

# Electrochemical Decomposition of CFC-12 Using Gas Diffusion Electrodes

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Chlorofluorocarbons (CFCs) were known to cause the depletion of the ozone layer at the stratosphere. A large amount of CFCs is still in use as a refrigerant or still present in the plastic forms. These CFCs should be collected and retreated to harmless compounds to the environment. Electrochemical decomposition of dichlorodifluoromethane (CFC-12) was carried out using 12 kinds of metal-supported gas diffusion electrodes (GDEs). Ag-, Cu-, In-, and Pb-supported GDEs showed high electrocatalytic activity of decomposition of CFC-12. Especially Cu-, In-, and Pb-supported GDEs showed almost 100% efficiency without producing the byproduct ( $H_2$ ). Zn-, Ag-, Cu-, and In-supported GDEs caused defluorination of CFC-12 as well as dechlorination and produced methane mainly. Pb-supported GDE induced only dechlorination of CFC-12 and produced difluoromethane (HFC-32) in high selectivity (92.6%). With the increase in the current density, the partial current density of methane formation at Cu-supported GDE was saturated at  $370 \text{ mA cm}^{-2}$ . The partial current density of HFC-32 formation at Pb-supported GDE was not saturated even at  $650 \text{ mA cm}^{-2}$  and kept high selectivity of HFC-32 formation.

## Introduction

Chlorofluorocarbons (CFCs) were known to cause the depletion of the ozone layer at the stratosphere (1), and the abolition of the production and the use of CFCs were strongly demanded (2). Recently, the production of specified CFCs was discontinued. However, a large amount of CFCs is still in use as a refrigerant or still present in the plastic forms. These CFCs should be collected and retreated to harmless compounds to the environment. At present, the treatment of chlorofluorocarbons is mainly carried out by the incineration method. Because CFCs are very persistent compounds originally, the combustion of CFCs needs high temperature. The cost of the construction of this high-temperature incinerator is very high. Moreover, HF and HCl generated by the combustion of chlorofluorocarbons corrode the incinerator and shorten its lifetime. To improve these disadvantages, the catalytic combustion method at low temperature (3, 4) and the catalytic hydrogenation method (5–8) have been studied. However, these methods are still in the experimental stage, because the catalyst is poisoned by HF and HCl.

The electrochemical method has the following advantages: (a) The reaction can proceed under a milder condition

than other methods. (b) The secondary pollution hardly occurs, because reactive chemical agents are not used in treatment. In spite of these advantages, electrochemical decomposition of CFCs is hardly studied. Only Tezuka and Iwasaki (9) reported dechlorination of difluorotetrachloroethane and trichlorotrifluoroethane in organic solvents using Hg-poor, Pt, and graphite paste electrodes as a cathode. Recently, we have carried out electrochemical reductive decomposition of chloroform in aqueous solution using 15 kinds of metal electrodes (10). By using Ag, Cu, Pd, Pb and Zn electrodes, decomposition of chloroform proceeded with very high efficiency. In this paper, we attempt to apply those metals that have high electrocatalytic activity of dechlorination of chloroform to the decomposition of difluorodichloromethane (CFC-12). Reductive decomposition of CFC-12 was carried out at room temperature using gas diffusion electrodes (GDEs), which are suitable for the electrochemical reaction of compounds in gas phase. GDE consists of two regions: a hydrophilic reaction region and a hydrophobic gas diffusion region (11). Electrolytic solution penetrates only into the reaction region, and a gaseous reactant is supplied through the gas diffusion region rapidly. Electrochemical reactions occur on the metal fine grains supported on the reaction region. GDE is porous and has a very large reaction area. Therefore, it is appropriate for electrochemical reaction at a high current density and often used for the reduction of  $CO_2$ ,  $NO_x$ , etc. (12–15). The activity of GDE for decomposition of CFC-12 depended on the kinds of metals that were supported on GDE. By using Cu-, Ag-, and In-supported GDE, defluorination of CFC-12 proceeded as well as expected dechlorination, and methane was mainly produced. By using Pb-supported GDE, only dechlorination occurred, and difluoromethane (HFC-32) was produced in high selectivity.

