energy Div. on special assignment with the Atomic Energy Commission's Atomic Power Lab. Currently, he is a member of the A.E.C.'s Advisory Committee on Industrial Information and of the Governor's Advisory Council on Atomic Energy of the State of Ohio.

Dr. Gray has been active in the affairs of The Electrochemical Society since becoming a member in 1940. He was Editor of the 1953 edition of "Modern Electroplating," part of The Electrochemical Society Series published by Wiley.

### Kemet to Produce Solid Tantalum Capacitor

A complete line of solid tantalum capacitors that will withstand vibrational acceleration up to 40 g's at frequencies from 5 to 2000 cycles, and temperatures up to 125°C, has been announced by Kemet Co., Div. of Union Carbide Corp. With high capacitance per unit volume, the extremely reliable capacitors are made by compressing finely powdered tantalum metal into plugs that are then hermetically sealed in cylindrical metal cans. Absence of a liquid electrolyte eliminates leakage problems and greatly increases shelf life.

"Kemet"\* solid tantalum capacitors are available in capacitances ranging from 5 to 120  $\mu$ f at working voltages from 6 to 30 v at 85°C. Other ratings can be provided on special order. Life tests in excess of 10,000 hr at rated voltage have revealed negligible changes in performance characteristics.

The dielectric excellence of tantalum oxide as a capacitor material has long been recognized, and the

\* Reg. trade-mark of Union Carbide Corp.

new construction extends its advantages over wider ranges of temperatures and dynamic loads.

Kemet Co. is not dependent on other suppliers for the mining or processing of tantalum, and is therefore able to exercise close quality control in each step of manufacture from raw materials to the finished capacitor.

For further information on the new "Kemet" solid tantalum capacitor, including performance curves, charge ratings, dimensions, and weights, write for Kemet's Electronics Products Engineering Bulletin No. 1 to: Kemet Co., Electronic Materials Sales, P. O. Box 6087, Cleveland 1, Ohio.

### Back Issues Wanted

If anyone wishes to sell his back issues of the JOURNAL, bound or unbound, or the TRANSACTIONS of the Society, for the last 20-25 years, up to and including 1956, please communicate direct with Nelson P. Nies, U. S. Borax Research Corp., 412 Crescent Way, Anaheim, Calif.

## Section News

### Speakers Needed

Local Sections, and particularly those in out-of-the-way locations, sometimes find it difficult to secure speakers due to financial limitations.

It is requested that potential speakers, Patron or Sustaining Members sending possible speakers into the Section area, offer services where possible. This could be done with the Local Section officer direct, or perhaps through Society Headquarters.

### Boston Section

The 12th meeting of the Boston Section was the annual business meeting. Reports of the year's activities were presented by the officers and committee chairmen, and reports from the recent National Meeting in New York City were given.

Newly elected officers are:

*Chairman*—Charles Levy

*Vice-Chairman*—Harry Gatos

*Secretary-Treasurer* — Worden Waring, Raytheon Manufacturing Co., 55 Chapel St., Newton, 58, Mass.

*Local Section Councilor (1958-1960)*—L. B. Rogers

The other Councilor (1957-1959) is Frank Benner.

The Executive Committee met and continued preparations for next year's program of meetings.

During the technical part of the meeting, Dr. Herbert Bandes, of Arthur D. Little, Inc., discussed "Applications of Chemistry in the Electronics Industry." He spoke of plating and etching problems in printed circuitry, of the plating of strip and wire for use in tubes, of chemical processes in the preparation of oxide cathodes and in the preparation of phosphors and their application to television tube screens, and of chemical refining in germanium purification. An interesting discussion, with various questions from the floor, followed Dr. Bandes' presentation.

The next meeting of the Boston Section is planned for October.

Worden Waring, *Sec.-Treas.*

### Indianapolis Section

The Indianapolis Section of the Society held its Spring Technical Meeting on Tuesday, April 22, 1958, at the Atherton Center (Student Union Bldg.) of Butler University in Indianapolis. The speaker was Dr. Karl Willson of the Mallory Battery Co., Cleveland, Ohio; his subject was primary batteries.

Dr. Willson reviewed the multiplicity of electrochemical systems being employed today for primary electrical power sources—ranging from the "workhorse" Leclanché system, through the more common alkaline mercuric oxide, copper oxide, manganese dioxide, and silver oxide types, to the magnesium-silver chloride and cuprous-chloride type reserve systems. He also touched upon the less well-known magnesium dry cell, Zamboni pile, air depolarized cells, solid electrolyte batteries, fuel cells, gas activated cells, fused salt electrolyte cells, radioactive batteries, and even more obscure combinations. He outlined their performance characteristics, economics, and fields of use. Factors leading to the wide variation in discharge character and

storage properties of different systems and designs were then related to electrode reactions. A number of samples of various-type primary battery systems and structures were exhibited at the end of the presentation. One point which was also emphasized was that equipment designers could usually save time and money for both themselves and the battery industry if they would first check with manufacturers concerning available battery designs, sizes, and characteristics, and use standard products whenever possible, rather than to design the product first and then request fabrication of special units to fit the space allowed.

During the accompanying business meeting, the following officers were elected for the next year (1958-1959):

*Chairman*—L. L. Deer

*Vice-Chairman*—C. T. Lattimer

*Secretary-Treasurer*—T. C. O'Nan, P. R. Mallory & Co., Indianapolis 6, Ind.

*Local Section Councilor*—J. M. Booe

Dr. F. C. Mathers was also appointed to continue as Councilor for an additional year to fill the unexpired term of Dr. A. Herczog who had moved from our area.

T. C. O'Nan, *Sec.-Treas.*

### News from India

*Indian Aluminium Co.'s Expansion Plans*—The Indian Aluminium Co. is installing a new smelter at Hirakud, Orissa State, with a capacity of 10,000 tons per year, and an eventual capacity of at least 60,000 tons. Operation is expected to begin early in 1959. The expansion, simultaneously under way, of the existing alumina plant at Muri to 18,000 tons capacity is also expected to be completed during this year, and further expansion to 30,000 tons of alumina will thereafter be undertaken for completion by 1961.

