April, 1991] © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 1305—1312 (1991)

Electrode Kinetics of the $[Fe(CN)_6]^{4-/3-}$ Complex Confined in Cationic Perfluoropolymer Films on Electrode Surfaces

Takeyoshi OKAJIMA,† Takeo OHSAKA,†† and Noboru OYAMA*
Department of Applied Chemistry, Tokyo University of Agriculture and Technology,
2-24-16 Nakamachi, Koganei, Tokyo 184
†Department of Industrial Chemistry, College of Science and Technology,
Nihon University, 1-8-14 Kanda-surugadai,Tokyo 101
††Department of Electronic Chemistry, Graduate School at Nagatsuta, Tokyo Institute of
Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

(Received December 27, 1990)

A heterogeneous electron-transfer process of the $[Fe(CN)_6]^{4-/3-}$ complex confined electrostatically in cationic perfluoropolymer (CPFP) films on graphite electrodes and a homogeneous charge-transport process within the films were examined by potential-step methods. The relevant kinetic parameters (i.e., standard rate constant; k°/cm s^{-1} and transfer coefficient; α) of the heterogeneous electron-transfer process and the apparent diffusion coefficient (D_{app}/cm^2 s^{-1}) of the homogeneous charge-transport process within the films were evaluated at various concentrations (C°) of the complex within the film. The values of D_{app} and k° slightly decreased with an increase in C°. The value of α was independent of C° (cathodic transfer coefficient, α_c=0.20, anodic transfer coefficient; α_a=0.80). The values of k°, α, and D_{app} were compared with those obtained previously for protonated poly(4-vinylpyridine) ($PVPH^+$)-$[Fe(CN)_6]^{4-/3-}$ system and poly(*N,N*-dimethylaniline) (PDMA)-$[Fe(CN)_6]^{4-/3-}$ system. It was found that k°, α_c, and D_{app} decrease, depending on the polymer film in which the complex is confined, in the following order: for D_{app} and k°, $PVPH^+$>PDMA>CPFP and for α_c, $PVPH^+\approx$PDMA>CPFP.

Thus far several polyelectrolytes (e.g., Nafion and protonated poly(4-vinylpyridine), shown in Fig. 1) have been used as an "electrode modifier" in the field of polymer-modified electrodes.[1–5] A number of papers dealing with Nafion film-coated electrodes have been reported since it was found that Nafion, which has the structure consisting of hydrophobic and hydrophilic domains,[6] could be used as an electrode modifier, because of its chemical stability and stable adhesion onto electrode surfaces.[6–21] A perfluoropolycarboxylic acid (PFPC) has also been used as electrode modifier.[5,22]

More recently, a new cationic perfluoropolymer membrane (CPFP, Fig. 1) has been produced by Tosoh Co., Ltd. This is a new cationic anion-exchange membrane with quaternary ammonium groups, in contrast to Nafion and PFPC which are anionic cation-exchange membranes with sulfonyl and carboxyl groups, respectively. In recent papers,[23–25] we have reported the preparation and the

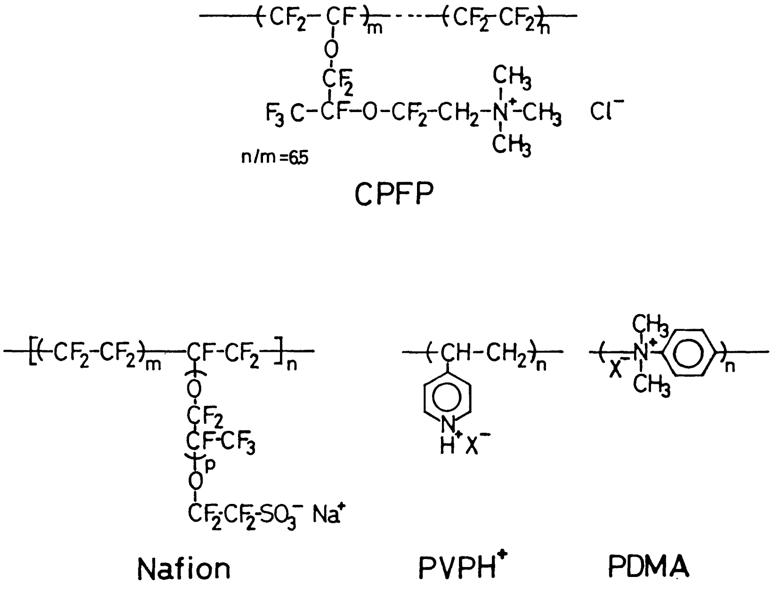

Fig. 1. Structures of cationic perfluolopolymer (CPFP), protonated poly(4-vinylpyridine) ($PVPH^+$), poly(*N,N*-dimethylaniline) (PDMA), and Nafion.

basic properties of the CPFP film as an electrode modifier and the charge-transport process within the film in which anionic Alizarine Red S dye is confined electrostatically as electroactive species.

In this work, we aim to examine the kinetics of the heterogeneous electron-transfer process of $[Fe(CN)_6]^{4-/3-}$ complex confined electrostatically in CPFP film on graphite electrode surfaces and the homogeneous charge-transport process within the film. The relevant kinetic parameters (standard rate constant: $k^\circ/\mathrm{cm\,s^{-1}}$, anodic and cathodic transfer coefficients: α_a and α_c) of the electrode reaction and apparent diffusion coefficient ($D_{app}/\mathrm{cm^2\,s^{-1}}$) of the homogeneous charge-transport process within the film are evaluated at various concentrations of the complex within the film. Further, the obtained values of k°,α_c, and D_{app} will be compared with those obtained previously for protonated poly(4-vinylpyridine) $(PVPH^+)$-$[Fe(CN)_6]^{4-/3-}$ system[26] and poly(*N*,*N*-dimethylaniline) (PDMA)-$[Fe(CN)_6]^{4-/3-}$ system.[27]

Experimental

Materials. CPFP membrane specimen was a gift of Tosoh Co., Ltd. Trifluoroacetic acid and sodium trifluoroacetate (Aldrich) used as supporting electrolytes and $K_3[Fe(CN)_6]$ (Merck) were of reagent grade and were used as received.

