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In-situ Kinetic Studies on Direct Fluorination of Thin Polyethylene Films with QCM

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Fluorination of polyethylene (PE) films with fluorine gas was studied by using the quartz crystal microbalance technique from the interest for the preparation of wet-proofed carbon black with fluorinated polyethylene (FPE) film for application to gas-diffusion electrodes in fuel cells. The fluorination reaction proceeds clearly in three separated steps, i.e., the first transient step, the 2nd step controlled by the chemical reaction between F_2 and PE molecules, and the 3rd step controlled by the diffusion rate of dissolved F_2 in FPE. The complete fluorination of PE films of ca. 2—10 μm in thickness can be achieved after sufficient reaction time. It was found that the fluorination at the 2nd step obeys the first order kinetics regarding F_2 concentration with the activation energy of only 34.3 $\mathrm{kJ\,mol^{-1}}$. The fluorination at the 3rd step proceeded linearly with the square-root of the reaction time. Diffusion parameters $S\sqrt{D}$ and apparent activation energies for the fluorination at the 3rd step were determined by solving Fick's diffusion equation based on those experimental data. Both of them were very large in comparison with that for un-reacting gases, which were ascribed to the fluorination step proceeded by the reactive diffusion process.

Polytetrafluoroethylene (PTFE) has been used in gas-diffusion electrodes for fuel cells, because of its superior hydrophobicity and thermal stability. The conventional gas-diffusion electrodes are composed of a mixture of fine particles of catalyzed carbon black (Pt/CB) and PTFE dispersion. The former can form an electrolyte network because of its contact angle for electrolytes smaller than 90°. On the other hand, PTFE can form a gas network by wet-proofing a part of the Pt/CB with its hydrophobic property. Balance of the networks has been controlled by the PTFE content. PTFE should cover the Pt/CB surface sufficiently to maintain the stable hydrophobic gas-network for the required lifetime. However, PTFE is difficult practically to cover it sufficiently with the film, because of its high melt-viscosity,[1)] and of the smallest particle-size available commercially (ca. 0.3 μm in diameter) which is more than ten times larger than that of CB. Therefore, the CB in gas-diffusion electrodes may be wetted with the electrolyte sooner or later as long as the conventional structure and materials are used in the catalyst layer. In order to overcome this problem, we have developed an ideal material and a new design concept for an advanced gas-diffusion electrode, i.e. noncatalyzed CB wet-proofed completely by a film of fluorinated polyethylene (FPE/CB) and an electrode structure in which the functions of the the electrolyte network and gas network are attributed to Pt/CB and FPE/CB.[2,3)] We have demonstrated a high and stable performance by applying them to phosphoric acid fuel cells (PAFCs).[4)]

FPE/CB was made by coating polyethylene (PE) completely over a noncatalyzed CB surface, followed by fluorination with fluorine gas (F_2). The resulting film has a molecular structure and physical or chemical properties similar to conventional PTFE.[4)] Since a patent was disclosed about the fluorination of polyethylene by Rudge in 1954,[5)] direct fluorination by F_2 has been recognized as a surface modification technique for various polymer resins to improve properties such as surface wetability, adhesion, or gas permeability.[6—10)] There are not many reports on the application of this method to bulky polymers due to the difficulty of the complete fluorination, e.g., Reglow attributed the difficulty to the steric hindrance of the substituted fluorine and Kiplinger reported the limited thickness of the fluorinated layer in PE films.[11—13)] We have applied these methods first successfully to coat with relatively thin FPE over a high surface area CB.[1)]

Several kinetic studies have also been done on the fluorination process. For example, the conventional gravimetry was used for examining the F_2 conversion, fluorinated depth and other characteristics of fluorinated resin by combining with ex-situ measurements by XPS or IR.[10,11,13—21)] Fluorinated depth of resins were estimated by the visual spectrum, then the ratio of substituted fluorine was estimated together with the weight gain.[22)] Recently, fluorination was studied by in-situ thermal gravimetry specially designed and the resulting film was examined with XPS and IR.[21] However, the gravimetry was not sensitive enough to detect the initial stage of the fluorination, which is not controlled by the diffusion process of F_2 in the film, due to the low resolution of only 1 μg to the weight change.

In spite of the many studies mentioned above, information on the kinetics at the initial stage and the following stage of the fluorination controlled by the chemical reaction process and the mass transport process in films, respectively, has not been investigated enough to prepare new material by this method. Here, we describe an in-situ study on the direct fluorination of PE by F_2 gas in detail by using a quartz crystal microbalance (QCM) technique which is sensitive enough to examine the process.

