Effect of Functional Group of Ferrocene Redox Substance on the Transport Properties of Newly Designed Ion Exchange Membrane Prepared from Polymer Gel

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ABSTRACT: A different newly designed cationic exchange polymer membrane and anionic exchange polymer membrane were introduced, and also the transport properties of these polymeric membranes were investigated in this study. The transport properties of these polymer membranes in contact with ferrocene redox derivatives were estimated by using electrochemical techniques such as cyclicvoltammetry, chronopotentiometry, and chronoamperometry techniques, respectively. The used ferrocene redox substances, which have different functional groups, were (Ferrocenylmethyl) trimethylamonium iodide, FcMA, Ferrocenedimethanol, FcDM, and Ferrocene carboxylic acid, FcCA. It indicated that the performance of a membrane depended on the content of polymer gel, anionic exchange polymer site (20 wt % and 50 wt %) or cationic polymer exchange site (20 wt % and 50 wt %), and the efficiency of the functional groups of cationic and anionic exchange polymer site as well. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1678–1685, 2008

Key words: AEM membrane; CEM membranes; ferrocene redox derivatives; CV; CP; CA

INTRODUCTION

Ion exchange membranes find application in diverse processes such as electrodialysis for the desalination of brackish water, the production of table salt, recovery of valuable metals from the effluents of metal-plating industry, recovery of acid–base from the spent leaching solution, and for other purposes.[1] Therefore, they are useful in energy saving and pollution control. The development of ion exchange membrane of high chemical, thermal and mechanical stabilities, which meet growing demands of aforementioned process, is of great importance. So far the works concerning the charged mosaic membranes have been reported to elucidate the mechanism of ion transport within membranes.[2–10] However, its interior are too complex to understand the function of mosaic polymer membranes clearly because the charged mosaic polymer membrane consist of two kinds of fixed charges, positive and negative polymeric exchange sites, and membrane matrix material. Then, to understand the performance of charged mosaic polymer membrane, the different charged parts such as cationic and anionic exchange polymeric sites are separated. Here in this study, two different ion exchange polymeric materials of charged mosaic membrane are prepared separately,[11] and the contribution of each polymeric site (cationic or anionic) to the membrane phenomena is separately examined. Also the material transports of the respective cationic and anionic exchange polymeric layers are examined independently. Thus, it is interesting to study the fundamental electrochemical properties of cationic and anionic exchange polymeric layers coated on Au electrode and its dependence on the contents of polymer gel materials as well.

Authors have also investigated the electrochemical behavior of conventional membrane like Nafion and Nafion blended with Collodion membrane caused by different redox substances.[12] The characteristics of these membranes have been examined in terms of membrane potential, salt flux, and water content. As a whole, the blended membrane indicated membrane performance comparable with the commercial ion-exchange membrane (Nafion).[13–15] The aim of this study is to introduce two newly designed polymer gel anionic exchange polymer membrane (AEM) and cationic exchange polymer membrane (CEM) incorporated with Nitrile-butadiene rubber matrix (H-NBR) as an alternative ion exchange membrane to be used in industry like electrodialysis or salt electrolysis. H-NBR was selected to use as a matrix because

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(a)

	(Ferrocenylmethyl)trimethyl-ammonium Iodide	Ferrocene-Dimethanol	Ferrocene Carboxylic acid
Type	FcMA	FcDM	FcCA
R_1	$CH_2 \ N^- \ (CH_3)_3$	CH_2OH	$COO \ H^+$
R_2	H	CH_2OH	H

(b)

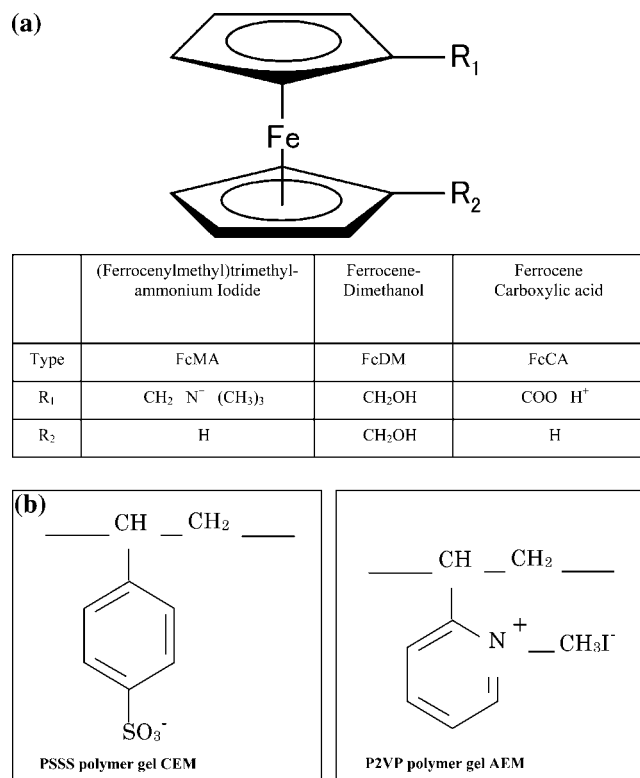
PSSS polymer gel CEM   P2VP polymer gel AEM