*Nickel-Free Coinage Alloys*—The National Metallurgical Lab., Jamshedpur, has developed nickel-free coinage alloys containing manganese. They have good flow-ability, ductility, brightness, shine, and ring, and faithfulness in reproduction of embossed impression. The Government of India Mint has produced beautifully finished coins utilizing these alloys and has confirmed the findings of the laboratory.

*Symposia in Electrochemistry and Metallurgy*—The Council of Scientific and Industrial Research, India,

### 1957 Bound Volume Available

A limited number of the bound volume of 1957 JOURNALS (Vol. 104) are available from Society Headquarters, 1860 Broadway, New York 23, N. Y., at \$18.00 per copy to nonmembers, including subscribers, and \$12.00 per copy to ECS members, subject to prior acceptance.

has approved the holding of the following symposia during 1958-1959; (a) Electrolytic Cells, and (b) Iron and Steel Industry in India.

T. L. Rama Char,  
*Regional Editor, India*

### India Section

The Section held a business meeting on March 20, 1958 at the Indian Institute of Science, Bangalore, with Mr. T. J. Varkey in the Chair. The minutes of the September 29, 1957 meeting were confirmed, and the Statement of Accounts for 1957 was approved.

The following were nominated officers of the Section for 1958-1959, as per the report of the Nominating Committee:

*Chairman*—M. S. Thacker  
*Vice-Chairmen*—A. Jogarao, J. Balachandra, and N. R. Srinivasan  
*Secretary*—S. Krishnamurthy, c/o B. V. Patankar, 311 Sixth Main Rd., Bangalore 3, India  
*Treasurer*—T. L. Rama Char

It was resolved to communicate the thanks of the Section to The Asia Foundation for continuing financial assistance to India Section members for 1958 Society dues, and to the Board of Directors of the Society for their help in the matter, as well as for agreeing to the proposal to establish the grade of "Associate" of the India Section.

T. L. Rama Char, *Treasurer*

### San Francisco Section

A special meeting of the Section was held on March 18, 1958 at the University of California Faculty Club. This was an informal meeting with Dr. Norman Hackerman, President of the Society, who reported on the state of the Society and on some of the problems we are facing. He then discussed some of the corrosion research projects which are in progress at the University of Texas.

At the regular Section meeting on March 26, the speaker was Dr. Norbert Ibl, of the Swiss Federal Institute of Technology, Zurich, and his topic was the "Study of Diffusion and Convection in Electrolysis." After reviewing various methods of studying cathode diffusion layers (e.g., current-voltage curves, quick-freezing of the boundary layer, sampling through a pinhole), Dr. Ibl presented his studies of the cathode film by interferometric techniques. In this method, part of a split beam of light is directed through the diffusion layer while the other part goes through a layer of electrolyte representative of the bulk of the solution. Since the refractive index changes from the body of the electrolyte through the boundary layer to the cathode, interference fringes will be bent in the latter region, the amount of bending being a function of concentration differences. Thus, concentrations in the immediate vicinity of a cathode can be determined, and concentration polarization can be calculated.

The interferometric method is extremely sensitive and is, therefore, mainly applicable to small concentration gradients (such as exist at low current densities). The technique has the advantage of not disturbing the electrode processes in any way.

Most of the studies dealt with vertical cathodes under conditions of natural convection. Good agreement was obtained between theory and experiment. Interferometry confirmed that the thickness of the diffusion layer changes from bottom to top of a vertical electrode.

Optical investigations of the hydrodynamic layer were also made, and flow velocities estimated. It was found that, at tall vertical electrodes, natural convective flow may become turbulent at higher current densities. Maximum velocities were observed about 0.5 mm away from

the electrode surface; these velocities, although low (of the order of 1 mm/sec), are sufficient to make natural convection stirring very effective.

Local Section officers for 1958-1959 will be:

*Chairman*—Morris Feinleib  
*Vice-Chairman*—T. R. Beck  
*Secretary*—R. A. Zimmerly, 1524 Maynard St., Concord, Calif.  
*Treasurer*—J. F. Aicher  
*Local Section Councilors*—R. F. Bechtold and C. W. Tobias

Morris Feinleib, *Chairman*

### Ontario-Quebec Section

The fourth and final meeting of the Ontario-Quebec Section for the 1957-1958 season was held at McGill University in Montreal, Friday afternoon, April 18. The meeting took the form of a symposium on "Surface Finishing of Metals" with Dr. A. E. Edwards, of Aluminium Laboratories Ltd., acting as Technical Chairman.

Four interesting papers were presented, followed by a lively discussion with speakers answering questions from the floor. Dr. W. A. Wesley, of the International Nickel Co., Bayonne, N. J., spoke on "Nickel-Chromium Coatings," covering recent theories and experimental work aimed at developing thin coatings having longer life in corrosive environment. Dr. R. C. Spooner, of Aluminium Laboratories Ltd., Kingston, Ontario, discussed "Inorganic Nonmetallic Coatings," outlining properties, application, and importance of the three types—chemical conversion, porcelain enamel, and oxide coatings, dwelling particularly on the anodizing of aluminum. Mr. E. M. Head, of Canadian Pittsburg Industries Ltd., Longbranch, Ontario, talked about properties and application of "Organic Coatings," mentioning the continuous research and development required to meet new demands

## December 1958 Discussion Section

A Discussion Section, covering papers published in the January-June 1958 JOURNALS, is scheduled for publication in the December 1958 issue. Any discussion which did not reach the Editor in time for inclusion in the June 1958 Discussion Section will be included in the December 1958 issue.

Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the Managing Editor of the JOURNAL, 1860 Broadway, New York 23, N. Y., *not later than September 1, 1958*. All discussions will be forwarded to the author(s) for reply before being printed in the JOURNAL.

by industry. Mr. W. Dingley, of the Dept. of Mines and Technical Surveys, Ottawa, discussed "Testing of Coatings," covering the purposes of testing, types of testing employed, and the techniques and methods developed for various tests.

L. G. Henry, *Sec.-Treas.*

## Division News

### Electric Insulation Division

At its annual business meeting on April 28, the Division elected the following officers:

*Chairman*—L. J. Frisco

*Vice-Chairman*—A. J. Sherburne

*Secretary-Treasurer*—T. D. Callinan, International Business Machines Corp., P. O. Box 390, Poughkeepsie, N. Y.

The following appointments were made by Mr. Frisco:

T. D. Callinan—Electric Insulation Division Editor of the JOURNAL

A. Gunzenhauser—Electric Insulation Division representative on the Membership Committee

The Division extended its sympathy and condolences to the family of the late Dr. John J. Chapman. Dr. Chapman, an internationally known expert on insulation, had served the Division as Vice-Chairman and as Divisional Editor of the JOURNAL.

T. D. Callinan, *Sec.-Treas.*

## New Members

In May 1958 the following were elected to membership in The Electrochemical Society by the Admissions Committee:

### Active Members Sponsored by a Sustaining Member

James L. Johnson, Upjohn Co., 301 Henrietta St., Kalamazoo, Mich. (Electro-Organic)

J. Paul Fisher, M. Ames Chemical Works, Inc., Glens Falls, N. Y. (Battery, Electrodeposition)

George M. Mason, Aluminum Co. of Canada, Ltd., 1700 Sun Life Bldg., Montreal, Que., Canada (Electrothermics & Metallurgy)

### Active Members

Enrico Arreghini, Fabbriche Accumulatori Henseberger, Via Mentana F, Monza, Milan, Italy (Battery)

Mary W. Barnes, National Bureau of

Standards; Mail add: 8606 Garfield St., Bethesda 14, Md. (Electrodeposition)

Myron E. Browning, Convair, Div. of General Dynamics; Mail add: 3145 Travis Ave., Fort Worth 10, Texas (Electrodeposition)

Alphonso W. Castillero, Electro Chem Mfg. Co.; Mail add: 7448 Rosemead Blvd., Rivera, Calif. (Electrodeposition)

David P. Fickle, National Bureau of Standards, Rm. 208 NW Bldg., Washington 25, D. C. (Electrothermics & Metallurgy)

Bruce A. Fountain, National Carbon Co.; Mail add: 917 Vanderbilt Ave., Niagara Falls, N. Y. (Electrothermics & Metallurgy)

Dewinn Fyffe, General Electric Co.; Mail add: Oakridge Rd., Auburn, N. Y. (Battery, Electrodeposition)

Robert A. Jewett, Sylvania Electric Products Inc., P. O. Box 70, Towanda, Pa. (Electronics)

Lloyd W. Johnson, General Electric Co.; Mail add: R.R. 1, Box 145-C, Acton, Ind. (Electrothermics & Metallurgy)

Rudolph F. Lia, Raytheon Mfg. Co.; Mail add: 239 Forest St., Medford 55, Mass. (Electronics)

Vernon A. Nelson, Allis-Chalmers Mfg. Co., Res. Div., Box 512, Milwaukee 1, Wis. (Electrodeposition, Theoretical Electrochemistry)

Johannes Niebuhr, Elchem, Hofenerstrasse 63a, Nürnberg, Western Germany (Electronics, Electrothermics & Metallurgy)

William W. Palmquist, National Carbon Co., P.O. Box 6087, Cleveland 1, Ohio (Industrial Electrolytic)

Philip E. Peterson, Northrop Aircraft, Inc.; Mail add: Apt. 312, 2444 Crenshaw Blvd., Los Angeles 16, Calif. (Corrosion, Electrodeposition, Electrothermics & Metallurgy, Theoretical Electrochemistry)

Nolan E. Richards, Reduction Research, Reynolds Metals Co., Box 191, Sheffield, Ala. (Electrothermics & Metallurgy, Theoretical Electrochemistry)

Searl J. Silverman, Bell Telephone Labs., Inc.; Mail add: 2532 Washington St., Allentown, Pa. (Electronics)

By action of the Board of Directors of the Society, all prospective members must include first year's dues with their applications for membership.

Also, please note that, if sponsors sign the application form itself, processing can be expedited considerably.

Alan J. Smith, Research Labs., Rohm & Haas Co., 5000 Richmond St., Philadelphia 37, Pa. (Corrosion, Industrial Electrolytic, Theoretical Electrochemistry)

Alvin M. Smith, Chemoalco; Mail add: 16932 Osage, Torrance, Calif. (Electrodeposition, Electronics, Theoretical Electrochemistry)

Douchan Stanimirovitch, Societe des Accumulateurs Fixes et de Traction, Romainville (Seine), France (Battery, Theoretical Electrochemistry)

Henry A. Tucker, U. S. Bureau of Mines; Mail add: 1717 31st St., S.E., Washington 20, D. C. (Electrothermics & Metallurgy)

J. Van Bladel, University of Wisconsin, Dept. of Electrical Engineering, Madison 6, Wis. (Electronics, Theoretical Electrochemistry)

John Wilson, General Electric Co., Large Lamp Div. 437, Nela Park, Cleveland 12, Ohio (Electronics)

Isador D. Yalom, Naval Ordnance Lab.; Mail add: 10813 E. Nolcrest Dr., Silver Spring, Md. (Battery)

### Student Associate Members—Cleveland Award Winners

James M. Barnewall, Baldwin Wallace College; Mail add: 2049 Elbur Ave., Lakewood 7, Ohio (Theoretical Electrochemistry)

Douglas H. Mercer, Hiram College; Mail add: 694 Hillsdale Dr., N.W., Warren, Ohio (Electrodeposition)