Experimental

The QCM analysis is known as an ultrahigh resolution gravimetry in an ultrahigh vacuum condition, gas phase and liquid phase. The theoretical basis for the analysis was established by Sauerbrey.[23] The resonance frequency shifts (ΔF), which have a linear relationship with the weight change, (Δm), in principle obeys the following equation:

$$\Delta F = \frac{-F_0^2\Delta m}{N\rho A} = \frac{-2.26\times10^{-6}F_0^2\Delta m}{A} \qquad (1)$$

where F_0 is a fundamental frequency (Hz) on QCM used, Δm is a weight change (g) on the QCM electrode, N is a frequency constant for the quartz (Hz cm), A is the electrode area and ρ is the specific gravity of quartz. In our experiments, planar (2.54 cm in diameter) AT-cut quartz crystals with gold electrodes on both sides (Torrane, CA) were operated at a fundamental frequency of 5 MHz. Frequency changes were detected by a universal counter (Hewlett-Packard: type-5334B), the resolution of which is 0.1 Hz. The decrease of 1.0 Hz corresponds to 17.8 $\mathrm{ng\,cm^{-2}}$ in weight gain. However, this relationship can only be held for an ideal rigid layer. Several factors, such as viscoelastic property or surface roughness or interfacial slippage, affect the frequency response.[24] So it is essential to calibrate the frequency responses to the practical weight changes.

PE thin films were formed on the above quartz crystals in the following manner. High density polyethylene (UltZex 2021L; Mitsui Sekiyu Kagaku Kogyo) was dispersed by 0.2 wt% in hexane. A certain amount of this dispersion was dropped on the crystal, followed by drying and then heat-treating to get smooth PE film on the gold electrode. This process was repeated until the required PE loading was obtained, where the PE loading of 0.2 $\mathrm{mg\,cm^{-2}}$ corresponded to about 2 μm thickness of the film.

The reactor attaching the QCM coated with PE is shown schematically in Fig. 1. Fluorination temperatures, which were detected by a thermocouple settled at about 1 mm height from the PE surface, were controlled at 25 to 100 °C by an oil bath. A planar quartz plate with PE film was placed on the fluorohydrocarbon rubber o-ring and sealed by a PTFE gasket. The chamber volume of the reactor was about 0.5 $\mathrm{cm^3}$. Commercialized 20% F_2 gas diluted with nitrogen (Kanto Denka Kogyo Co., Ltd.) was used by diluting further with pure nitrogen to a series of F_2 concentrations with mass flow controllers. In all experiments, the total flow rate was fixed at 12.0 $\mathrm{cm^3\,min^{-1}}$, which corresponded to the contact time of 2.5 s. Fluorination reactions were carried out under F_2 concentrations of 5, 10, 15, and 20%, and the reaction temperatures of 27, 53, 76, and 100 °C. The fluorinated state was analyzed by ex-situ analysis with an XPS spectrometer (Shimadzu ESCA-750S) with an Mg $K\alpha$ and an IR spectrometer (JASCO FT/IR-500).

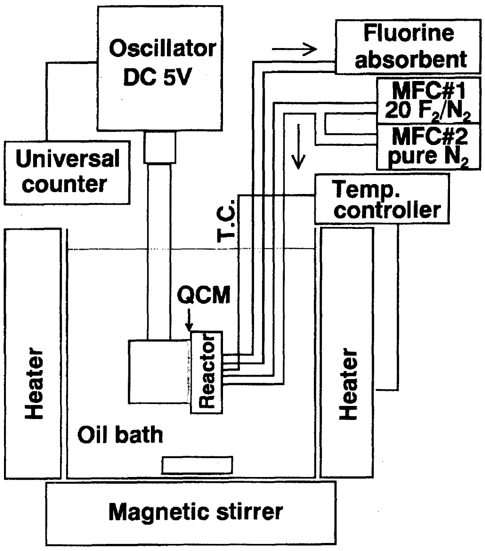

Fig. 1. Apparatus attached with QCM, used in the direct fluorination of polyethylene (PE) film by F_2 gas.

Results and Discussion

Fluorination Reaction Steps. Weights of a series of thickness PE films and some of the fluorinated ones, which were determined by conventional gravimetry, are plotted in Fig. 2 as a function of the frequency changes in the QCM responses accompanied with the loadings. The relationship shows a good proportionality. The sensitivity of the QCM estimated by the least-square method was 37.2 $\mathrm{ng\,Hz^{-1}}$, which was approximately double that of the ideally rigid layer, 17.8 $\mathrm{ng\,Hz^{-1}}$. Since the discrepancy from the theoretical value was caused by the properties of the present polymer samples, we calculated weight changes (ΔW; $\mathrm{ng\,cm^{-2}}$) which occurred during the fluorination reaction by using the conversion factor of the above 37.2 $\mathrm{ng\,Hz^{-1}}$ to multiple to the corresponding frequency changes (ΔF; Hz).