Figure 1 Schematic diagram of the chemical structure of Ferrocene redox substance (a), and the chemical structure of anionic and cationic exchange polymer gel membranes (b).

the polymer gel was smoothly dispersed into H-NBR matrix without segregation and the swelling was not observed during the experiment because of hydrophobic nature of H-NBR. The elucidation of transport properties in terms of diffusion coefficient of these membranes in contact with redox substances, which represent the different cation, anion, and neutral species were also investigated.

EXPERIMENTAL

Materials

Supporting electrolyte, (0.1M KCl) was used to enhance the electricity of the system. The redox substances, (Ferrocenylmethyl) trimethylammonium Iodide (FcMA), Ferrocenedimethanol (FcDM), and Ferrocene carboxylic acid (FcCA) were obtained from Aldrich. Twice distilled water was used to make the aqueous electrolyte solutions. The chemical structure of Ferrocene derivatives were shown in Figure 1(a).

Preparation of ionic exchange membrane

Synthesis of microsphere polymer gels (polystyrene sodium sulfonate, PSSS and poly (2-vinylpyridine),

P2VP), which are components of cationic and anionic exchange membranes, were described in elsewhere.[8,11,16] The cationic exchange polymer film, PSSS was mixed with hydrogenated acrylonitrile butadiene rubber (H-NBR) with the ratios of 50 : 50 and 20 : 80 wt %. Also, the anionic exchange polymer film, P2VP mixed with the H-NBR with ratios of 50 : 50 and 20 : 80 in wt %, respectively. Then, the mixed solutions were coated onto the surface of Au electrodes. The cationic films were named cationic exchange polymer membrane (CEM). The modified Au-electrodes with anionic films were quaternized by methyl iodide and the positive charges were fixed to them.[11] The film was named anionic exchange polymer membrane (AEM). The compositions of mixed solutions for coating are shown in Table I.

The film thicknesses of the polymer films were about 100–250 μm as average value. The size of spherical particles was 200–300 nm and the charge densities of polymer gel were 4.0 meq/g for PSSS and 8.6 meq for P4VP and P2VP according to literatures.[8,16] The Au-electrodes coated with polymer films of AEM and CEM, were soaked in 1 mM of redox substances containing 0.1M KCl to equilibrate before measurement. The chemical structure of ion exchange polymer membrane CEM and AEM are shown in Figure 1(b).

Experimental apparatus

The used experimental cell for diffusion coefficient of redox substances measurements was shown elsewhere.[11,12] It consists of four electrodes, which was connected to potentiostat/galvanostat (P/G Stat), (Hokuto Denko), model HA-151, X-Y-t recorder (Riken Denshi), model F35c, and Function generator (Hokuto Denk), model HB-111. The current density was determined from the WE (Au-working electrode) by dividing the current by its area. The potential imposed on WE was measured against a reference electrode, RE (Ag/AgCl/3M NaCl). To measure the potential accurately a counter electrode (CE) of a Pt wire was used. It is known in electrochemistry the use of four electrode system[17,18] is recommended to

TABLE I
Compositions of Cation and Anion Polymer Exchange Membranes

Membrane	Polymer gel/content (wt %)	Membrane matrix content (wt %)
1	PSSS/CEM-50	50
2	PSSS/CEM-20	80
3	P4VP/AEM-20	80
4	P2VP/AEM-50	50
5	P2VP/AEM-20	80

get exact values of peak current, I_p, when the resistance of system is high. The current-potential plot known as cyclicvoltammetry (CV), the current-time plot known as chronoamperometry (CA), and potential-time plot known as chronopotentiometry (CP) were obtained. The diffusion coefficients of redox substances were measured by the CV and CP according to the conventional methods.[12,18,19] Also the concentrations of redox substances in the CEM and AEM were measured by CA. However, the concentration values of the redox substances in the AEM were approximately detected nearly to 0.