## Experimental Section

Electrolyses were carried out in a stainless steel autoclave as shown in Figure 1. All electrolyses were carried out at 7 atm and room temperature. A cell equipped with GDEs was made of poly(vinyl chloride), which is resistant to corrosion by HF. GDEs and Pt- and Ru-supported GDEs were purchased from Tanaka Noble Metal Ltd. and used as working electrodes. Other metals were supported on the GDE by the impregnation method. The detailed procedure of impregnation has already been described in a previous paper (16). A GDE (1 cm in diameter) was fixed to the cell with a cap made of phenol resin. The electrode potential of a cathode was measured with respect to an Ag/AgCl/saturated KCl reference electrode. A Pt wire was used as an anode. The aqueous electrolyte was 1.0 M NaOH (GR Wako Pure Chemical), which was purified by pre-electrolysis with a Pt black cathode to eliminate heavy metal impurities. Purified  $N_2$  gas was bubbled into the solution at least for 20 min to remove the dissolved oxygen. CFC-12 (Mitsui-Dupont Fluorochemical Ltd) was introduced directly into the autoclave. Electrolyses were carried out galvanostatically (passage of 250 C) using a potentiostat–galvanostat (Hokuto Model HA-501) connected in series with a Coulomb–Ampere–hour meter (Hokuto Model HF-201). The potential of a cathode was corrected with an IR compensation instrument (Hokuto Model HI-203). The sampled gas from the autoclave was analyzed by gas chromatography. An Ohkura GC-802 instrument equipped with an activated carbon column (4 mm  $\times$  2 m) and a thermal conduction detector (TCD) for  $H_2$ , an Ohkura GC-202 instrument equipped with a VZ-10 column (4 mm  $\times$  2 m) and a flame ionization detector (FID) for

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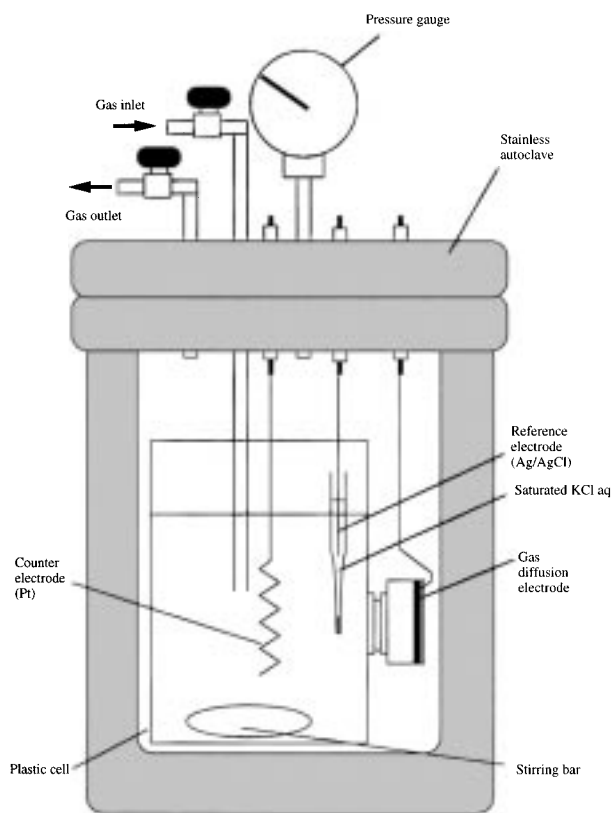


FIGURE 1. Stainless steel autoclave and the electrolysis cell for the electrochemical reduction of CFC-12 at 7 atm.

hydrocarbons, and an Ohkura GC-103 instrument equipped with a Porapak QS column (4 mm × 2 m) and a FID for HCFC-22 and HFC-32 were used for this purpose. The identification of fluorocarbons produced by electrolyses was carried out with a gas chromatography–mass spectrometer (Hitachi Model M-80) equipped with a Porapak Q column (4 mm × 2 m).

