

# Contents

I	INTRODUCTION	1
	A. Fundamental Concepts in Electrochemistry	1
	B. Topics Covered	9
	C. Literature	9
	References	10
II.	THE OXYGEN ELECTRODE AT REST	13
	A. Theoretical Calculated Values	13
	B. Observed Experimental Values	15
	1. The Oxide Theory	16
	a. The Oxides of Pt	17
	b. The Metal-Metal Oxide Potentials	18
	c. Application of Oxide Theory to the Pt Electrode	18
	2. The Peroxide Theory	20
	3. Constant Current Charging Curves	21
	a. The Thickness of the Adsorbed Oxygen Film	23
	b. Number of Arrests in Charging Curve	24
	c. The Ratio $Q_a/Q_c$	24
	d. Effect of pH	26
	4. Potential Sweep Techniques	27
	5. Optical Methods	31
	6. The Mixed Potential Theory	32
	C. Consensus on the Rest Potential of the Pt/O <sub>2</sub> Electrode	38
	1. The PtO/Pt-O Controversy	39
	2. The Normal O <sub>2</sub> Electrode	44
	3. Rest Potential in Alkaline Solution	46
	D. The Rest Potential on Other Noble Metals	47
	1. Gold	47
	a. Charging Curves	48
	b. Potential Sweep Traces	49
	c. Problem of Adsorbed Oxygen on Gold	49
	d. Potential-Determining Mechanisms	52
	2. Palladium	53
	a. Charging Curves	53
	b. Potential Sweep Traces	54
	c. Potential-Determining Mechanisms	54

3.	Rhodium.....	56
a.	Charging Curves.....	56
b.	Potential Sweep Traces.....	56
c.	Potential-Determining Reactions.....	57
4.	Iridium.....	59
a.	Charging Curves.....	59
b.	Potential Sweep Traces.....	59
c.	Potential-Determining Reactions.....	60
5.	Ruthenium and Osmium.....	63
a.	Electrochemical Data.....	63
E.	Peroxide Stabilized Systems.....	64
1.	Rest Potential on Noble Metals.....	65
a.	The Mixed Potential Theory.....	65
2.	Catalytic Decomposition of $H_2O_2$ .....	68
F.	Other Oxygen Electrode Systems.....	69
1.	The Antimony Electrode.....	69
a.	Metal-Metal Oxide Couples of Sb.....	69
b.	Experimental Observations.....	70
c.	Potential-Determining Reactions.....	70
2.	The Arsenic Electrode.....	72
3.	Other Examples.....	72
	References.....	73
III.	THE ANODIC EVOLUTION OF OXYGEN.....	81
A.	Platinum.....	81
1.	Steady-State Polarization Curves.....	82
2.	Mechanisms.....	86
3.	Effects of pH.....	89
4.	Effects of Adsorbed Ions.....	91
5.	Effect of Nonaqueous Media.....	96
6.	Photo-Effects.....	96
B.	Gold.....	97
C.	Palladium.....	102
D.	Rhodium.....	105
E.	Iridium.....	107
F.	Noble Metal Alloys.....	110
	References.....	113
IV.	THE CATHODIC REDUCTION OF OXYGEN..	117
A.	Platinum.....	117
1.	Steady-State Polarization Curves.....	117

2. Mechanisms . . . . .	122
3. Effects of pH . . . . .	128
4. Effects of Adsorbed Ions . . . . .	129
B. Gold . . . . .	129
C. Palladium . . . . .	131
D. Rhodium . . . . .	132
E. Iridium . . . . .	132
F. Alloys . . . . .	133
G. Peroxide-Stabilized Systems . . . . .	134
1. Low Current Density Studies . . . . .	134
2. Anodic Polarization Studies . . . . .	135
3. Cathodic Reduction Studies . . . . .	138
References . . . . .	140
V. THE REVERSIBLE OXYGEN ELECTRODE . . . . .	143
References . . . . .	151
VI. ELECTROANALYTICAL CHEMISTRY . . . . .	153
A. The Dropping Mercury Electrode . . . . .	157
1. The Electrochemistry of the Hg/O <sub>2</sub> System . . . . .	159
a. The Oxides of Hg . . . . .	159
b. Charging Curves on Hg Electrodes . . . . .	160
c. Oxygen Overvoltage Studies on Hg . . . . .	161
2. Polarographic Studies . . . . .	162
3. Use of DME in Analysis . . . . .	167
B. The Noble Metal Indicator Electrode . . . . .	170
1. Properties of the Pt Indicator Electrode . . . . .	171
2. Polarography at Solid Electrodes . . . . .	175
a. The Stationary Pt Wire Electrode . . . . .	175
b. The Rotated Pt Wire Electrode . . . . .	177
c. The Rotated Gold Electrode . . . . .	180
d. Membrane-Covered Electrodes . . . . .	182
3. Reduction of O <sub>2</sub> in Nonaqueous Solutions . . . . .	186
C. Galvanic Oxygen Detectors . . . . .	187
1. Fuel Cells . . . . .	188
2. Membrane-Covered Galvanic Devices . . . . .	189
a. O <sub>2</sub> Detectors with Pb Anodes . . . . .	190
b. O <sub>2</sub> Detectors with Cd Anodes . . . . .	192
D. Application of O <sub>2</sub> Electrodes to Biological Systems . . . . .	192
1. Determination of O <sub>2</sub> in Natural Waters . . . . .	193
2. Determination of O <sub>2</sub> in Sewage Wastes . . . . .	195