Cyclicvoltammetry

To investigate the diffusion behavior of redox substances inside the membranes qualitatively, CV was employed. A 1 mM solution of redox substances was prepared in the presence of KCl (0.1M KCl), as support electrolyte. The Au-electrode modified with polymer film was dipped in 1 mM redox solution, and then equilibrated before measurements. The potential imposed on electrode was varied from 0.2–0.65 V potential. The potential was scanned in triangular wave form, and then current-potential plots were recorded. The CV of bare Au-electrode was carried out at a very slow scan rate (0.5 mV/s.) to obtain 2.6 µA peak current. To estimate the exact surface value of Au electrode, slow scan is preferred to avoid experimental inaccuracy. The following eq. (1) gives S the electrode area

$$I_p = 2.69 \times 10^5 \ n^{2/3} \ S \ D^{1/2} \ v^{1/2} \ C \qquad (1)$$

where I_p is peak current (A), n is the electron transfer number of redox substance, v is scan rate, i.e., mV/s, and C is concentration of redox substance (mol/cm^3). Using the well-known diffusion coefficient, D of [Fe(CN)$_6$]$^{4-}$ = 1.18×10^{-5} cm^2/s, the electrode area was calculated to be 0.0248 cm^2.

Chronopotentiometry measurements

Chronopotentiometry is an electrochemical characterization method that measures the electric potential response of a system to an imposed current. Compared with other dynamic measurements methods, i.e. CV, it allows a direct access to the voltage contributions in different states of the solution-membrane system. Compared with steady state voltage or current sweeps, more information is obtained by CP because the dynamic voltage response in time can be analyzed. The transition time τ was determined from chronopotentiogram, that is, τ was determined from the intersection between abrupt rising lines of CP at different current densities (µA). The relation between I and τ in CP is called a Sand equation.[17]
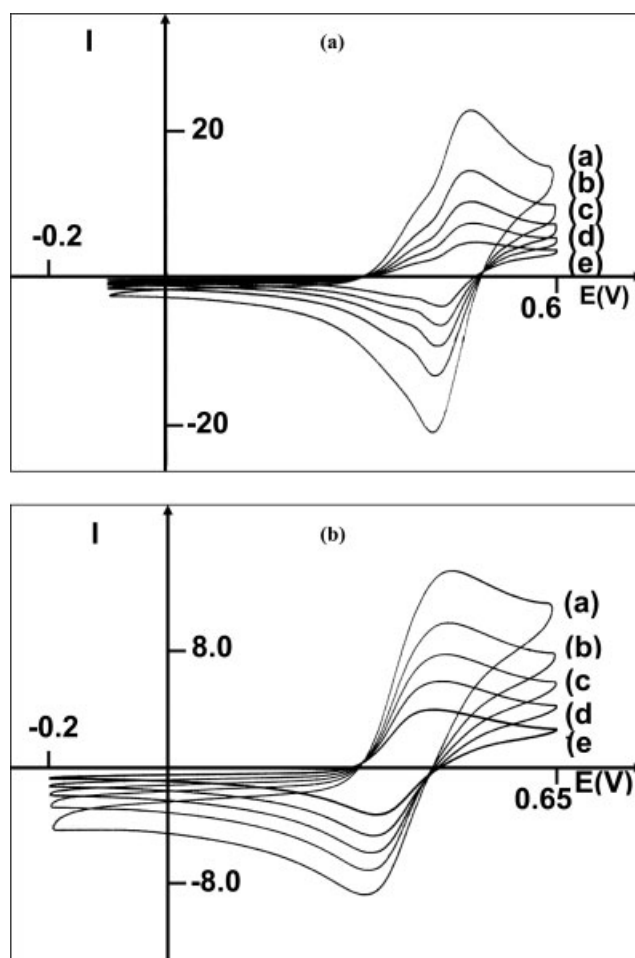
Figure 2 Typical cyclicvoltammograms of (a) bare Au electrode (b) CEM/50 wt % polymer gel membranes coated onto Au electrode in contact with 1 mM FcMA in 0.1M KCl of (E: 0.2–0.65 V vs. Ag/AgCl) at scan speed, v: (a) 500, (b) 200, (c) 100, (d) 50, (e) 20 mV/s, respectively.