## Results and Discussion

The faradaic efficiencies of main products by electrolyses using 12 kinds of metal-supported GDEs are summarized in Table 1, where faradaic efficiency is defined as the ratio of charge used for the formation of the product to the total charge of electrolysis. As shown in Table 1, the total faradaic efficiency of each metal-supported GDE varied widely. For easy comparison of the activity of metal-supported GDEs, we tentatively define the efficiency of decomposition of CFC-12 and the selectivity of products by

$$E_f = \frac{FE_T - FE_H}{FE_T} \quad (1)$$

$$Se_c = \frac{FE_c}{FE_T} \quad (2)$$

$$Se_d = \frac{FE_d}{FE_T} \quad (3)$$

$E_f$  is the efficiency of decomposition of CFC-12,  $Se_c$  and  $Se_d$  are the selectivity of the production of hydrocarbons and that of the production of difluoromethane (HFC-32), where,  $FE_c$ ,  $FE_d$ ,  $FE_H$  and  $FE_T$  are the faradaic efficiencies of hydrocarbons, HFC-32, hydrogen, and the total of them, respectively. As shown in Table 1, the efficiencies of electrolyses were largely dependent on the kind of metals

supported on the GDEs. Ag, Cu, Pb, and In showed very high activity in the decomposition of CFC-12. Especially, Cu-, Pb-, and In-supported GDEs decomposed CFC-12 with almost 100% efficiencies. Electrolysis at each active GDE was carried out at least three times with an error of at most 5% in faradaic efficiency. Other metals (Ni, Pt, Ru, Pd, Co, Cr, Zn, and Sn) showed low or no activity. The products of electrolyses were also dependent on the supported metals. Cu-, In-, Ag-, and Zn-supported GDEs produced methane, chlorodifluoromethane (HCFC-22), and HFC-32. Ag-, Cu-, and Zn-supported GDEs produced ethane and ethylene with low efficiencies. Pb-supported GDE produced HFC-32 with very high selectivity (92.6%). These results indicate that Cu-, In-, Ag-, and Zn-supported GDE are able to cause defluorination of CFC-12 as well as dechlorination. The C–F bond of CFCs is very strong and difficult to cut off. Generally, a very high energy [e.g., high temperature (17), plasma (18), supercritical state (19), etc.] is needed to break it. The experimental condition of the present study is 7 atm and room temperature. As far as we know, this is the mildest condition of CFC-12 decomposition in which the C–F bond of CFC-12 can be broken. This suggests that Cu-, In-, Ag-, and Zn-supported GDEs have very strong electrocatalytic activity of electrochemical decomposition of CFC-12.