Basal-plane pyrolytic graphite (BPG) (Union Carbide Co.) was used as a working electrode material. The BPG disk electrodes were prepared and mounted into a glass tube with a heat-shrinkable polyolefin tube. The exposed area of these electrodes was 0.194 cm^2. Before use of electrodes, they were cut with a scalpel and their fresh surfaces were exposed. Aqueous solutions were prepared from doubly distilled water. Other chemicals were of reagent grade.

Preparation of CPFP Film-Coated Electrodes. The stock solution of CPFP, which was prepared as reported previously,[23] was diluted twice with $H_2O/C_2H_5OH/2$-C_3H_7OH(1/1/1(volume ratio)) mixed solvent. Then, the concentration of CPFP in the diluted stock solution was 10.5 mg ml^{-1}. For the preparation of CPFP film-coated electrodes, aliquots (usually 4 μl) of the diluted stock solution were spread by a microsyringe on the freshly cleaved disk surface of BPG electrode, and then were air-dried to remove the solvent at room temperature.

Measurement of the Film Thickness. The film thickness was measured as follows. The glass slide (ca. 1 cm×1 cm) was coated with silicone film (PRX 305-Clear, Toray Silicone Co., Ltd.), keeping a portion of ca. 0.20 cm^2 uncoated. Aliquots of the CPFP stock solution were spread with a microsyringe on the uncoated portion of the glass slide, and they were dried. After that, the silicone film was stripped. With a Surfcom 550A (Surface texture measuring instruments, Tokyo Seimitsu Co., Ltd.), the average difference between the surface profile of the glass slide and that of the CPFP film was measured. As seen from the inset in Fig. 2 this difference was taken as a film thickness under the dry state. After the glass slide which was used to measure the film thickness under the dry state was soaked overnight in a supporting electrolyte aqueous solution (0.2 M $CF_3COONa+CF_3COOH$, pH 1.0, 1 M=1 mol dm^{-3}) and water on the CPFP film was removed, the film thickness was measured again as that under the wet state. The clear difference between the film thicknesses under the dry and wet states was not observed, and thus the film thickness under the wet state was regarded as equal to that under the dry state within experimental errors. Figure 2 shows a linear plot of the film thickness under the dry state (μm in unit) vs. the coverage of the CPFP stock solution (μl in unit). The film thickness on the CPFP film-coated electrode, which was used to examine the kinetics of charge-transfer reaction, was estimated to be ca 1.0×10^{-4} cm from this linear relationship.

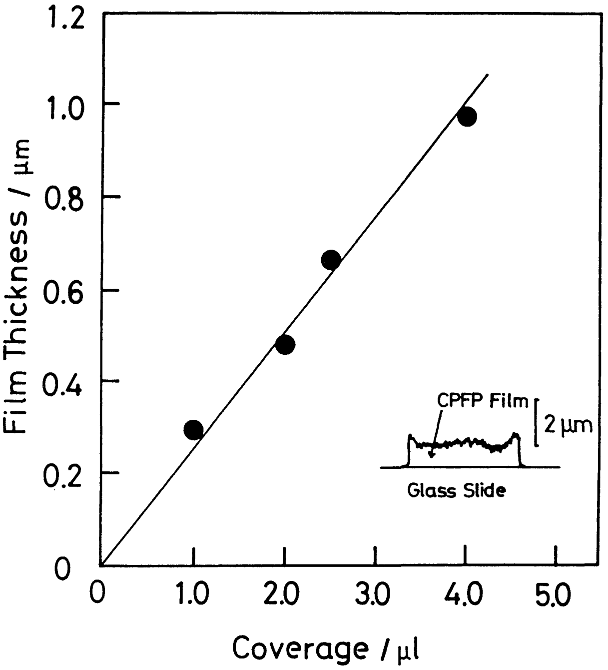

Fig. 2. Correlation between film thickness of CPFP and its coverage.
The coverage means the amount of the CPFP stock solution (see Experimental section) put and solvent-evaporated on the slide glass of a known area. The inset shows a typical vertical sectional profile of the CPFP film prepared on slide glass.

Apparatus and Procedures. The same standard three-electrochemical cell and electrode assembly as described previously were used in this work.[37] Electrode potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode (SSCE).

For cyclic voltammetry, potential-step chronoamperometry, potential-step chronocoulometry, and normal pulse voltammetry, the same instruments as described previously were used.[26,27] In potential-step chronoamperometric and chronocoulometric experiments, the electrode potentials were stepped from 0.8 to −0.2 V vs. SSCE for the reduction and from −0.2 to 0.8 V vs. SSCE for the oxidation. Then, the time of pulsed electrolysis was 40 ms for each case. In normal pulse voltammetric experiments, the electrode potentials were stepped from 0.8 V vs. SSCE for the reduction and from −0.2 V vs. SSCE for the oxidation, and then the height of pulsed wave was increased with 10 mV after each waiting period (usually 30—60 s). Currents were sampled in the range from 2 to 24 ms. A positive feedback circuit was used to compensate IR drop of applied voltage resulting from the resistances of the solution and the coating films.