Paul L. Reeder, College of Wooster; Mail add: Box 6, Fredericksburg, Ohio (Theoretical Electrochemistry)

Linda M. Wick, Western Reserve University; Mail add: 1346 Addison Rd., Cleveland 3, Ohio (Electro-Organic)

### Reinstatement to Active Membership

Walter R. Binai, Manufacturers Representative and Consulting Engineer, 3916 No. Parker Ave., Indianapolis 5, Ind. (Corrosion, Electrodeposition, Electrothermics & Metallurgy, Industrial Electrolytic, Theoretical Electrochemistry)

### Transfer from Associate to Active Membership

S. Soundararajan, Dept. of General Chemistry, Indian Institute of Science, Bangalore 3, India (Electro-Organic, Theoretical Electrochemistry)

### Deceased Members

Solomon E. Barr, Trenton, N. J.  
Carl F. Brenthel, Nürnberg, Western Germany  
P. Grodzinski, London, England

## Personals

**Ernest Paskell** recently joined the staff of the Delco Radio Div., General Motors Corp., Kokomo, Ind., as supervisor of the Transistor Pilot Production Line.

**George E. Best**, of the Baltimore plant (Mutual Chromium Chemicals), Solvay Process Div., Allied Chemical Corp., has transferred to Solvay's research center at Syracuse, N. Y., as technical advisor to the general manager of the technical service department. Since joining Mutual in 1948, Mr. Best has been associated with technical service work on chromium chemicals.

**A. C. Makrides**, formerly at the Dept. of Chemistry, University of Texas, Austin, recently accepted a position as research chemist at the Metals Research Labs., Electro Metallurgical Co., Niagara Falls, N. Y.

**Maurice Lang**, formerly technical director of the Battery Research Dept. at U. S. Electric Corp., has joined Yardney Electric Corp., New York City, as head of the Primary Battery Div. Mr. Lang will coordinate all activities of the division—research and development, mechanical, and engineering.

**Clyde E. Williams** has been elected a director of Fansteel Metallurgical Corp., North Chicago, Ill. Dr. Williams served as chief executive officer of Battelle Memorial Institute, Columbus, from 1934 until his retirement in 1957. He is now president of Clyde Williams and Co., consultants, in Columbus.

**Gerald L. Moran** has been appointed vice-president of the Chemical and Metallurgical Div. of Sylvania Electric Products Inc., Towanda, Pa., with over-all responsibility for the company's Chemical and Metallurgical Div., Parts Div., and Sylvania Home Electronics, a Sylvania division. Mr. Moran also will continue as general manager of the Chemical and Metallurgical Div.

**Fred J. Kirkman**, executive vice-president and general manager of Burgess Battery Co., Freeport, Ill., has been elected president and also a director. Starting with Burgess in 1934 as an employee in the engineering department's test laboratory, Mr. Kirkman later was named assistant chief engineer. He then was transferred to the Burgess plant in Niagara Falls, Canada, where he advanced to general manager of the company's Canadian operations. He subsequently was named vice-presi-

dent and general manager of U. S. and Canadian plants and, in 1955, was elected executive vice-president.

**S. Krishnamurthy** has been nominated as a representative of the Indian Telephone Industries Ltd., Bangalore, on the Chemicals for Electroplating Sub-Committee of the Fine Chemicals Sectional Committee, Indian Standards Institution.

**K. Seshadri** has been appointed senior scientific officer, Central Salt Research Institute, Bhavnagar.

**K. S. Rajagopalan** has been nominated by the C.S.I.R. as a representative on the ISI panel for corrosion research on light gauge steel structures.

**K. S. Gururaja Doss** has been appointed director, Central Electrochemical Research Institute, Karai-kudi.

**N. R. Srinivasan** has been deputed for advanced training to the U.S.S.R.

### John J. Chapman

John J. Chapman, research contract director, the Johns Hopkins University, Dielectrics Lab., Baltimore, Md., died on April 27, 1958 at the age of 45.

Dr. Chapman was born on February 12, 1913 in Baltimore, Md. He received his B.E. degree in electrical engineering from the Johns Hopkins University in 1935 and his doctorate in 1940. In 1939, he joined the engineering staff of the General Electric Co. where he conducted research in the electric insulation field. In 1945, he returned to Johns Hopkins where he continued his research in dielectrics, and was named director of the Dielectrics Lab. in 1952. In spite of a prolonged illness, he published many papers describing his work in the field of solid dielectric breakdown.

Dr. Chapman became a member of The Electrochemical Society in 1950, and served, since 1952, as the Electric Insulation Division Editor on the JOURNAL. He was also a member of the American Institute of Electrical Engineers, serving as a member of the AIEE Dielectrics Committee; the American Society for Testing Materials; and was a Fellow of the American Association for the Advancement of Science.

His honorary society memberships included Tau Beta Pi and Sigma Xi.

### Polykarp Herasymenko

Dr. Polykarp Herasymenko, research professor at New York University's College of Engineering,

died suddenly on April 6, 1958. He was 57 years old.

Dr. Herasymenko had been associated with New York University since 1952, conducting fundamental research in process metallurgy, titanium metallurgy, and thermodynamics. In the course of his career in both Europe and the United States, he made important contributions to these fields, as well as to the ionic theory of steelmaking and the problems of hydrogen pick-up in liquid steel.

Born and educated in the Ukraine, Dr. Herasymenko emigrated to Czechoslovakia in 1921 and received his doctorate from Charles University in Prague in 1925. An International (Rockefeller) Research Foundation grant awarded in 1928 enabled him to do research in physical chemistry at Kings College, London University. In 1930, he became head of the metallurgical and physical chemistry sections of the research laboratories of the Skoda works in Pilsen. Dr. Herasymenko held this position until August 1945 and then emigrated to West Germany. From 1948 to 1951, he served as research metallurgist in the United Steel Cos., Sheffield, England. He came to the United States in 1951. His many papers and articles have appeared in leading scientific journals the world over.