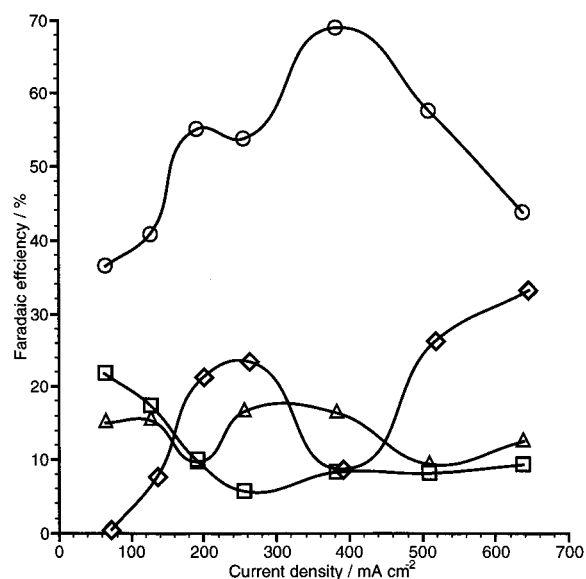
In the electrochemical reaction in aqueous medium, reductive reactions on the electrode compete with the reduction of water. Therefore, the products of electrolyses are expected to depend on the hydrogen overvoltage of the electrodes. Hydrogen overvoltage means the potential of an electrode where hydrogen begins to be produced. The value of the hydrogen overvoltage is largely dependent on the metals used as the electrode. In a general electrochemical reaction, the electrode with a low hydrogen overvoltage mainly produces hydrogen, and the electrode with a high hydrogen overvoltage is liable to reduce other reactants. This tendency is adapted to electrolysis of CFC-12 to a certain extent. As shown in Table 1, Pt-, Pd-, and Ru-supported GDEs with low hydrogen overvoltage produced H<sub>2</sub> with greater than 90% efficiencies, while Zn-, Sn-, and Pb-supported GDEs with high hydrogen overvoltage indicated the activity of electro-decomposition of CFC-12 to some extent. However, this tendency is not adapted to the metals with intermediate hydrogen overvoltages. For Cu, Ni, and Ag, the order of the hydrogen overvoltage is Cu > Ni > Ag (20). As was shown in Table 1, Ag- and Cu-supported GDEs have a high activity of decomposition of CFC-12, while Ni-supported GDE has no activity. In addition, Zn- and Sn-supported GDEs were less active than Cu- and Ag-supported GDEs, although Zn and Sn have larger hydrogen overvoltages than Cu and Ag. These results suggest that the electrocatalytic activity of decomposition of CFC-12 is affected by factors other than hydrogen overvoltage. One factor would be the degree of adsorption of CFC-12 on the surface of the fine grains of metal. The detailed mechanism of decomposition of CFC-12 cannot be obtained from the data in this paper. However, judging from the products of electrolyses, decomposition of CFC-12 would consist of three stages; i.e., (1) the adsorption of CFC-12 on the surface of the fine grain of metal, (2) the elimination of Cl<sup>-</sup> ion induced by electron transfer from the GDE, and (3) the elimination of F<sup>-</sup> ion induced by electron transfer from the GDE. The second and the third processes would be accompanied by hydrogenation caused by the adsorbed hydrogen on the electrode surface. The first process would determine the electrocatalytic activity of metals supported on GDEs, and the third process would determine the final products of electrolyses. Pb seems to have very low electrocatalytic activity of defluorination.

The dependence of faradaic efficiencies of products of electrolysis on the current density using a Cu-supported GDE was shown in Figure 2. Electrolysis at each current density

**TABLE 1. Faradaic Efficiency and Efficiency and Selectivity of Products Defined by Eqs 1–3 of Electrochemical Decomposition of CFC-12 Using Various Metal-Supported Gas Diffusion Electrodes**

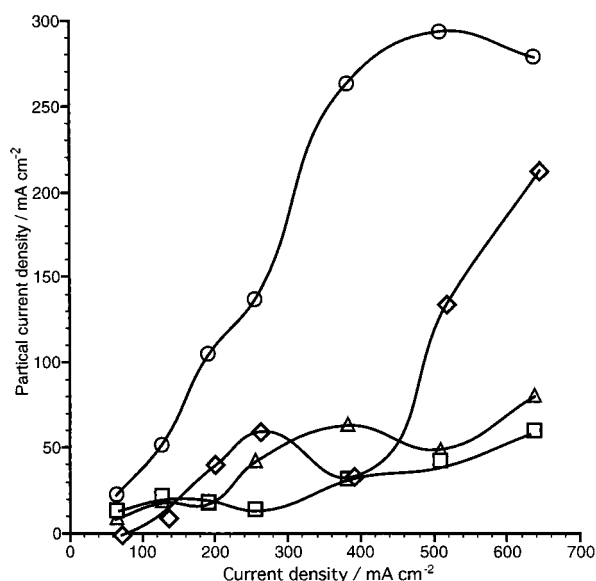
supported metal	$E^b$ (V)	faradaic efficiency (%)							efficiency (%) de.CFC-12 <sup>c</sup>	selectivity (%)	
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	CHClF <sub>2</sub>	CH <sub>2</sub> F <sub>2</sub>	total		hydrocarbons	HFC-32
Ni	-1.46	1.1	nd <sup>d</sup>	1.9	88.3	2.5	3.9	97.7	9.6	3.1	4.0
Pt	-2.00	2.0	1.5	nd	95.6	3.1	6.5	108.7	12.1	3.2	6.0
Zn	-1.74	14.9	0.7	0.4	65.3	8.4	14.2	103.9	37.2	15.4	13.7
Ag	-1.54	16.3	0.6	0.4	17.8	13.2	50.8	99.1	82.0	17.5	51.3
Cu	-1.52	36.6	0.8	1.7	0.7	22.1	15.5	77.4	99.1	50.5	20.0
Ru	-1.07	2.0	nd	nd	89.4	2.5	nd	93.9	5.0	2.1	0
Pd	-1.39	1.7	nd	nd	71.2	3.0	10.1	86.0	17.2	2.0	11.7
Pb	-1.41	1.6	nd	nd	nd	4.3	74	79.9	100	2.0	92.6
Co	-1.42	nd	nd	nd	96.4	nd	1.8	98.2	1.9	0	1.9
Cr	-1.65	nd	nd	nd	72.1	nd	7.7	79.8	9.6	0	9.6
Sn	-1.65	4.2	nd	nd	75.3	6.1	11.5	97.1	22.5	4.3	11.8
In	-1.45	37.6	nd	nd	1.2	6.1	33.5	78.4	98.5	48.0	42.7