The kinetic measurements were carried out in 0.2 M $CF_3COONa+CF_3COOH$ aqueous solutions (pH 1.0) containing $[Fe(CN)_6]^{3-}$ in the concentration range from 10^{-5} to 10^{-4} M to keep its concentration within the film a given constant value.

The surface concentration (Γ/mol cm^{-2}) of $[Fe(CN)_6]^{4-/3-}$ within the CPFP film was estimated from graphical integration of the cyclic voltammogram, which was obtained at slow potential sweep rates (2—5 mV s^{-1}), with correction of background current for the oxidation and reduction. After substituting dissolved oxygen in a solution with a purified nitrogen gas, all electrochemical measurements were carried out under an atmosphere of nitrogen gas at room temperature.

The temperature dependence of formal potential ($E^{\circ\prime}$) was examined using a "non-isothermal electrochemical cell"[31,32] having a thermally jacketed compartment for the working and counter electrodes and a separate compartment for the reference electrode which was connected to the cell with a 3 M NH_4Cl salt bridge. The reference electrode was maintained at a fixed temperature (25±0.2 °C). The temperature of the cell was varied in the range of 3—37 °C. The values of $E^{\circ\prime}$ were estimated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms.

Results

Cyclic Voltammetry. The cyclic voltammetric experiments were performed with the CPFP-film coated and naked BPG electrodes in a 0.2 M $CF_3COONa+CF_3COOH$ aqueous solution (pH 1.0) containing 0.2 mM $[Fe(CN)_6]^{3-}$. When the CPFP-film coated BPG electrode was immersed into the solution, the anodic and cathodic peak currents (i_p^a and i_p^c) of the cyclic voltammogram gradually increased as the electrode potential was scanned repeatedly between 0.8 and −0.2 V vs. SSCE. After about an hour, as shown in Fig. 3(A), these peak currents indicated constant values, and the steady-state cyclic voltammogram was obtained. In this case, the values of i_p were about 10 times as large as those obtained at the naked BPG electrode in the same solution as used in Fig. 3(A). Then, C° was ca. 0.15 M and was by a factor of about 750 larger than the concentration (0.2 mM) of $[Fe(CN)_6]^{3-}$ in the bulk solution.

Further, the formal redox potential ($E^{\circ\prime}=0.310$ V vs. SSCE) of $[Fe(CN)_6]^{4-/3-}$ couple confined in the CPFP film was different from that (0.367 V vs. SSCE) of the same couple in the bulk solution. This indicates that the environment around the redox couple within the film is different from that in the bulk solution. In this case, it may be presumed that the oxidized half of the redox couple exists within the film more stably than in the bulk solution and/or the reduced one exists in the bulk solution more stably than within the bulk. When the CPFP film-coated electrode used in Fig. 3(A) was transferred into the supporting electrolytic solution containing no $[Fe(CN)_6]^{3-}$, i_p gradually decreased, suggesting the releasing of the complex into the bulk solution. However, when this electrode was re-transferred into the same solution as used in (A), i_p increased and the same cyclic voltammograms as shown in (A) were obtained. From this fact, it is obvious that the CPFP film stably adsorbed on the electrode surfaces. Further, it has previously been demonstrated that two kinds of anionic metal complexes can be simultaneously concentrated into the CPFP film.[23]

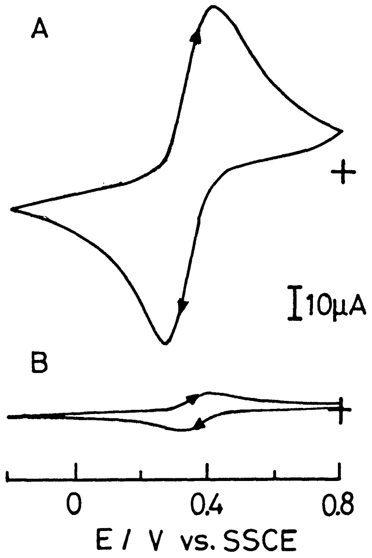

Fig. 3. (A) Steady-state cyclic voltammogram obtained for CPFP film-coated BPG electrode in 0.2 M CF_3COONa aqueous solution (pH 1.0) containing 0.2 mM $[Fe(CN)_6]^{3-}$. Thickness of CPFP film: 3.0×10^{-4} cm. Surface concentration (Γ) of quaternized ammonium site in CPFP film: 5.2×10^{-7} mol cm^{-2} (volume concentration: 1.7 M). (B) Cyclic voltammogram obtained for bare BPG electrode in the same solution as that used in A. In both cases, potential scan rate: 50 mV s^{-1}.

As described above, the overall electrode process at the CPFP film-coated electrode consists of two processes. One is the heterogeneous electron-transfer reaction which is characterized by standard rate constant (k°) and transfer coefficient (α). The other is the homogeneous charge-transport reaction which is characterized by apparent diffusion coefficient (D_{app}). These reactions were quantitatively examined with electrochemical pulse methods, as shown below.