PE may be fluorinated through the following two reaction steps,

$$-(\mathrm{CH_2})- \xrightarrow{\text{fluorine}} -(\mathrm{CFH})- + \mathrm{HF} \xrightarrow{\text{fluorine}} -(\mathrm{CF_2})- + \mathrm{HF} \qquad (2)$$

where the consumption of one molar F_2 should show the weight gain of 18 g. Therefore,

$$\Delta M = \frac{\Delta W}{18} = 2.1\times10^{-9}\Delta F \qquad (3)$$

where ΔM is the molar number of replaced F_2 with hydrogen (mol cm^{-2}) in polymer chain. Figure 3 shows an example of the weight change with time through the fluorination of PE at 76 °C under F_2 partial pressure of 0.2 atm. The weight increases with increasing time and reaches a maximum steady value which corresponded to the full conversion of PE to FPE as will be mentioned later. The weight change $\triangle W$ was lowered by lowering the reaction temperature and/or F_2 partial pressure. The reaction rate (R) can be expressed by the following equation:

$$R = \frac{dM}{dt} \tag{4}$$

Figure 4 shows the change of R with time. The R increases steeply just after F_2 introduction (step 1), reaches a peak within a few minutes (step 2), and then slowly decreases with time (step 3). Since the contact time of F_2 gas with PE was 2.5 s, F_2 concentration on the PE surface was considered to be in equilibrium with F_2 in the gas phase at the beginning of step 2, so that the peak reaction rate may be controlled by the chemical reaction at the PE surface layer, and step 1 may be controlled by the F_2 supplying process from the gas phase to PE surface.

Weight changes were plotted as a function of the square-root of reaction time (Fig. 5). The weight increases proportionally to $\sqrt{t}$ in the wide range of step 3 before achieving the maximum saturated value. From this behavior, it becomes clear that the diffusion of F_2 in polymer film is the rate determining step and the maximum value may indicate the full conversion of PE to FPE. This also suggests that F_2 must be consumed immediately through the fluorination reaction shown by Eq. 2 and form a completely fluorinated PE layer, namely the FPE layer, from outside to inside when it diffuses into the PE layer, since the reaction step 3 is slow enough compared to the chemical fluorination process in the 2nd step. The diffusion controlling step has been reported by several authors at the fluorination of PE,[14—16,21] and of other transparent polymer films.[22]

After the fluorination described above, the FPE films were analyzed by XPS in comparison with PE film. Carbon 1s XPS spectra are shown in Fig. 6 for the source PE and the FPE obtained by fluorination for more than

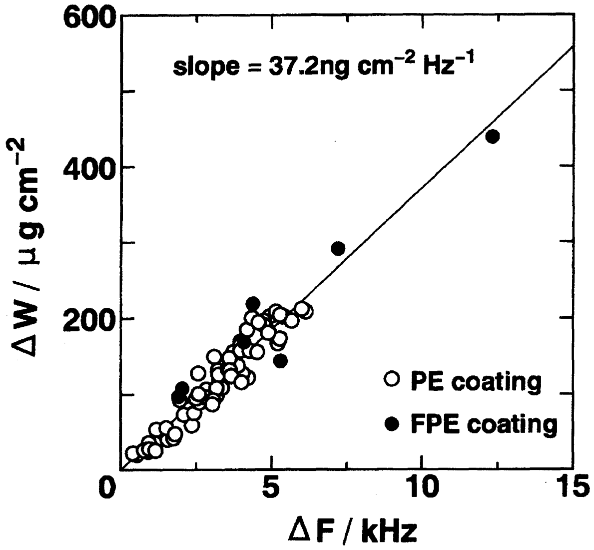

Fig. 2. The plots of QCM frequency changes as a function of the weights determined by conventional gravimetry for the samples of PE or those of fluorinated ones (FPE) coated on QCM electrodes, which were used for the conversion of frequency changes to weights during the direct fluorination of PE.

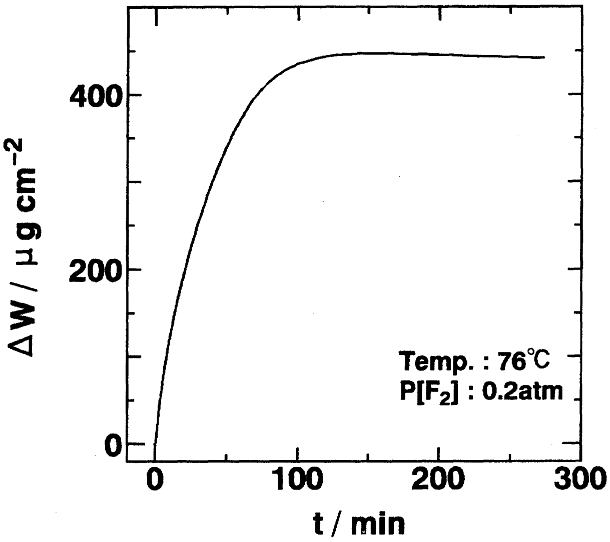

Fig. 3. Weight gain of PE film 2 μm in thickness with the fluorination as a function of the reaction time. The contact time of 20% F_2; 2.5 s, Reaction temperature; 75 °C.