Dr. Herasymenko was elected to membership in The Electrochemical Society in February 1956.

He is survived by his wife, Anna.

## Book Reviews

**The True Story of Aluminum**, by Alfred Cowles. Published by Henry Regnery Co., Chicago, 1958. 251 pages.

Technicians are usually too busy to write down the stories of their discoveries, and after their deaths it is always difficult for the historian to gather material from their families and from the companies for which they worked. This is especially true for the work of Hall and Heroult, who were lazy writers; the documentation left to their biographers is rather sketchy. More than 70 years after the first aluminum was made by fusion electrolysis of alumina in cryolite, one of the descendants of the Cowles brothers wrote a book about this subject, using some family documents. This fills an important gap. The Cowles brothers, as may be recalled, played a considerable role in the development of electric furnaces, and they had Hall

working for one year (mid 1887-1888) in their Lockport plant, at their expense, on his aluminum process, for which they had acquired an option. Never before has the background of Hall's contribution been illuminated so well in book form, and the presentation of the most important patent references as well as the bibliography of the evidence displayed in court are most valuable. The latter should be published *in extenso* some day, to make it available to the broad public.

This book, which tries to destroy a legend, has some weaknesses, mainly as to the metallurgical problems involved. The art as it existed when Hall-Heroult applied for their patents in 1886 is not clearly established. Especially, Sainte-Claire Deville's basic work is not well appreciated as to its impact on both inventors, who learned their art from his book on aluminum, published in 1859. Ste.-Claire reduced industrially various aluminum halide combinations with sodium, because he had nothing but batteries at his disposition to electrolyze them. On account of the low boiling point of  $\text{AlCl}_3$ , which he used by preference, he had to stabilize his salt with an addition of  $\text{NaCl}$ . Also, he could not go above the boiling point of sodium,  $880^\circ\text{C}$ , which restricted his use of the high melting cryolite. He discovered, however, the cleansing action of fluorides, including cryolite, for aluminum, which he attributed to their property of dissolving alumina. His disciples, Le-Chatelier, Lontin, and Minet, made use of this idea in their fusion electrolysis, and either embedded the alumina in the carbon anode before firing it as done also by Ste.-Claire, or later dropped it around the anode. But they stuck obstinately to Ste.-Claire's cryolite mixture, which, because of its  $\text{NaCl}$  content, had only a small solubility for alumina. Hall and Heroult, the latter very hesitantly, switched to cryolite alumina with no chloride addition; but, already in 1887, Minet had started producing industrially, using Ste.-Claire's electrolyte, and in one year he made 500 kilos of the metal at the Calypso plant. It took Heroult two, Hall four more years before they could duplicate Minet's show, mainly because both wasted their time to produce a 10-20% aluminum bronze, used in gun castings. Also, they had trouble with the corundum, which they added to their bath, which did not dissolve easily and was too impure. Hall, as shown by his testimony in court, made electrolytic aluminum powder in 1886, when Minet already had produced kilos of fused electro-

lytic aluminum. Hall abandoned chloride additions only after 1890.

The Ste.-Claire-Minet idea of  $\text{NaCl}$  addition to cryolite was basically wrong for aluminum electrolysis, but it yielded the metal. In this chloride-fluoride bath, recently rediscovered and patented in its application to titanium, the electrolysis proceeds on account of the aluminum of the cryolite. Chlorine is liberated at the anode,  $\text{NaF}$  builds up in the bath which progressively changes its composition, and the chances of reconditioning it by reaction of carbon and chlorine with alumina are remote, because of the low solubility of this oxide in the  $\text{NaCl}$ -bearing electrolyte. This is a camouflaged chloride electrolysis. Some time elapsed before the true chemistry of the Hall-

Heroult bath and of Minet's was recognized. It was Haber who established the facts, and even today few electrochemists are aware of the differences. Hall-Heroult operate with a permanent bath, constantly reconditioned by alumina addition, which is decomposed by the current. Minet depletes the aluminum content of the cryolite added and only very little repletion can take place by way of a chlorine-alumina-carbon reaction at the anode, forming  $\text{AlCl}_3$ . Alumina being cheaper than cryolite as a source of the metal, Minet's bath could not possibly compete industrially with Hall-Heroult's. Nor is chlorine evolution desirable.

A weakness of Cowles' book concerns the means of internal heating of the cell. The Cowles brothers, if

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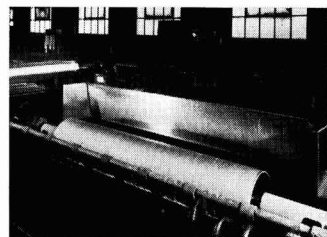
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we disregard the heat supplied by carbon-metal oxide reactions, mixed up two different heating principles: internal heating by radiation of an arc, and internal heating by resistance, or, as they called it, by "incandescent or submerged arc." The furnace, which they describe in their U. S. Patent 319,795 of 1885, concerns internal heating exclusively by the electric current, by way of broken or pulverized carbonaceous resistor matter. This is the principle and furnace used later in silicon carbide production and in infringement of Cowles' rights, by Carborundum, for which the company had to pay heavily after an infringement suit. It certainly has no bearing on the resistance heating of a fused salt bath. The principle of salt bath heating

had been used almost 80 years before Cowles by Davy, in making sodium or potassium by fusion electrolysis of the hydroxides, i.e., with no external heat. As to internal arc radiation heating, it was common knowledge already at the time when Hare, in 1839, described his controlled-atmosphere arc melting device, which is the prototype of our modern titanium melting furnaces. However, if there was any novelty in internal heating of a salt bath by electricity at the time of Cowles, it certainly is fully disclosed in Bradley's U. S. Patent 468,148 of 1883, which is of marvelous clarity and which mentions cryolite. It never was applied by the inventor, but his right was thoughtfully bought by the Cowles brothers and used in their

litigation against Hall, who, after 1889, gave up external heating of graphite-lined iron pots and used the current alone to keep the bath fused. This procedure was certainly not a money-saving one, at least not at that time, but it was the only practical way for such a high-temperature operation.

