

Electroreduction of a Chlorofluoroethane on a Solid Polymer Electrolyte Composite Electrode

Minoru Inaba,* Ken Sawai, Zempachi Ogumi, and Zen-ichiro Takehara

Division of Energy & Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01

(Received February 16, 1995)

The dechlorination of 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124) was carried out electrochemically on a solid polymer electrolyte composite electrode (Pd-Neosepta). As the sole product 1,1,1,2-tetrafluoroethane (HFC-134a) was obtained. Irradiation with light of a xenon arc lamp enhanced the dissociation of C—Cl bond of the reactant adsorbed on Pd, resulting in an increase in the rate for HFC-134a formation.

It is known that chlorine radical formed from chlorofluorocarbons (Freon) destroys the stratospheric ozone layer, and it is desired to establish safe and economical methods for the destruction or transformation of chlorofluorocarbons to less harmful substances.¹ Electrochemical dechlorination of chlorofluorocarbons is one of promising methods for this purpose.^{2,3}

We have so far reported on the application of solid polymer electrolyte (SPE) electrolyzers to organic synthesis.⁴⁻⁸ The SPE method eliminates the need for a supporting electrolyte, the addition of which often leads to difficulties in subsequent product purification processes and to unwanted side reactions. As is shown by the fact that SPE composite electrodes are being developed for use in fuel cells,⁹ the structure of the SPE composite electrodes is suitable for gas electrodes; hence, the SPE method is promising for electrochemical reactions of gaseous organic compounds such as chlorofluorocarbons. In the present work, we studied the electrochemical dechlorination of a gaseous chlorofluoroethane, 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), using an SPE composite electrode. The effects of the irradiation of light was examined, and the reaction mechanism was discussed.

Solid polymer electrolyte composite electrodes were prepared by an electrodeless plating method as described previously.⁴ An anion-exchange membrane, Neosepta[®] AM-1 (Tokuyama Soda, Co., Ltd.), was used as the SPE material. An aqueous hydrochloric acid solution containing PdCl₂ was used as a palladium source, and a hydrazine solution as a reductant. Figure 1 shows the electrochemical cell used in this study. The cell was composed of two polytetrafluoroethylene compartments, which were separated by the SPE composite electrode. The volumes of the cathode and anode compartments were 0.56 and 12.56 cm³, respectively. The geometric surface area of the SPE composite electrode was 3.1 cm². A platinum wire was used as the counter electrode. The reactant gas, HCFC-124 (Showa Denko) was passed through the cathode compartment at a constant rate. The anodic compartment was filled with aqueous 0.1 mol dm⁻³ (M) NaOH. Electrode potential was measured vs. a Ag/AgCl reference electrode using a Luggin capillary placed in the anode compartment. Electrolysis was carried out potentiostatically. The cathode compartment was fitted with a quartz glass window. A xenon arc lamp (500 W) was placed at 15 cm apart from the electrode surface. During runs the surface of the electrode material was irradiated with the xenon arc lamp through the optical window and the current feeder (Ti mesh coated with Au). A quartz glass cell of 1 cm in thickness was filled with water, and placed between the lamp and the electrolytic cell to avoid heating. Electrolytic products were analyzed by GC-MS and gas chromatog-

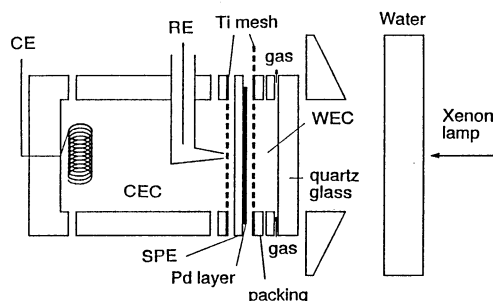
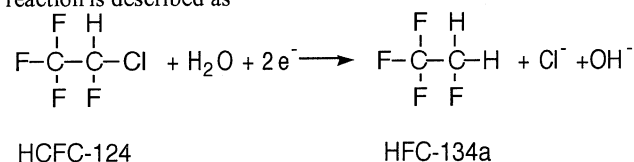


Figure 1. Schematic diagram of the electrolytic cell; SPE = Neosepta[®] AM-1; CE = Pt wire; RE = Ag/AgCl; WEC = cathode compartment; CEC = anode compartment.

raphy.