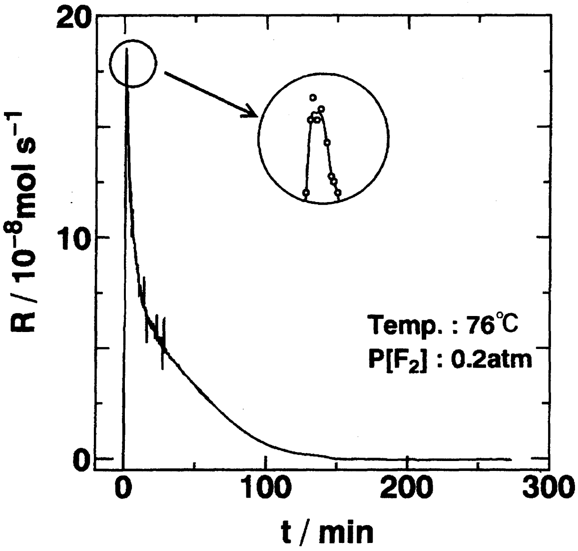

Fig. 4. The reaction rates for the direct PE fluorination controlled by the chemical reaction process as a function of the reaction time. The data correspond to that appearing in Fig. 3.

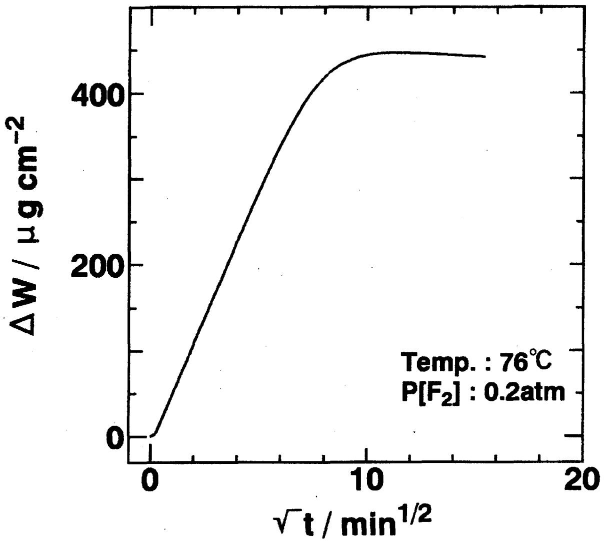

Fig. 5. Weight gain of PE film 2 μm in thickness with the fluorination as a function of the square-root of reaction time. The data correspond to that which appear in Fig. 3.

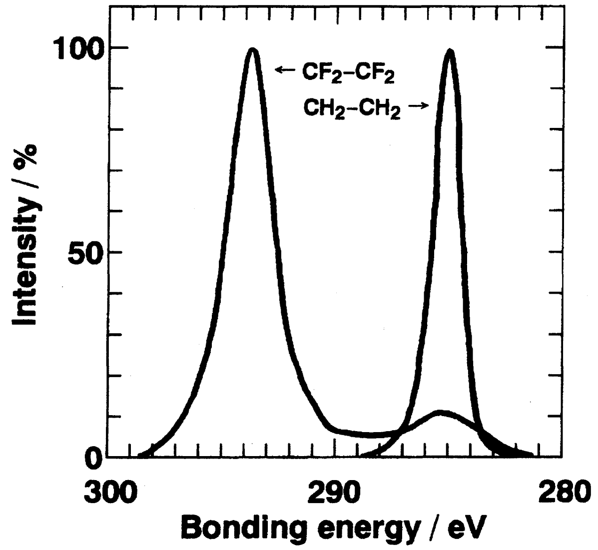

Fig. 6. C_{1s} XPS spectra of PE film 2 μm in thickness and the completely fluorinated one (FPE).