Potential-Step Chronoamperometry (PSCA) and Chronocoulometry (PSCC). The curves A-1 and B-1 shown in Fig. 4 show current-time and coulomb-time responses, respectively, which were obtained with PSCA and PSCC for the reduction of $[Fe(CN)_6]^{3-}$ incorporated into the CPFP film on the electrode. In these figures, the dashed lines show the data of blank experiments obtained at the $[Fe(CN)_6]^{3-}$-free CPFP

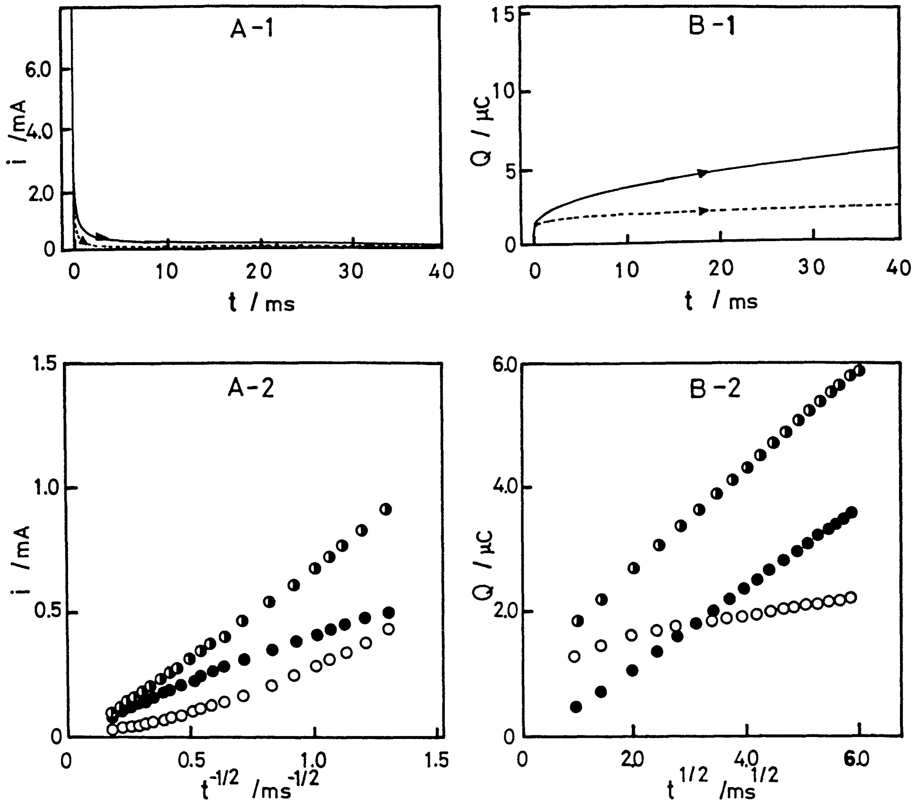

Fig. 4. Typical potential-step (A-1) chronoamperometric and (B-1) chronocoulometric responses for the reduction of $[Fe(CN)_6]^{3-}$ complex confined in the CPFP film on BPG electrode in 0.2 M CF_3COONa solution (pH 1.0). A-2 and B-2 represent chronoamperometric and chronocoulometric Cottrell plots for the data shown in A-1 and B-1, respectively. The dashed lines correspond to the background current responses obtained at the CPFP film (containing no $[Fe(CN)_6]^{3-}$)-coated BPG electrode in 0.2 M CF_3COONa solution (pH 1.0). Open and half-solid circles correspond to the dashed and solid lines in A-1 and B-1, respectively, and solid circles represent the background-current-corrected response.

film-coated electrodes. In these measurements the potential was stepped from 0.8 to −0.2 V vs. SSCE, and the time of pulsed electrolysis was 40 ms. Within this time window, a thickness of diffusion layer, which can be estimated to be ca. $(1-2)\times10^{-5}$ cm based on the D_{app} values obtained (shown below), is much thinner than the film thickness (1.0×10^{-4} cm). Therefore, the homogeneous charge-transport reaction can be regarded as a semi-infinite diffusion. The Cottrell equation and its integrated form were used to analyze the obtained curves.[28]

The plots A-2 and B-2 in Fig. 4 show the Cottrell plots for the data of A-1 and B-1, respectively. The values of D_{app} were estimated from the slopes of the plots which were corrected with the data of blank experiments for A-1 and B-1. The obtained values of

Table 1. Kinetic Parameters of the Heterogeneous Electron-Transfer Process at the Electrode/Film Interfaces and the Homogeneous Charge-Transport Process in the Films for the $[Fe(CN)_6]^{3-/4-}$/CPFP Film-Coated BPG Electrode System[a]

Film	Electrode process[b]	C°/M	D_{app}/cm^2 s^{-1}	k°/cm s^{-1}	α_a,α_c[c]
CPFP	Ox	8.9×10^{-2}	1.2×10^{-9}	$(5.4\pm2.0)\times10^{-5}$	0.80 ± 0.02
CPFP	Red	3.2×10^{-2}	2.4×10^{-9}	$(7.6\pm1.7)\times10^{-5}$	0.20 ± 0.03
CPFP	Red	1.0×10^{-1}	1.8×10^{-9}	$(6.7\pm1.6)\times10^{-5}$	0.21 ± 0.03
PDMA[d]	Red	1.2×10^{-1}	5.0×10^{-9}	1.2×10^{-4}	0.30 ± 0.03
PVPH$^+$[e]	Red	1.1×10^{-1}	2.5×10^{-8}	1.0×10^{-3}	0.30

a) Supporting electrolyte: 0.2 M $CF_3COONa+CF_3COOH$ (pH=1.0). b) Ox: oxidation process; Red: reduction process. c) α_a: anodic transfer coefficient, α_c: cathodic transfer coefficient. d) Ref. 27. e) Ref. 26.