RESULTS AND DISCUSSION

Cyclicvoltammograms measurements

The typical plots of the cyclicvoltammograms of bare Au-electrode, and the Au-electrode modified with CEM, PSSS, (PSSS, CEM/50 wt %) in contact with 1 mM FcMA solution were shown in Figure 2(a,b), respectively. The difference between the cyclicvoltammograms of bare Au electrode [Fig. 2(a)] and CEM coated onto Au-electrode [Fig. 2(b)] indicated that the presence of FcMA species in the CEM membranes. One can note the shape and peak strength of cyclicvoltammograms depended strongly on the scan speed (V/s). The cyclicvoltammogram, CV of bare Au-electrode [Fig. 2(a)] showed a small shoulder. While the CV of cationic exchange polymeric membrane PSSS/50 wt % coated onto Au-electrode [Fig. 2(b)] showed no shoulder. The shoulder formation may be attributed to the superimposition of iodide ion that exist at the positive species FcMA and bare
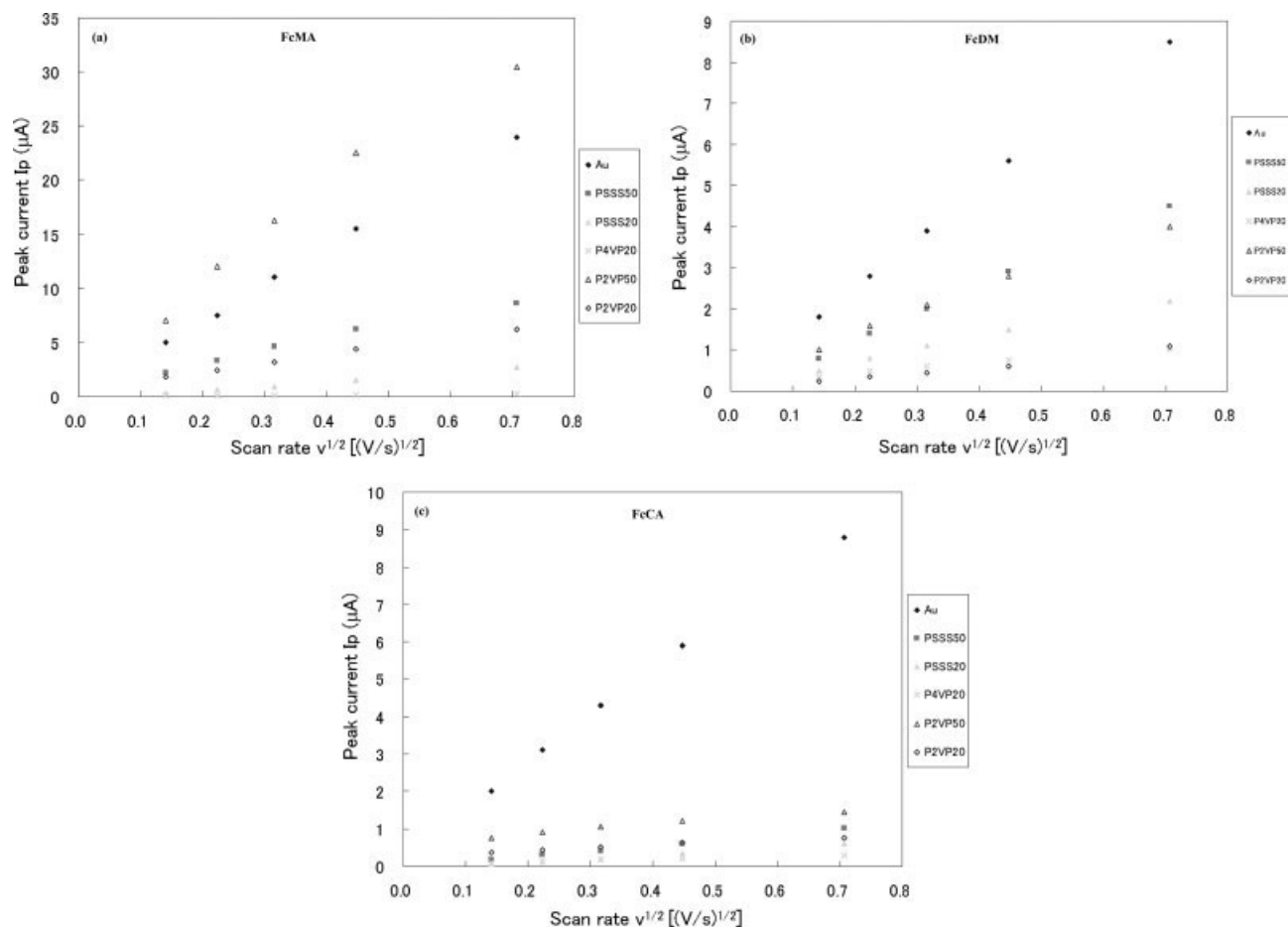
Figure 3 Relationships between peak current, I_p and square root of scan speed, $v^{1/2}$ for CEM and AEM polymer gel membrane in contact with 1 mM (a) FcMA, (b) FcDM, and (c) FcCA, respectively.