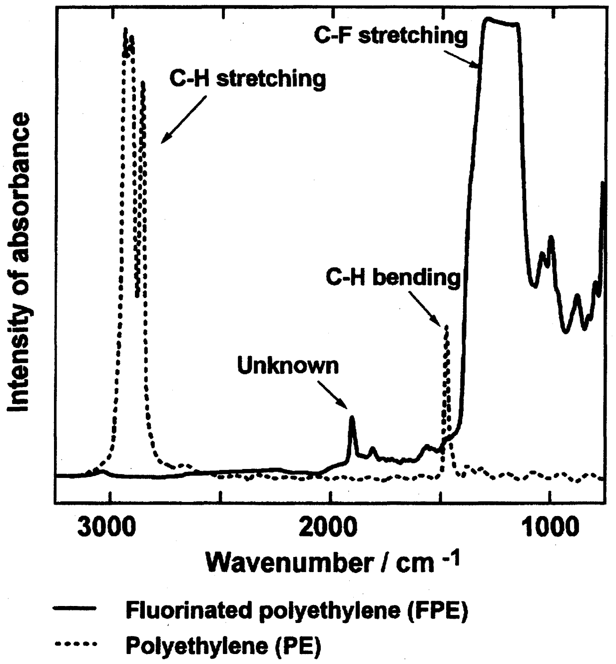

Fig. 7. IR spectra of PE film 10 μm in thickness and the completely fluorinated one (FPE).

200 min under the condition shown in Fig. 3. A main peak for the PE at 285 eV, assigned to CH_2–CH_2, shows a remarkable shift in the direction of higher bonding energy after the fluorination. The peak at 292 eV for the FPE is assigned to CF_2–CF_2 bonding. In the case of the fluorination not completed, peaks of the transition components such as CH_2–CHF, CHF–CHF, CF_2–CH_2, etc. appeared between 292 and 285 eV.[16—18,20] In the curve fitting data of the FPE spectrum, no transition peak can be seen. Thus, the complete fluorination of PE film can be certificated. A small peak at 285 eV in the spectrum of FPE is ascribed to a residual carbon contamination, which is commonly seen in XPS experimental systems. Figure 7 shows an IR spectra on a fluorinated PE 10 μm in thickness, which was fluorinated at 100 °C for about 15 h in 0.2 atm F_2 reactant gas. The absorption corresponding to C–F stretching appears around 1300 cm^{-1} instead of the complete disappearances of those corresponding to C–H stretching at around 2900 cm^{-1} and C–H bending at around 1500 cm^{-1}, so that it is clear that PE films can be fluorinated completely by a sufficient reaction time.

Surface Fluorination Reaction. The reaction rate at step 2 under enough F_2 supply was considered to be controlled by that of chemical fluorination (R_C). Figure 8 shows the relation between the R_C and F_2 partial pressures $P[F_2]$ at various temperatures. The R_C obeys good first-order kinetics regarding $P[F_2]$.

$$R_C = kP[F_2] \tag{5}$$

From the experimental data at 27, 53, 76, and 100 °C, the rate constants were obtained. Figure 9 shows their Arrhenius plots. The data at 27 °C deviates from the others, perhaps due to the deviation of the real temperature of the PE sample surface from that detected with thermocouples, which was caused by over-heating of the PE surface with the reaction heat although the thermocouples could not detect any temperature increase throughout the experiments at 27 °C. From this apparent rate constant, the surface temperature of PE was predicted to become about 46 °C, at least for a short time. The activation energy of this surface reaction is estimated to be 34.3 kJ mol^{-1}.

Bulk Fluorination Reaction. Since the 3rd step reaction is controlled by the diffusion step as mentioned above, the reaction rate will be a function of both dis-

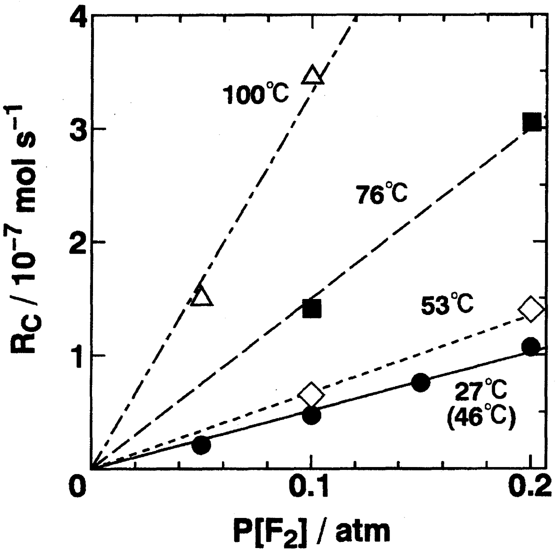

Fig. 8. The relationship between the reaction rates (R_C) for the direct PE fluorination controlled by the chemical reaction process and the partial pressure of F_2 gas, shown at various reaction temperatures. The temperature shown in parenthesis is the estimated real value in the PE film.