Figure 2 shows cyclic voltammograms on Pd-Neosepta when unirradiated [curve (a)] and irradiated [curve (b)] with light of the xenon arc lamp. The cathodic reduction of HCFC-124 proceeded at potential more negative than -850 mV accompanied with hydrogen evolution. The cathodic current was enhanced by the irradiation of light.

The electroreduction of HCFC-124 was carried out potentiostatically without and with irradiation, and the effect of light was examined. In both cases 1,1,1,2-tetrafluoroethane (HFC-134a) was obtained as the sole product, and hence the electrode reaction is described as



While the product is recovered as a gas mixture, the Cl⁻ and OH⁻ anions move to the anolyte as the counterion of the anion-exchange membrane. Figure 3 shows the rates of HFC-134a production plotted against electrode potential. The production rate of HFC-134a remained unchanged at potentials more negative than -0.9 V without irradiation. With irradiation the rate was much higher than that without irradiation, and increased with increasing electrode potential in the negative direction; that is, the irradiation enhanced the electrochemical reduction of HCFC-124. Nevertheless, the current efficiency for HFC-134a production was 6.1% at -1.2 V because hydrogen evolution occurred as a competitive reaction at this potential.

Electrochemical reduction of organic compounds are classified into two mechanisms.¹⁰ One is a mechanism in which an organic compound receives electrons directly from an electrode, and the other is catalytic reduction by active hydrogen atoms formed on an electrode. It is reported that the reaction of chlorofluorocarbon in the former mechanism occurs at potential more negative than -2.0 V vs. NHE and is difficult to proceed on electrodes with low hydrogen overvoltage such as palladium.² In the latter mechanism electrodes with high catalytic activity are preferable.

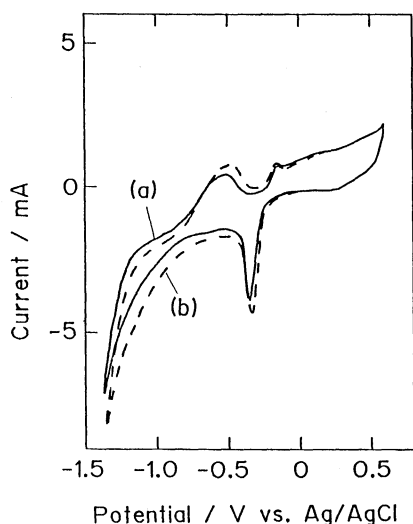


Figure 2. Cyclic voltammograms on Pd-Neosepta (3.1 cm^2) (a) without and (b) with irradiation of light. $\nu = 10 \text{ mV s}^{-1}$. Aqueous 0.1 M NaOH was filled in the anode compartment, and HCFC-124 was passed through the cathode compartment.

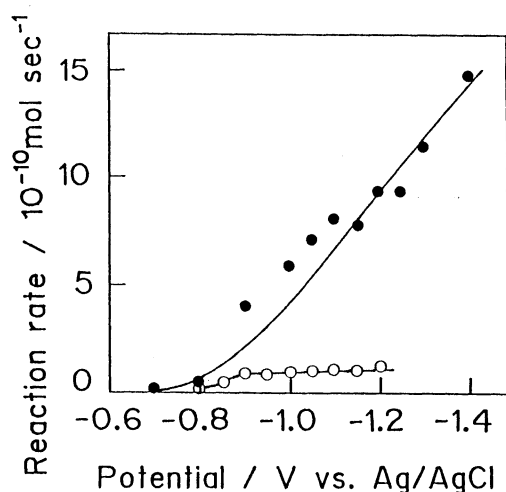


Figure 3. HFC-134a formation rates (O) without and (●) with irradiation of light plotted vs. electrode potential. Aqueous 0.1 M NaOH was filled in the anode compartment, and HCFC-124 was passed through the cathode compartment.