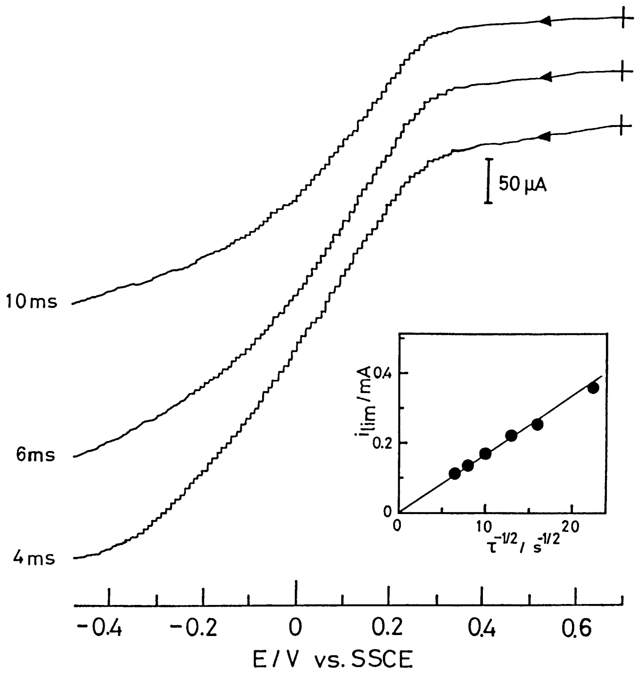

Fig. 5. Typical normal pulse voltammograms for the reduction of $[Fe(CN)_6]^{3-}$ complex confined in the CPFP film on BPG electrode in 0.2 M CF_3COONa solution (pH 1.0) containing 1.0×10^{-5} M $[Fe(CN)_6]^{3-}$. Concentration of $[Fe(CN)_6]^{3-}$ complex confined in the film: 3.2×10^{-2} M. The dashed lines show the background current responses. The inset shows a typical normal pulse voltammetric Cottrell plot of limiting current, i_{lim}, vs. (sampling time)$^{-1/2}$, $\tau^{-1/2}$.

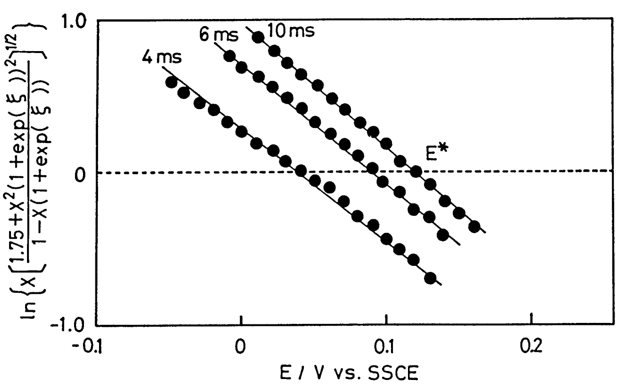

Fig. 6. Modified log-plots for the normal pulse voltammograms shown in Fig. 5. Sampling times are indicated on each straight line.

D_{app} are shown in Fig. 7.

Normal Pulse Voltammetry. Figure 5 shows typical normal pulse voltammograms obtained for the reduction of $[Fe(CN)_6]^{3-}$ confined in the CPFP film at various sampling times (τ/ms). At sufficiently negative applied potentials, the limiting currents (i_{lim}) were obtained. The dependence of the limiting currents (i_{lim}) of these normal pulse voltammograms on τ was examined. As shown in the inset of Fig. 5, i_{lim} was plotted against $\tau^{-1/2}$. This plot gave a straight line and passed through the origin. From this fact, it was found that the homogeneous charge-transport reaction within the film was controlled by diffusion and obeyed Fick's law.[26–28] The values of D_{app}, obtained from the slopes of such linear plots, are shown in Fig. 7 and Table 1. Further, the kinetic parameters (i.e., k° and α) of the heterogeneous electron-transfer reaction were estimated from the conventional analysis of the rising part of each normal pulse voltammogram.[26,27,29] Figure 6 shows the modified log-plots of $\ln(x[\{1.75+x^2(1+\exp(\xi))^2\}/\{1-x(1+\exp(\xi))\}]^{1/2})$ vs. E for each voltammogram shown in Fig. 5, where x is the ratio of the current at potential E to the limiting