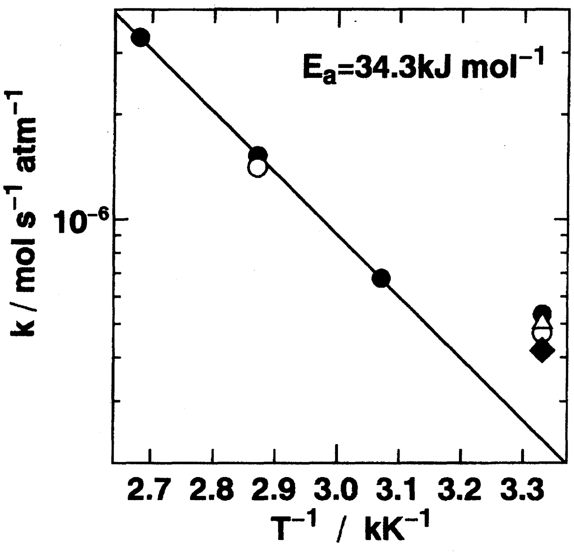

Fig. 9. Arrhenius plots of the rate constants for the direct PE fluorination controlled by the chemical reaction process at various partial pressures of F_2 (◆: 0.05 atm, ○: 0.10 atm, △: 0.15 atm, ●: 0.20 atm).

tance and time, and therefore we shall represent it by Fick's Second Law for planar diffusions with the F_2 concentration $C(X,t)$, where X and t stand for the distance from the film surface and the reaction time, respectively;

$$\frac{\partial C(X,t)}{\partial t} = D\frac{\partial^2 C(X,t)}{\partial X^2} \tag{6}$$

In this notation, when a time period of the appearance of the 3rd step of the fluorination processes is denoted by t_0, the initial condition may be specified approximately by

$$C(X,t) = 0, \quad 0 \leqq t \leqq t_0 \tag{7}$$

since t_0 is negligibly small under the present experimental conditions, e.g. a few minutes, compared to that for the 3rd step reaction. Under the following boundary conditions, Eq. 8 is solved.

$$X \to \infty \;\; C(X,t) \to 0, \;\; X = 0 \;\; C(X,t) = C_0, \;\; t_0 < t \tag{8}$$

where C_0 is the F_2 concentration at the film surface of the fluorinated PE. Consequently, at any subsequent time t, and at any value of X, the concentration, which may be illustrated schematically as Fig. 10, is given by

$$C(X,t) = C_0 \mathrm{erfc}\left[\frac{X}{2\sqrt{Dt}}\right] \tag{9}$$

where erfc [ ] denotes a function known as the error function compliment and D denotes a diffusion coefficient. By differentiating Eq. 9 at the surface ($X=0$), the following equation can be obtained for the diffusion rate of F_2 through the film surface.

$$R_{X=0} = -D\left[\frac{\partial C(X,t)}{\partial X}\right]_{X=0} = \frac{C_0\sqrt{D}}{\sqrt{\pi t}} \tag{10}$$

Therefore, the total amount of F_2 taken into the film (V) is,

$$V = 1.23\times 10^3 \times \Delta M = \int R_{X=0}\mathrm{d}t = \frac{C_0 2\sqrt{Dt}}{\sqrt{\pi}} = \frac{2P[F_2]S\sqrt{Dt}}{\sqrt{\pi}} \tag{11}$$

where S is the solubility coefficient of F_2 for the fluorinated PE (cm^3 [STP] · cm^{-3}[FPE] · $\mathrm{atm.}^{-1}$). In the Eq. 11, V (cm^3 [STP] · cm^{-2}) consists of a sum of reacted F_2 (V_r) and unreacted F_2 (V_{ur}). V_{ur} must be located between the film surface and the reacting plane interfaced with FPE of the reaction product and PE unreacted as devolved F_2 with a concentration profile as shown in Fig. 10. Since no data on F_2 solubility has

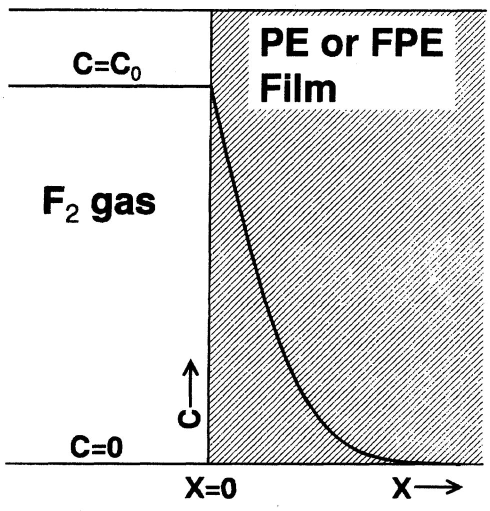

Fig. 10. Schematic illustration of the diffusion profile of F_2 gas in PE or FPE layers.

been reported not only in the FPE but also PTFE, we estimate very roughly the order of the maximum solubility, or the order of maximum $V_{\rm ur}$, provided that F_2 solves uniformly in the whole film with solubility the same as that of O_2 at 25 °C.[25] This is only 1.0×10^{-7} g, which can be completely neglected as compared with the total V which is in the order of 4.5×10^{-4} g evaluated from the data shown in Fig. 3. It is revealed, therefore, that the most F_2 taken into the film was consumed for the fluorination of PE, i.e. $V \fallingdotseq V_{\rm r}$.