Hence, the reaction on Pd-Neosepta in this study is considered to have proceeded through the latter mechanism.

Irradiation with light enhanced the rate for HFC-134a production. This indicates that the dissociation of C—Cl bond is involved in the overall electrode reaction as a rate determining

step. The dissociation energies of C—Cl are 70, 100 and 83 kcal/mol for CFCl_3 , CF_3Cl and CH_3Cl , respectively,¹¹ and photon energies required for decomposition of CFCl_3 and CH_3Cl are 213.9 and 184.9 nm in vapor phase, respectively.^{12,13} The spectrum of xenon arc lamp is continuous over the range between 250 to 1300 nm with the peak intensity at about 500 nm,¹⁴ but it does not extend to vacuum ultraviolet region. It is hence difficult to dissociate C—Cl bond using photons emitted from xenon arc lamp. However, chlorocarbons adsorbed on highly catalytic metals such as Pt and Pd decompose when irradiated with photons of longer wavelengths. For example, CH_3Cl adsorbed on such metals decomposes when irradiated with light of a wavelength ranging from 229 to 280 nm.¹⁵⁻¹⁸ The observed increase in reaction rate indicates that HCFC-124 is adsorbed on Pd and that the irradiation enhances the radical formation from the adsorbed reactant.

This work was partly supported by Grant-in-Aids for Scientific Research (No. 05235107) from Ministry of Education, Science and Culture, Japan.

References and Notes

- 1 S. Morikawa, *Kagaku*, **45**, 84 (1990).
- 2 M. Tezuka, *Kagaku Kogyo*, **1991**, 456.
- 3 M. Tezuka and T. Yajima, *Denki Kagaku*, **59**, 517 (1991).
- 4 Z. Ogumi, K. Nishio, and S. Yoshizawa, *Denki Kagaku*, **49**, 212 (1981).
- 5 Z. Ogumi, M. Inaba, S. Ohashi, M. Uchida, and Z. Takehara, *Electrochim Acta*, **33**, 365 (1988).
- 6 Z. Ogumi, T. Mizoe, C. Zhen, and Z. Takehara, *Bull. Chem. Soc. Jpn.*, **63**, 3365 (1990).
- 7 M. Inaba, J. T. Hinatsu, Z. Ogumi, and Z. Takehara, *J. Electrochem. Soc.*, **14**, 706 (1993).
- 8 M. Inaba, Z. Ogumi, and Z. Takehara, *J. Electrochem. Soc.*, **141**, 2579 (1994).
- 9 G. A. Eisman, *J. Power Sources*, **29**, 289 (1990).
- 10 L. G. Feoktistov, in "Organic Electrochemistry", ed by M. M. Baizer and H. Lund, Marcel Dekker, New York (1983) Chap. 7.
- 11 N. W. Luft, *J. Chem. Phys.*, **23**, 973 (1955).
- 12 R. E. Robberts and P. J. Ausloos, *J. Photochem.*, **4**, 419 (1975).
- 13 D. M. Shold and R. E. Robberts, *J. Photochem.*, **9**, 499 (1978).
- 14 D. A. Skoog and J. J. Leary, "Principles of Instrumental Analysis", 4th ed., Saunders (1993) p. 76.
- 15 B. Roop, K. G. Lloyd, S. A. Costello, A. Campion, and J. M. White, *J. Chem. Phys.*, **91**, 5103 (1989).
- 16 S. K. Jo and J. M. White, *J. Phys. Chem.*, **94**, 6852 (1990).
- 17 F. Solymosi, A. Berko, and K. Revesz, *Surf. Sci.*, **240**, 50 (1990).
- 18 F. Solymosi, J. Kiss and K. Revesz, *J. Chem. Phys.*, **94**, 8510 (1991).