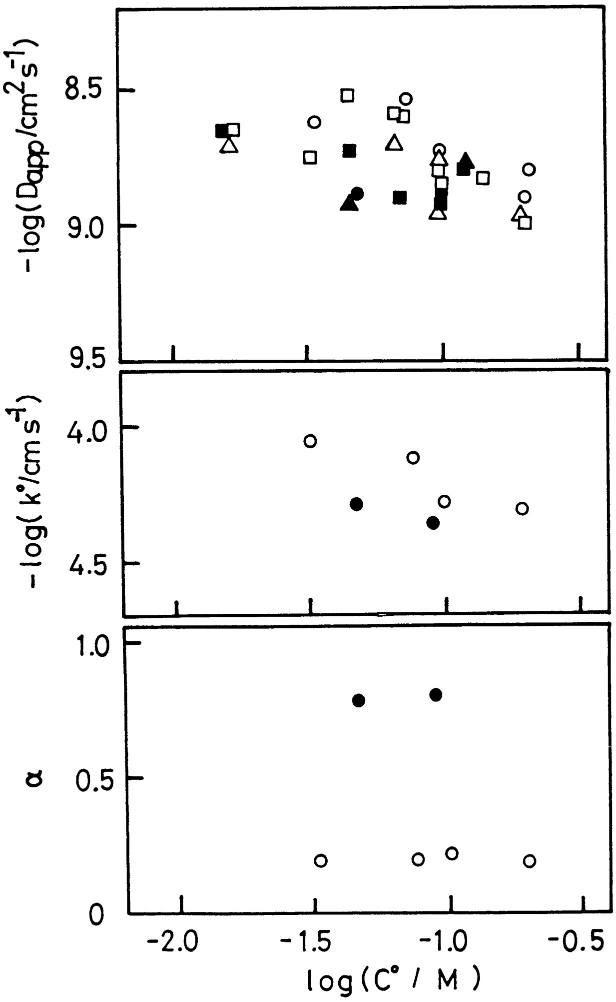

Fig. 7. Dependences of D_{app}, k°, and α on C°. Thickness of CPFP film: 1.0×10^{-4} cm. Supporting electrolyte: 0.2 M $CF_3COONa+CF_3COOH$ (pH 1.0). C° denotes the volume concentration of $[Fe(CN)_6]^{3-}$ (or $[Fe(CN)_6]^{4-}$) complex confined in CPFP film. The data shown by squares, triangles, and circles were obtained by PSCA, PSCC, and NPV, respectively. Solid and open symbols correspond to the anodic and cathodic processes, respectively.

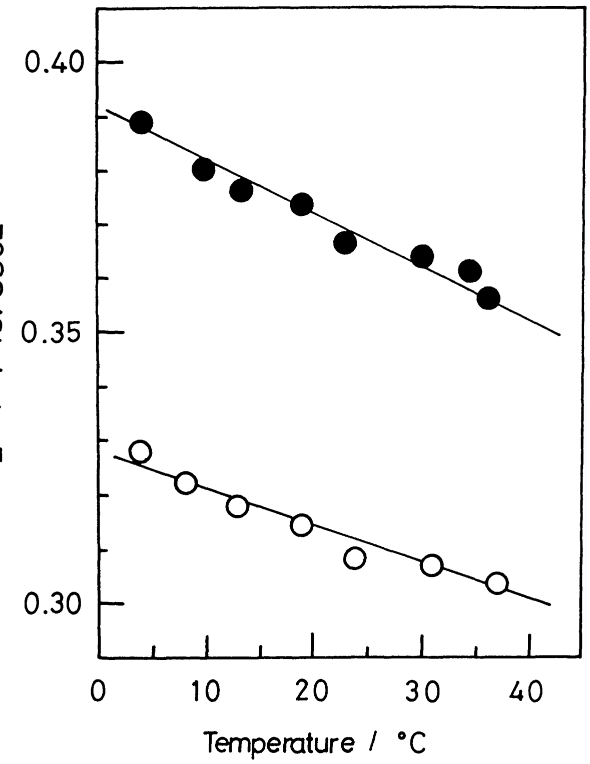

Fig. 8. Temperature dependences of formal potential ($E^{\circ\prime}$) of $[Fe(CN)_6]^{4-/3-}$ redox couple confined in the CPFP film and dissolved in 0.2 M CF_3COONa solution. Solution composition: 0.2 M $CF_3COONa+CF_3COOH$ (pH 1.0) $+1.0\times10^{-5}$ M $[Fe(CN)_6]^{3-}$. Thickness of CPFP film: 1.0×10^{-4} cm, (●) at bare BPG electrode, (○) at CPFP film-coated electrode.

diffusion current expressed by the Cottrell equation[26,27,29] and ξ is the dimensionless parameter expressed as $\{(nF/RT)(E-E^{\mathrm{r}}_{1/2})\}$ ($E^{\mathrm{r}}_{1/2}$: the reversible half-wave potential, n: the number of electrons involved in the heterogeneous electron-transfer reaction, F: the Faraday constant, R: the gas constant, T: the absolute temperature). The plots gave the straight lines with the almost same slope at different sampling times. The transfer coefficient (α) was determined from the slopes of the plots in Fig. 6, and the standard rate constant (k°) was determined from the difference between the reversible half-wave potential ($E^{\mathrm{r}}_{1/2}$) and the intercept potential (E^*) on the potential axis.[29] The obtained values of k° and α are shown in Fig. 7 and Table 1.

Figure 8 shows the temperature (T) dependence of the formal potential ($E^{\circ\prime}$) for the $[Fe(CN)_6]^{4-/3-}$ couple confined in the CPFP film and dissolved in solution. The linear relationships between $E^{\circ\prime}$ and T were obtained and thus the reaction entropy differences ($\Delta S^\circ_{\mathrm{rc}}$) for the couple were estimated by using the equation:[31,32]

$$\Delta S^\circ_{\mathrm{rc}} = S^\circ_{\mathrm{red}} - S^\circ_{\mathrm{ox}} = F\left(\frac{\mathrm{d}E^{\circ\prime}}{\mathrm{d}T}\right) \qquad (1)$$

where S°_{red} and S°_{ox} are absolute ionic entropies of the reduced and oxidized halves of the redox couple and F is the Faraday constant. The $\Delta S^\circ_{\mathrm{rc}}$ values were estimated to be -24 ± 2 and -14 ± 2 cal mol^{-1} K^{-1} for the bulk solution (0.2 M $CF_3COONa+CF_3COOH$, pH 1.0) and the CPFP film, respectively.