The diffusion parameters $S\sqrt{D}$ relating to the 3rd reaction step were calculated from the experimental plots between $\triangle W$ and $\sqrt{t}$ based on Eq. 11 at various reaction temperatures and partial pressures of F_2 gases, and the results are shown in Fig. 11. Few studies have been published on the solubility or diffusion coefficient of halogen, particularly F_2, in even PTFE. Therefore, we compare $S\sqrt{D}$ for F_2 in FPE at 25 °C with that for O_2 in PTFE, which behaves similarly in polymers. The former is 4.5×10^{-3}, which is two orders of magnitude larger than 8.3×10^{-5} of the latter, perhaps due to the consumption of F_2 on the way of diffusion, which can be called a reactive diffusion. Figure 12 shows the Arrhenius plots for the $S\sqrt{D}$. All of the data except that at 27 °C fall into a regression line and are independent on F_2 partial pressure as expected. The data at 27 °C deviates from this regression linear plot due to the deviation of the detected sample temperature from the real one. The real temperature was estimated to be 47 °C by extrapolation of the line to $S\sqrt{D}=1.5\times10^{-2}$, which is quite consistent to that estimated in the proceeding section based on the kinetic-controlled reaction rates, i.e., 46 °C. The apparent activation energies are 76.6 kJ mol^{-1}, although that for O_2 in PTFE was estimated to be 11.9 kJ mol^{-1}.[25] The large $S\sqrt{D}$ values or the apparent activation energies for F_2 diffusion may mainly be ascribed to the D since the S may not be considered to change much in the present small variation of the experimental temperature range. The fact that the D has very large values in spite of the large activation energies must suggests that the diffusion coefficient has large frequency factors probably brought by the reactive diffusion of F_2 mentioned above, which is different from the conventional diffusion of nonreactive gases such as O_2 in polymers.

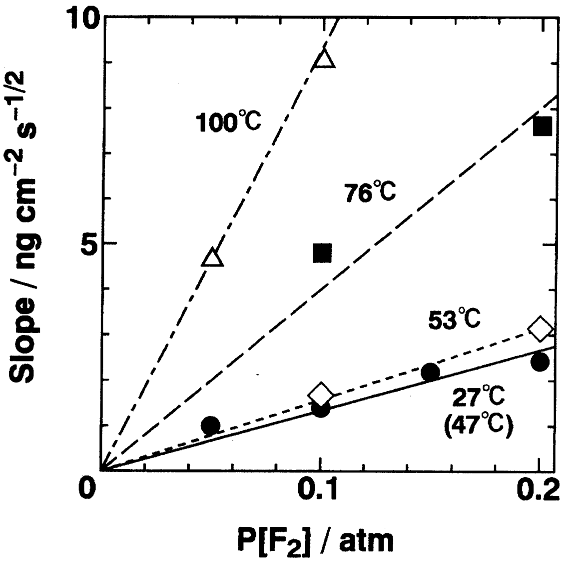

Fig. 11. The relationship between the slopes, which were calculated from the experimental data plots between $\sqrt{t}$ and $\triangle W$, and the partial pressure of F_2 gas, which is shown at various reaction temperatures. The temperature shown in parenthesis is the estimated real value in the PE film.

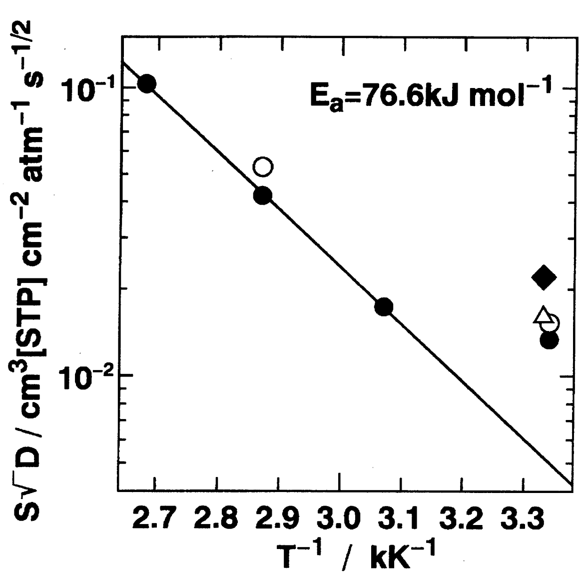

Fig. 12. Arrhenius plots of diffusion parameters $S\sqrt{D}$ for the direct PE fluorination controlled by the F_2 diffusion process, shown at various partial pressures of F_2 (◆: 0.05 atm, ○: 0.10 atm, △: 0.15 atm, ●: 0.20 atm).