<sup>a</sup> Under the condition: current density 63.7 mA cm<sup>-2</sup> at 7 atm of CFC-12 and at room temperature. <sup>b</sup> Potential (V) corrected with an IR compensation instrument (vs Ag/AgCl). <sup>c</sup> Decomposition of CFC-12. <sup>d</sup> Not detected.



**FIGURE 2.** Current density dependence of faradaic efficiencies of products using Cu-supported GDE. (○) methane, (△) HFC-32, (□) HCFC-22, (◇) H<sub>2</sub>.

was carried out at least twice with an error of 5% at most in faradaic efficiency. Faradaic efficiency of methane increased with the increase in the current density until 400 mA cm<sup>-2</sup> and then decreased. Faradaic efficiency of hydrogen increased with the increase in the current density. Faradaic efficiencies of HCFC-22 and HFC-32 were almost independent of the current density. Figure 3 is the relationship between the partial current density of products formation and the current density at a Cu-supported GDE. The partial current density is defined as the product of faradaic efficiency by current density. It means the amount of charge that is used for the formation of the compound on 1 cm<sup>2</sup> of electrode in a second. The uncertainty of partial current density is within 5% of the value of current density at each point. The partial current density of methane formation increased in proportion to the current density and was saturated at 500 mA cm<sup>-2</sup>. The maximum of the partial current density of methane formation was 290 mA cm<sup>-2</sup>. The dependence of faradaic efficiencies of products on the current density using a Pb supported GDE was shown in Figure 4. Faradaic efficiency of HFC-32 formation was almost independent of the current density; about 80%. Faradaic efficiencies of other products were also independent of the current density and almost 0%. It should be noted that a Pb-supported GDE



**FIGURE 3.** Relationship between current density and partial current density of products using Cu-supported GDE. (○) methane, (△) HFC-32, (□) HCFC-22, (◇) H<sub>2</sub>.

kept quite a high selectivity in the formation of HFC-32 even at a high current density. The relationship between the partial current density of products formation and the current density at a Pb-supported GDE was shown in Figure 5. The partial current density of HFC-32 formation increased proportionally to the current density and did not reach saturation even at 650 mA cm<sup>-2</sup>. The partial current density of the formation of other products (methane, H<sub>2</sub>, and HCFC-22) increased gradually with the increase in the current density. However, those values were much lower than that of HFC-32.