Discussion

Figure 7 shows dependence of D_{app} on C°. When C° was increased from 0.01 to 0.2 M, D_{app} slightly decreased from 2.3×10^{-9} cm^2 s^{-1} to 1.2×10^{-9} cm^2 s^{-1}. As shown in Fig. 1, the structure of CPFP consists of the hydrophobic perfluorocarbon chain and ether-bond part and the hydrophilic quaternary ammonium sites, and the former occupies most of the structure. From this fact, it is assumed that the CPFP film as well as Nafion film[6,10,30] may have the domain structure which consists of the hydrophobic and hydrophilic parts in a solvent-swollen state, and that three-dimensional micro channels of the quaternary ammonium ion sites may exist within the CPFP film. Therefore, $[Fe(CN)_6]^{3-}$ (or $[Fe(CN)_6]^{4-}$) may diffuse within such channels with an electrostatic interaction with positively charged sites of the CPFP film and a hydrophobic interaction with the hydrophobic domain.[10,12,30] The fact that D_{app} slightly decreased with an increase in C° may be explained by an electrostatic cross-linking[1-5,7,10,11,14,15,22-27,33-39] of the polyelectrolyte coatings occurring when the multiply charged electroactive species are incorporated into organic polyelectrolyte coatings having the opposite charge, because the electrostatic cross-linking of the film hinders the physical diffusion of electroactive species itself and the motion of counterions associated with the redox reaction, which occurs to keep a charge neutrality.

If an electrostatic cross-linking which is often observed in a well-swollen film (e.g., $PVPH^+$ film) occurs, it could be expected that D_{app} largely decreases with an increase in C°.[26,38,39] However, in the case of the CPFP film, the dependence of D_{app} on C° is small. The CPFP film contains a far more hydrophobic domain compared to the $PVPH^+$ film. The distance between the positively charged sites was calculated to be 3—8 and 19—23 Å for the $PVPH^+$ film and the CPFP film, respectively by assuming a simple cubic lattice model for the statistical distribution of ammonium or pyridinium sites in these films. Therefore, the smaller effect of the electrostatic cross-linking in the CPFP film compared to the $PVPH^+$ film can be ascribed to the lower degree of swelling of this film, as supported by the experimental result that the thickness of a given film under the wet state is almost the same as that under the dry state.

The C° dependence of D_{app} may also be thought to reflect a single-file diffusion effect,[10,11,22,40] because $[Fe(CN)_6]^{4-}$ (or $[Fe(CN)_6]^{3-}$) ions which must move between more or less fixed sites within the CPFP matrix are considered to have their rate of motion limited by the decreasing availability of sites as C° increases.

In Fig. 7 are also shown the dependences of k° and α on C°. The dependence of k° on C° is similar to that of D_{app} on C°, and k° slightly decreases when C° is increased. In contrast, α is almost independent of C°, and α values of anodic and cathodic processes (α_a and α_c) are ca. 0.80 and ca. 0.20, respectively. In addition, the sum of α_a and α_c is ca. 1.0, indicating that the anodic and cathodic reactions occur by way of the same activated state.[44]

The values of D_{app}, k°, and α_c obtained for the CPFP-$[Fe(CN)_6]^{3-}$ system are compared with those obtained previously for $PVPH^+$-$[Fe(CN)_6]^{3-}$ system[26] and PDMA-$[Fe(CN)_6]^{3-}$ system[27] (Table 1). At almost the same concentration of $[Fe(CN)_6]^{3-}$ in the films, the values of D_{app} and k° decrease in the following order; $PVPH^+$ film system>PDMA film system>CPFP film system. For example, when C° is $(1.0-1.2)\times 10^{-1}$ M, the D_{app} for the CPFP film is about 1/3 and 1/13 of those for the PDMA and $PVPH^+$ films,[26,27] respectively. This may be ascribed to a different extent of the electrostatic cross-linking of these films by $[Fe(CN)_6]^{3-}$ (and $[Fe(CN)_6]^{4-}$) ions which is considered to originate from their different morphologies in the solvent-swollen states. The α_c value for the CPFP film system is ca. 0.2 and is smaller than those (0.30) for the $PVPH^+$ film and PDMA film systems.[26,27] Such different α_c values for different film systems may reflect the different reaction positions of $[Fe(CN)_6]^{4-/3-}$ complex (e.g., with respect to the outer Helmholtz plane) in the transition state of the electron-transfer reaction and/or the existence of the potential-independent chemical reaction preceeding the electron-transfer reaction proper.[14,41–44]

The reaction entropy ΔS°_{rc} is an important parameter in considering the factors influencing the kinetics of electron-transfer process, since it provides a sensitive monitor of the changes in solvent polarization that are necessary in order for electron transfer to occur. The negative value (-24 ± 2 cal mol^{-1} K^{-1}) was obtained for the $[Fe(CN)_6]^{4-/3-}$ couple dissolved in 0.2 M $CF_3COONa+CF_3COOH$ solution (pH 1.0) in qualitative agreement with the expectation from an electrostatic treatment such as the Born model.[31,32] Assuming that the equivalent radii of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are 2 and 2.5 Å, respectively, ΔS°_{rc} is roughly estimated to be -19 cal mol^{-1} K^{-1}.[32] In the case of the $[Fe(CN)_6]^{4-/3-}$ couple confined in the CPFP film, the negative ΔS°_{rc} (-14 ± 2 cal mol^{-1} K^{-1}) was also obtained, but its value is more positive compared to that for the solution-phase $[Fe(CN)_6]^{4-/3-}$ couple. This fact suggests that the degree of the entropy in the oxidized form is smaller in the CPFP film than in the bulk solution and/or the degree of the entropy in the reduced form is larger in the film than in the solution. In other words, $[Fe(CN)_6]^{3-}$ (or $[Fe(CN)_6]^{4-}$) ions seem to interact more strongly (or weakly) with their surroundings within the CPFP film matrix than in the solution.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 01470064 from the Ministry of Education, Science and Culture. The authors express their appreciations to Tosoh Co., Ltd. for providing CPFP membranes.