Summary

The kinetic studies of the fluorination of PE film with fluorine gas was examined by using the QCM technique. The fluorination reaction processes were clearly separated in 3 steps, i.e., the first transient step until the accomplishment of the steady surface concentration of F_2, the 2nd step controlled by the chemical reaction between F_2 and PE molecules, and the 3rd step controlled by the diffusion rate of dissolved F_2 in FPE. The complete fluorination of PE film even at ca. 10 μm in thickness can be achieved after a sufficient reaction time. It was found that the fluorination at the 2nd step obeys the first order kinetics with regard to F_2 partial pressure and the activation energy calculated based on the reaction rate constants at various temperatures is relatively small. The fluorination at the 3rd step was revealed to proceed linearly with the square-root of the reaction time, showing a diffusion controlled reaction. The diffusion parameters $S\sqrt{D}$ were determined by solving Fick's diffusion equation based on this experimental data. Apparent activation energies based on the resulting $S\sqrt{D}$ values were very large compared with that for unreacting gases. It is indicated that the fluorination of the 3rd step proceeded by the reactive diffusion process. Separated determination of each value of D and S for this process will be examined with the QCM method by us in the future and published elsewhere.

References

1) B. Chu, J. Wang, and W. H. Tuminello, *J. Appl. Polym. Sci.*, **49**, 97 (1993).

2) M. Watanabe, C. Shimura, K. Tsurumi, and N. Hara, *Chem. Lett.*, **1991**, 1113.

3) M. Watanabe, K. Tsurumi, and N. Hara, U. S. Patent 5137754 (1992).

4) N. Hara, K. Tsurumi, and M. Watanabe, *J. Electroanal. Chem.*, in press.

5) A. J. Rudge, British Patent 710523 (1954).

6) H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.*, **12**, 1231 (1968).

7) D. D. Dixon, D. G. Manly, G. W. Recketenwald, and M. A. Williams, U. S. Patent 3862284 (1975).

8) B. D. Buman, R. K. Mebts, and M. A. Williams, U. S. Patent 4764405 (1988).

9) M. Eachway, R. Bonn, and H. Neumann, U. S. Patent 4869859 (1989).

10) Y. Chong and N. Watanabe, "The Meeting of Electrochem. Soc. of Jpn.," Yokohama, 1989, Abstr., No. 2D08.

11) R. J. Lagow and J. L. Margrave, *Polym. Lett. Ed.*, **12**, 177 (1974).

12) O. Levespiel, "Chemical Reaction Engineering," John Wiley and Sons Inc., New York (1962), p. 357.

13) C. L. Kiplinger, D. F. Persico, R. J. Lagow, and D. R. Paul, *J. Appl. Polym. Sci.*, **31**, 2617 (1986).

14) T. Volkmann and H. Widecke, *Macromol. Chem.*, **25**, 243 (1989).

15) D. T. Clark, W. J. Feast, W. K. R. Musgrave, and I. Ritchie, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem.*, **34**, 307 (1974).

16) D. T. Clark, W. J. Feast, W. K. R. Musgrave, and I. Ritchie, *Polym. Sci. Technol.*, **5A**, 373 (1974).

17) D. T. Clark, W. J. Feast, W. K. R. Musgrave, and I. Ritchie, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 857 (1975).

18) M. Anand, R. E. Cohen, and R. F. Baddour, *Polymer*, **22**, 361 (1981).

19) G. A. Corbin, R. E. Cohen, and R. F. Baddour, *Polymer*, **23**, 1546 (1982).

20) C. Bliefert, *Metalloberfläche*, **41**, 371 (1987).

21) R. D. Sanderson, F. J. Du Toit, P. A. B. Carstens, and J. B. Wagener, *J. Therm. Anal.*, **41**, 563 (1994).

22) J. Shimada and M. Hoshino, *J. Appl. Polym. Sci.*, **19**, 1439 (1975).

23) G. Sauerbrey, *Z. Phys.*, **155**, 206 (1959).

24) D. A. Buttry and M. D. Ward, *Chem. Rev.*, **92**, 1355 (1992).

25) S. Pauly, "Polymer Handbook," 3rd ed, John Wiley and Sons Inc., New York (1989), Vol. 4, p. 357.