3. Determination of O <sub>2</sub> in Blood . . . . .	196
4. Determination of O <sub>2</sub> in Cells and Tissues . . . . .	198
5. Determination of O <sub>2</sub> in Photosynthesis Studies . . . . .	200
6. Determination of O <sub>2</sub> in Biological Cultures . . . . .	202
7. Determination of O <sub>2</sub> in Other Media . . . . .	202
References . . . . .	204
<b>VII. THE OXYGEN ELECTRODE ON SOME ACTIVE METALS . . . . .</b>	<b>211</b>
<b>A. Silver . . . . .</b>	<b>211</b>
1. The Oxides of Silver . . . . .	212
a. Preparation of Silver Oxides . . . . .	214
b. Standard Potentials of Silver Oxide Couples . . . . .	215
c. Charging Curves on Silver Electrodes . . . . .	219
d. X-ray Studies . . . . .	226
e. Potential Sweep Traces on Silver Electrodes . . . . .	231
f. Fundamental Battery Studies . . . . .	232
2. Anodic Evolution of Oxygen on Silver . . . . .	234
3. Cathodic Reduction of Oxygen on Silver . . . . .	236
<b>B. Lead . . . . .</b>	<b>238</b>
1. The Oxides of Lead . . . . .	239
a. Pb <sub>2</sub> O . . . . .	240
b. PbO . . . . .	240
c. Pb <sub>3</sub> O <sub>4</sub> . . . . .	242
d. PbO <sub>2</sub> . . . . .	242
e. Pb <sub>12</sub> O <sub>19</sub> . . . . .	245
f. Pb <sub>2</sub> O <sub>3</sub> . . . . .	246
g. Basic Lead Sulfates . . . . .	247
2. The Electrochemistry of the Oxides of Lead . . . . .	248
a. Standard Electrode Potentials . . . . .	248
b. Charging Curves . . . . .	251
3. The Oxygen Overvoltage Studies on Lead . . . . .	259
a. Rest Potentials . . . . .	260
b. Steady-State Polarization Studies . . . . .	262
c. Mechanisms . . . . .	263
4. Fundamental Battery Studies . . . . .	264
a. Cell Voltage . . . . .	265
b. Battery Paste . . . . .	265
c. Grid Corrosion . . . . .	267
<b>C. Nickel . . . . .</b>	<b>271</b>
1. The Oxides of Nickel . . . . .	273

2.	The Electrochemistry of the Oxides of Nickel	276
a.	Standard Electrode Potentials.....	276
b.	Charging Curves.....	277
c.	Potential-Sweep Traces.....	282
3.	Anodic Evolution of Oxygen.....	284
4.	Cathodic Reduction of Oxygen.....	290
5.	Fundamental Battery Studies.....	291
	References.....	293
<b>VIII</b>	<b>POROUS OXYGEN ELECTRODES.....</b>	<b>307</b>
A.	The Oxides of Carbon.....	313
1.	The Forms of Carbon.....	313
2.	Gaseous Oxides of Carbon.....	316
3.	Adsorbed Oxygen Films.....	318
4.	Solid Oxides of Carbon.....	318
B.	The Oxygen Electrode on Carbon.....	321
1.	The O <sub>2</sub> Anode in Acid Solutions... ..	321
2.	The Carbon Indicator Electrode... ..	322
3.	Steady-State Polarization Studies... ..	324
C.	The Oxygen Diffusion Electrode... ..	327
1.	Porous Carbon Electrodes.....	328
2.	Porous Metal Electrodes.....	333
3.	Composite Porous Electrodes.....	334
4.	Pasted Diffusion Electrodes.....	335
D.	Redox Oxygen Electrodes.....	338
E.	High Temperature Oxygen Electrodes.....	340
1.	Solid Oxide Cells.....	340
2.	Molten Salt Cells.....	343
F.	Other Oxygen Electrodes.....	347
	References.....	348
<b>IX.</b>	<b>THE ROLE OF OXYGEN IN CORROSION MECHANISMS</b>	<b>357</b>
A.	Differential Aeration Processes.....	361
1.	Partially Immersed Metal Plates.....	362
2.	Totally Immersed Metal Plates.....	366
3.	Corrosion Under Drops.....	368
4.	Pitting.....	369
5.	Mutual Protection.....	371
6.	Stress Corrosion.....	372
7.	Corrosion Inhibitor Addition Agents.....	374

B. Bimetallic Corrosion Processes	380
C. Anodic Corrosion Processes...	381
D. Accelerated Corrosion Tests..	385
References.....	387
<b>AUTHOR INDEX.....</b>	<b>393</b>
<b>SUBJECT INDEX.....</b>	<b>419</b>