References

1) N. Oyama and F. C. Anson, *J. Electrochem. Soc.*, **127**, 247 (1980).
2) N. Oyama, T. Shimomura, K. Shigehara, and F. C. Anson, *J. Electroanal. Chem.*, **112**, 271 (1980).
3) F. C. Anson, J. M. Savéant, and K. Shigehara, *J. Am. Chem. Soc.*, **105**, 1096 (1983).
4) I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **102**, 6642 (1980).
5) Y. M. Tsou and F. C. Anson, *J. Electrochem. Soc.*, **131**, 595 (1984).
6) H. L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1880 (1981).
7) H. S. White, J. Leddy, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4811 (1982).
8) T. P. Henning, H. S. White, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 5862 (1982).
9) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **104**, 4824 (1982).
10) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **105**, 685 (1983).
11) Y. M. Tsou and F. C. Anson, *J. Phys. Chem.*, **89**, 3818 (1985).
12) C. R. Martin and K. A. Dollard, *J. Electroanal. Chem.*, **159**, 127 (1983).
13) N. Oyama, T. Ohsaka, K. Sato, and H. Yamamoto, *Anal. Chem.*, **55**, 1431 (1983).
14) T. Ohsaka, H. Yamamoto, M. Kaneko, A. Yamada, M. Nakamura, S. Nakamura, and N. Oyama, *Bull. Chem. Soc. Jpn.*, **57**, 1844 (1984).
15) T. Ohsaka, N. Oyama, K. Sato, and H. Matsuda, *J. Electrochem. Soc.*, **132**, 1871 (1985).
16) I. Rubinstein, *J. Electroanal. Chem.*, **188**, 227 (1985).
17) C. M. Elliott and J. G. Redepenning, *J. Electroanal. Chem.*, **181**, 137 (1984).
18) Z. Lu and S. Dong, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2979 (1988).
19) D. W. DeWulf and A. J. Bard, *J. Electrochem. Soc.*, **135**, 1977 (1988).
20) Z. Ogumi, T. Mizoe, and Z. Takehara, *Bull. Chem. Soc. Jpn.*, **61**, 4183 (1988).
21) K. Uosaki, J. Wang, and H. Kita, *J. Electroanal. Chem.*, **273**, 275 (1989).
22) N. Oyama, T. Ohsaka, T. Ushirogouchi, S. Sanpei, and S. Nakamura, *Bull. Chem. Soc. Jpn.*, **61**, 3103 (1988).
23) N. Oyama, T. Ohsaka, and T. Okajima, *Anal. Chem.*, **54**, 979 (1986).
24) T. Ohsaka, Y. Takahira, O. Hatozaki, and N. Oyama, *Bull. Chem. Soc. Jpn.*, **62**, 1023 (1989).
25) T. Ohsaka, Y. Takahira, S. Nakamura, and N. Oyama,

J. Electroanal. Chem., **247**, 339 (1988).

26) N. Oyama, T. Ohsaka, M. Kaneko, K. Sato, and H. Matsuda, *J. Am. Chem. Soc.*, **105**, 6003 (1983).

27) T. Ohsaka, T. Okajima, and N. Oyama, *J. Electroanal. Chem.*, **215**, 191 (1986).

28) A. J. Bard and L. Faulkner, "Electrochemical Methods," Wiley, New York, N.Y. (1985), Chap. 5.

29) H. Matsuda, *Bull. Chem. Soc. Jpn.*, **53**, 3439 (1980).

30) I. Rubinstein, J. Rishpon, and S. Gottesfeld, *J. Electrochem. Soc.*, **133**, 729 (1986).

31) E. L. Yee, R. J. Çave, K. L. Guyer, P. D. Tyma, and M. J. Weaver, *J. Am. Chem. Soc.*, **101**, 1113 (1979).

32) T. Ohsaka, H. Yamamoto, and N. Oyama, *J. Phys. Chem.*, **91**, 3775 (1987).

33) P. Daum, J. R. Lenhard, D. Rolison, and R. W. Murray, *J. Am. Chem. Soc.*, **102**, 4649 (1980).

34) J. Facci and R. W. Murray, *J. Electroanal. Chem.*, **152**, 97 (1983).

35) N. Oyama and F. C. Anson, *J. Electrochem. Soc.*, **127**, 640 (1980).

36) N. Oyama and F. C. Anson, *Anal. Chem.*, **52**, 1192 (1980).

37) F. C. Anson, T. Ohsaka, and J. M. Saveant, *J. Phys. Chem.*, **87**, 640 (1983).

38) N. Oyama, S. Yamaguchi, Y. Nishiki, K. Tokuda, H. Matsuda, and F. C. Anson, *J. Electroanal. Chem.*, **139**, 371 (1982).

39) K. Sato, S. Yamaguchi, H. Matsuda, T. Ohsaka, and N. Oyama, *Bull. Chem. Soc. Jpn.*, **56**, 2004 (1983).

40) K. Heckmann, "Biomembranes," ed by A. L. Manson, Plenum Press, New York (1972), Vol. 3, p. 127.

41) N. Oyama, T. Ohsaka, and T. Ushirogouchi, *J. Phys. Chem.*, **88**, 5274 (1984).

42) M. J. Weaver, *J. Phys. Chem.*, **83**, 1748 (1979).

43) W. R. Fawcett, *J. Electroanal. Chem.*, **22**, 19 (1969).

44) R. Tamamushi, "Denki Kagaku," Tokyo Kagaku Dojin, Tokyo (1967), Chap. 5.