All this should not detract from the pioneering merits of the Cowles brothers, who were the first to use electrothermal methods on a commercial scale to reduce various ores with carbon. Their first furnace constructions were not well adapted for the smelting of slags and metals, since the hearth was laid out horizontally. Heroult, with no hesitation, switched to the Siemens arc furnace arrangement with a vertical hearth, for his electrolytic cell as well as for the ferroalloy and steel-making furnace which carries his name. Confusion was also introduced in Cowles' work by the fact that only direct current was available at that time, obtained from Siemens-Gramme generators. This naturally led to electrolytic phenomena, superimposed on thermal reduction by carbon, which brought about unwarranted claims, as, for instance, the one of alumina electrolysis in the presence of carbon.

Some high lights of the present book may be stressed. The author claims, rightly so, that "there is little resemblance between the modern process of producing aluminum and Hall's Lockport (1888) version, which depended on copper anodes and external heat to fuse a bath consisting of the fluorides of aluminum and potassium." Also, in a passage in Hall's letter to his promoter, R. C. Cole, of August 23, 1889, Hall writes, "Simple cryolite plus alumina quickly spoils and is no good." This was, however, the basis of his patent application.

As a matter of fact, the work done by Ste.-Claire up to his death in 1881 had sufficiently cleared the road of the metallurgist for a successful use of the fusion electrolysis, so that, at the moment the Siemens-Gramme dynamo appeared, numerous inventors literally burst into this new field. However, it took even the ablest of them, Hall and Heroult, some time before they understood and did what they had recommended intuitively in their patents, and which had the hallmark of Ste.-Claire. But, even if they were called only promoters of the aluminum industry, their role as creators of this metal puts them on a level with the greatest men the world has borne.

W. J. Kroll



**Organic Electrode Processes**, by Milton J. Allen. Published by Reinhold Publishing Corp., New York, 1958. 174 pages; \$6.50.

This book is aimed at the classical synthetic organic chemist and actually does not have much to offer to ECS members. Most of the material is already known to members of the Electro-Organic Division, and the rest of the membership would presumably not be too interested.

The opening chapter on basic principles is simple and, on the whole, correct. But, the author draws a distinction between "chemical reversibility" and "thermodynamic reversibility" which escapes this reviewer, at least. Furthermore, the author is still in the gaslight era of bubble overpotential and "decomposition potential." He has the irritating habit of referring to the reactant as the "depolarizer" and he speaks of the "so-called 'diffusion layer.'"

In the chapter on instrumentation and techniques, he states that, as soon as gas evolution commences, the potential of the working electrode vs. a reference "becomes meaningless." The recommended power supply instrumentation seems far too complex and too expensive for the average organic chemist to go into. For example, he recommends an instrument with a 440-volt, 60-cycle, 3-phase, 5-hp induction motor to drive the d-c generator, as part of the apparatus. Also, the author speaks approvingly of a British apparatus and even shows a coded schematic diagram, without giving the code or the values of the components.

The main portion of the book is devoted to the electrochemical organic reactions. These include reduction of nitro compounds, imines, imidic esters, carbonyls, alkaloids, hydrogenation, dehalogenation, halogenation, the Kolbe reaction, oxida-

tion of alcohols, carbonyls, heterocycles, aromatics, etc. The emphasis is placed on organic mechanisms and yields. This material seems accurate except that, on page 124, quaternary ammonium nitrogen is shown with 5 covalent bonds.

In this portion of the text, however, there is an interesting statement. The author believes that 2 electrons are transferred in reduction at a low overvoltage cathode, while only one is transferred at a high overvoltage cathode. This, he states, is because the diffusion away of the unadsorbed reduction product at the high overvoltage cathode is more rapid than the transfer of the electron.

In this reviewer's opinion, this work is inferior to the chapter by Swann in Volume II of "Techniques of Organic Chemistry."

H. W. Salzberg

**Batteries of Today**, by Alfred B. Garrett. Published by Research Press, Inc., 137 No. Perry St., Dayton, Ohio, 1957. 216 pages; \$9.00.

There has long been a need for a brief elementary survey of batteries written for the interested layman, and this book seems to me to satisfy this need. It is comprehensive, simply written, and understandable.

The author starts with an elementary outline of battery electrochemistry and then gets down to cases. He discusses storage batteries in general, and the lead-acid, Edison, and nickel-cadmium cells in particular, leaving out, however, the silver oxide-zinc cell, which he apparently considers to be a primary only. In each case, he goes into history, construction, reactions, characteristics, uses, and good and bad points. The chapter on battery charging discusses charging methods, apparatus, effects, and precautions.

The section on primaries goes into the Leclanché cell, the magnesium cell, and special purpose cells, including the Daniell cell, the Weston cell, the silver oxide-zinc cell, and the silver chloride cell.

Finally, special chapters are devoted to fuel cells, photocells and solar barrier cells, and nuclear batteries.

At this point, the author should have stopped, his mission accomplished. Instead, he included a completely pointless 31-page listing of battery patents, by class, subclass, and number. This might possibly be of interest to a patent searcher, but not to either a layman or an electrochemist.

One further drawback to the book is the price; \$9.00 seems to me too high for the descriptive information contained in 165 pages, 5 in. x 8 in., of large-sized widely set type, having on the average 10 words to a line and 28 lines to the complete page.

H. W. Salzberg

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## Announcements from Publishers

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"Ceramic Fabrication Processes," W. D. Kingery, Ed. Published by John Wiley & Sons, Inc., New York, 1958. 235 pages; \$9.50.

"Physical Methods in Physiology," by W. T. Catton. Published by Philosophical Library, New York, 1957. 375 pages; \$10.00.