For the actual treatment of CFC-12, the conversion to economically valuable compounds is most desirable. In the system of this paper, Pb-supported GDE is the most appropriate electrode. Pb-supported GDE was found to produce HFC-32 with high selectivity even at a high current density. HFC-32 is the one of the substitutes of CFCs with no ozone depletion potential. The catalytic conversion of CFC-12 to HFC-32 has already been reported (7, 8). This method needs hydrogen, high temperature, and noble metal catalysis to convert CFC-12 into HFC-32. Electrochemical decomposition method requires only aqueous solution as the hydrogen source, a Pb-supported GDE, and the electric current. In addition, HF and HCl, which deactivate the catalysis, are able to be neutralized and fixed in solution

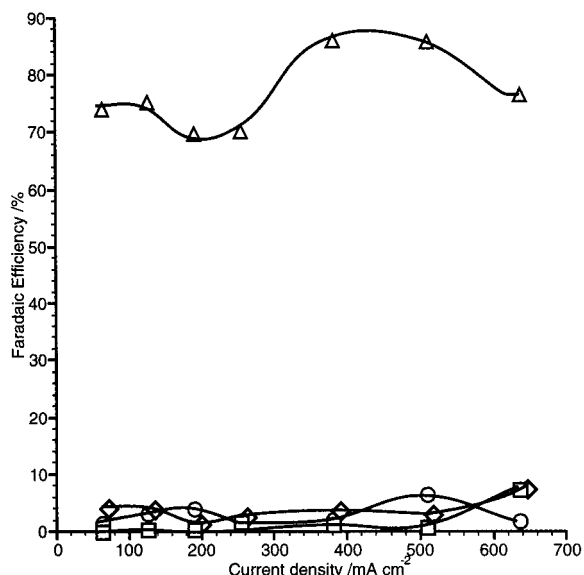


FIGURE 4. Current density dependence of faradaic efficiencies of products using Pb-supported GDE. (○) methane, (△) HFC-32, (□) HCFC-22, (◇) H<sub>2</sub>.

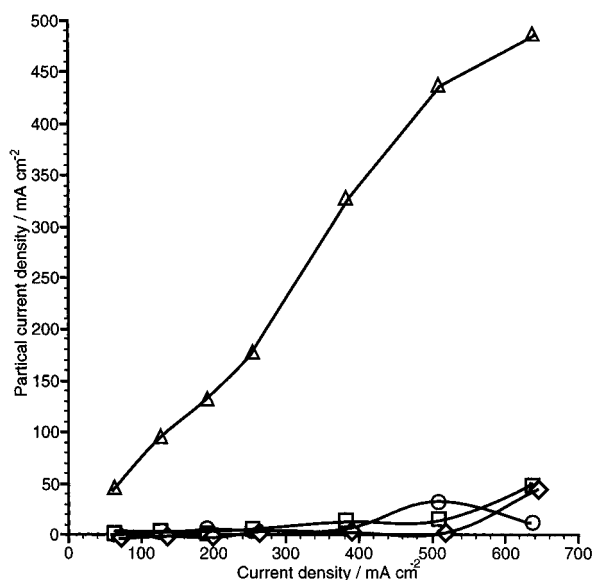


FIGURE 5. Relationship between current density and partial current density of products using Pb-supported GDE. (○) methane, (△) HFC-32, (□) HCFC-22, (◇) H<sub>2</sub>.

immediately by adding alkaline to the electrolytic solution. These advantages of the electrochemical method suggest the possibility that, by further investigation and improvement, it can be appropriate for the conversion of CFC-12 to HFC-32 in small scale.

From the above results, it is concluded as follows: Ag-, Cu-, In-, and Pb-supported GDEs have high electrocatalytic activity in electrochemical decomposition of CFC-12. Ag-, Cu-, In-, and Zn-supported GDEs decompose CFC-12 into methane, while Pb-supported GDE produced HFC-32 in high selectivity. With the increase in the current density, the partial current density of methane formation by Cu-supported GDE arrived at saturation. Pb-supported GDE produced HFC-32 in high selectivity even at 650 mA cm<sup>-2</sup>. HFC-32 can be recycled as substitutes of CFCs with no ozone depletion potential. Therefore, Pb-supported GDE is the most desirable in metal-supported GDEs for the actual treatment of CFC-12.

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