"Qualitative Testing and Inorganic Chemistry," by Joseph Nordmann. Published by John Wiley & Sons, Inc., New York, 1957. 488 pages; \$6.25.

## Manuscripts and Abstracts for Spring 1959 Meeting

Papers are now being solicited for the Spring Meeting of the Society, to be held at the Sheraton Hotel in Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959. Technical sessions probably will be scheduled on Electric Insulation, Electronics (including Luminescence and Semiconductors), Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of abstracts (*not to exceed 75 words in length*) must be received at Society Headquarters, 1860 Broadway, New York 23, N. Y., *not later than January 2, 1959. Please indicate on abstract for which Division's symposium the paper is to be scheduled, and underline the name of the author who will present the paper.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.

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The Fall 1959 Meeting will be held in Columbus, Ohio, October 18, 19, 20, 21, and 22, 1959, at the Deshler-Hilton Hotel. Sessions will be announced in a later issue.

"Fundamental Concepts of Inorganic Chemistry," by Esmarch S. Gilreath, professor of chemistry, Washington and Lee University. Published by McGraw-Hill Book Co., New York, 1958. 421 pages; \$7.50.

This text is the outgrowth of more than a dozen years' experience in the teaching of a course entitled Advanced Inorganic Chemistry at Washington and Lee University. It is designed for advanced undergraduate students and provides materials for a one-semester course in the fundamental concepts of inorganic chemistry. As such, it is intended to supply certain essential scientific knowledge that is not transmitted in the first two years of chemistry and physics.

"Qualitative Analysis," An Introduction to Equilibrium and Solution Chemistry, by Therald Moeller, professor of inorganic chemistry, University of Illinois. Published by McGraw-Hill Book Co., 1958. 550 pages; \$6.50.

"1954-1955 Bibliographic Survey of Corrosion." NACE Publication No. 58-1. Compiled by A. Irene Humphrey. Published by National Association of Corrosion Engineers, 1061 M & M Bldg., Houston 2, Texas, 1957. 468 pages. Price: non-members NACE, \$20.00; members NACE, \$15.00.

This is the sixth in a series of NACE bibliographies on corrosion literature. The preceding five volumes, covering 1945-1953, contained 15,758 abstracts. Compiled in the new volume are 4287 abstracts of articles on corrosion and corrosion prevention published in 1954-1955. Also included are a number of abstracts published from 1945 to 1953 which were not available for use in earlier bibliographies. Abstracts are arranged topically in eight main groups: general, testing, characteristic corrosion phenomena, corrosive environments, preventive measures,

materials of construction, equipment, and industries. Each main group is subdivided and topical cross references are appended.

"Nickel and Its Alloys," by J. G. Thompson. National Bureau of Standards Circular 592, issued Feb. 5, 1958 (supersedes Circular 485). 87 pages; 60 cents. (Order from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.)

The current revision was sponsored by the International Nickel Co., Inc., under the Bureau's Research Associate plan. A review of the available literature through 1956 is presented, as well as some 1957 references and unpublished information. About 800 supplementary references are listed as sources of further information.

### New Free Price List of AEC Reports Published

A new free price list of Atomic Energy Commission unclassified reports for sale by the Office of Technical Services, U. S. Dept. of Commerce, is now available on request.

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Price lists are issued semiannually, and the next list will be available in August 1958. OTS also publishes U. S. Government Research Reports, a monthly publication which lists new research reports as soon as they are released by the AEC. It also describes reports from the Army, Navy, Air Force, and other Government agencies available to the public through OTS. This publication can be obtained on a subscription basis from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., at \$6.00 a year.

### "Unconventional" Sources of Electrical Power Surveyed

An Air Force-sponsored survey of means of converting solar, thermal, chemical, and mechanical energies into electricity has resulted in the selection of five "unconventional" power sources which appeared most promising. A two-part report of the survey has been released to industry through the Office of Technical Services, U. S. Dept. of Commerce.

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The study involved the theoretical and practical limitations and capabilities of power generation by means other than rotating machinery, conventional batteries, or radioactivity. The data, drawn from the literature and limited laboratory work, were intended to determine where emphasis should be placed in a possible development program.

The most practical of the unconventional sources appeared to be the oscillating electromagnetic generator, thermopile generator, ion exchange membrane, fuel cell, and photovoltaic battery. These underwent detailed study described in Part 2 of the report.

In the preliminary survey, described in Part 1, data and theory were also compiled on the Workman-Reynolds effect, emission, pyro-electricity, thermomagnetic generators, electrokinetic transducers, electrostatics, piezoelectricity, and magnetorestriction.

The survey was conducted by A. L. Betts and P. A. McCollum, Oklahoma A & M College, for Wright Air Development Center, U. S. Air Force. The reports are PB 131411, *Unconventional Power Sources, Part 1*, Sept. 1954, 74 pages, \$2.00; and PB 131218, *Unconventional Power Sources, Part 2*, Sept. 1955, 75 pages, \$2.00. The volumes can be ordered from OTS, U. S. Dept. of Commerce, Washington 25.

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**Manuscripts** submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½-4 cm (1-1½ in.) margins.

**Title** should be brief, followed by the author's name and his business or university connection.

**Abstract** of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

**Drawings** will be reduced to column width, 8.3 cm (3¼ in.), after reduction should have lettering at least 0.15 cm (1/16 in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

**Photographs** must be glossy prints and mounted flat.

**Captions** for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

**General**—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

SYMBOLS

If more than a few symbols are used, these should be defined in a list at the end of the paper, for example:

- $a, b \dots$  = empirical constants of Brown equation  
 $f_i$  = fugacity of pure  $i$ th component, atm  
 $D_r$  = bulk diffusion coefficient, cm<sup>2</sup>/sec

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

- R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).  
H. T. S. Britton, "Hydrogen Ions," Vol **1**, p. 309, D. Van Nostrand Co., New York (1943).  
H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

REFERENCES

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

In reporting electrode potentials, the sign of the standard Zn/Zn<sup>++</sup> electrode potential should be taken as negative; Cu/Cu<sup>++</sup> as positive.

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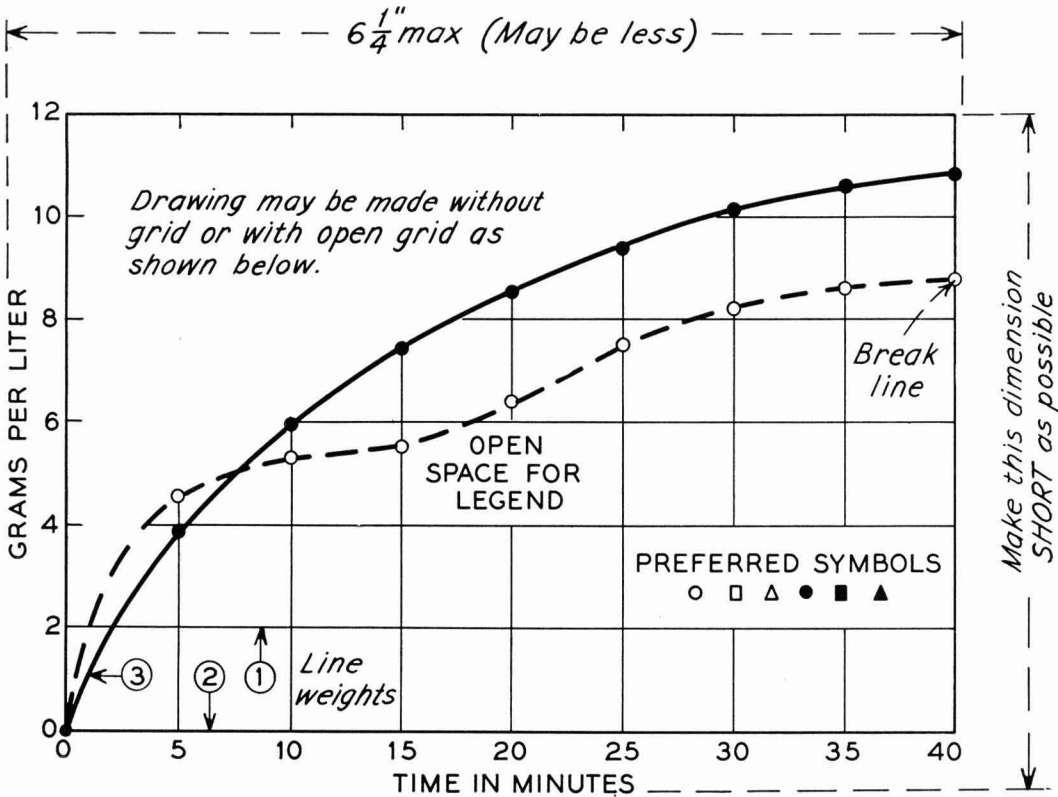
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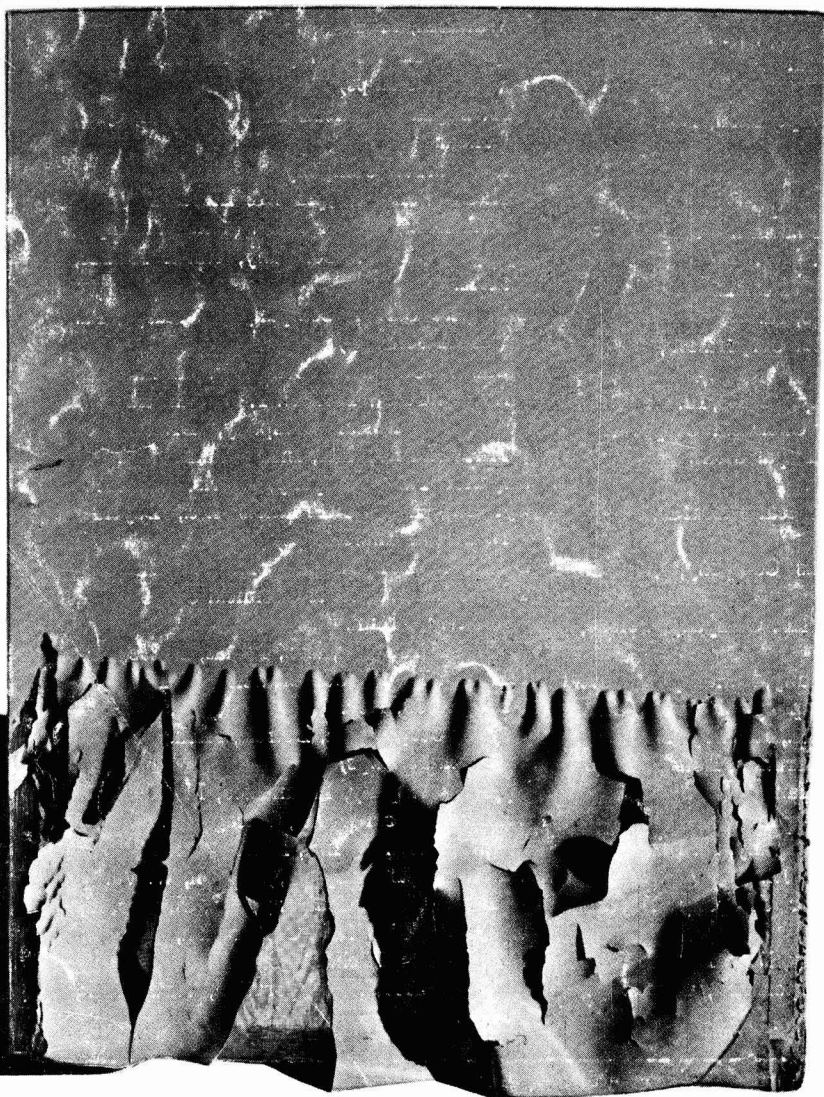
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