Au-electrode. On the other hand, the presence of SO_3^- group of the PSSS in the cationic exchange polymer membrane polymer film of CEM polymer forbids the approach of iodide ion of FcMA to Au-electrode, and formation of shoulder.

Diffusion coefficients of redox substances

To investigate the difference between the diffusion coefficients of the cationic sulfonate groups of PSSS polymer exchange membrane and the anionic N^+—CH_3Cl^- groups of P2VP polymer exchange membrane, the CV were discussed using eq. (1).

Figure 3(a–c) shows that the plots of peak current I_p vs. $v^{1/2}$ in the presence of 1 mM of FcMA, FcDM, and FcCA, respectively. The plots I_p vs. $v^{1/2}$ showed almost linear relationship. The values of the diffusion coefficients, D, were calculated from Figure 3(a–c) and provided in Table II. Table II indicates that the diffusion coefficients of FcMA, FcDM, and FcCA in the CEM (CEM/50 wt %) were higher than that of CEM/20 wt %, and AEM/20 wt %. All the diffusion coefficients values of the cationic and anionic polymer

films showed small values compared with that of bare Au electrode. It indicated that the diffusion coefficient values depended on the cationic or anionic exchange polymer site in the membrane, charge of redox substance, and the content of membrane matrix material, H-NBR. Table II shows that the diffusion coefficients of FcDM and FcCA in the anionic exchanger polymer membrane (P2VP) AEM/50 wt % were higher than that of CEM/20 wt % and AEM/20 wt % polymer membranes. But the diffusion coeffi-

TABLE II
Diffusion Coefficient ($\times$ 10^{-6} cm²/s) Obtained from CV For CEM and AEM in the Presence of Ferrocene Redox Derivatives

Reagent	FcMA	FcDM	FcCA
Charge	+	0	−
Au	3.4	3.2	3.3
PSSS/CEM-50	2.6	1.0	0.05
PSSS/CEM-20	0.2	0.2	0.02
P4VP/AEM-20	0	0.03	0.002
P2VP/AEM-50	0	0.5	0.1
P2VP/AEM-20	0	0.05	0.02

cient values of FcMA through AEM/20 and AEM/50 wt % polymer gel membranes were not detected, and were almost zero. These results explain that the interaction between SO_3^- groups of PSSS polymer inside the CEM membrane and positive charge of FcMA species enhances the diffusion of FcMA species. While the higher diffusion coefficient value of FcDM in the CEM/50 wt % species was attributed to the neutral charge of FcDM. Also, the hydrophobic property of FcDM facilitate the diffusion of FcDM through the membrane. The diffusion coefficient of negative species FcCA in the CEM/50 wt % polymer membrane showed low value compared with the diffusion coefficients values of positive and neutral charge of FcMA and FcDM, respectively. This indicated that the electrostatic repulsion between SO_3^- groups of PSSS in the CEM/50 wt % and negatively species FcCA occurred. The diffusion coefficients of positively charged FcMA in the anionic exchange polymer membranes, AEM/50 wt % and AEM/20 wt %, were not remarkably observed. This means that the repulsion force between positive charge of N^+—CH_3Cl group of anionic exchange polymer membrane, P2VP (AEM) and the positive charge of FcMA occurred. The interaction force between positive charge of N^+—CH_3Cl^- group of AEM and negative charge of FcCA facilitate the diffusion of FcCA in the AEM/50 wt %.

Reversibility

The typical CP of bare Au and Au-coated with CEM and AEM in contact with 1 mM FcMA were given in Figure 4(a–c), respectively. One can obtain the transition time, τ that gives electrochemically important information. The reversibility of CEM and AEM were discussed qualitatively based on the CP's results.

To discuss the reversibility of the Au-coated polymer membranes, CEM and AEM in quantitative way, the relation between the response potential, E, transition time, τ and time t was described in eq. (2).[17,18]

$$E = E_{\tau/4} + RT/nF \ln(\tau^{1/2} - t^{1/2})/t^{1/2} \quad (2)$$

Where $E_{\tau/4}$ is the quarter-wave potential; τ, transition potential; and t, time respectively.

The transition time, τ was obtained from the sharp rise up in CP curves and substituted into eq. (2). The linear relationship between E and $\ln(\tau^{1/2} - t^{1/2})/t^{1/2}$ was observed in Figure 5(a–c). This means that the electrochemical reactions on Au electrodes are almost reversible because the slope value was close to the ideal value, i.e. 59 mV. The slopes in Figure 5(a–c) were calculated and provided in Table III. Table III indicated that the cationic and anionic exchange polymer membranes behave in a reversible manner, if the slope values (RT/nF) were close to 58–60 mV. In the
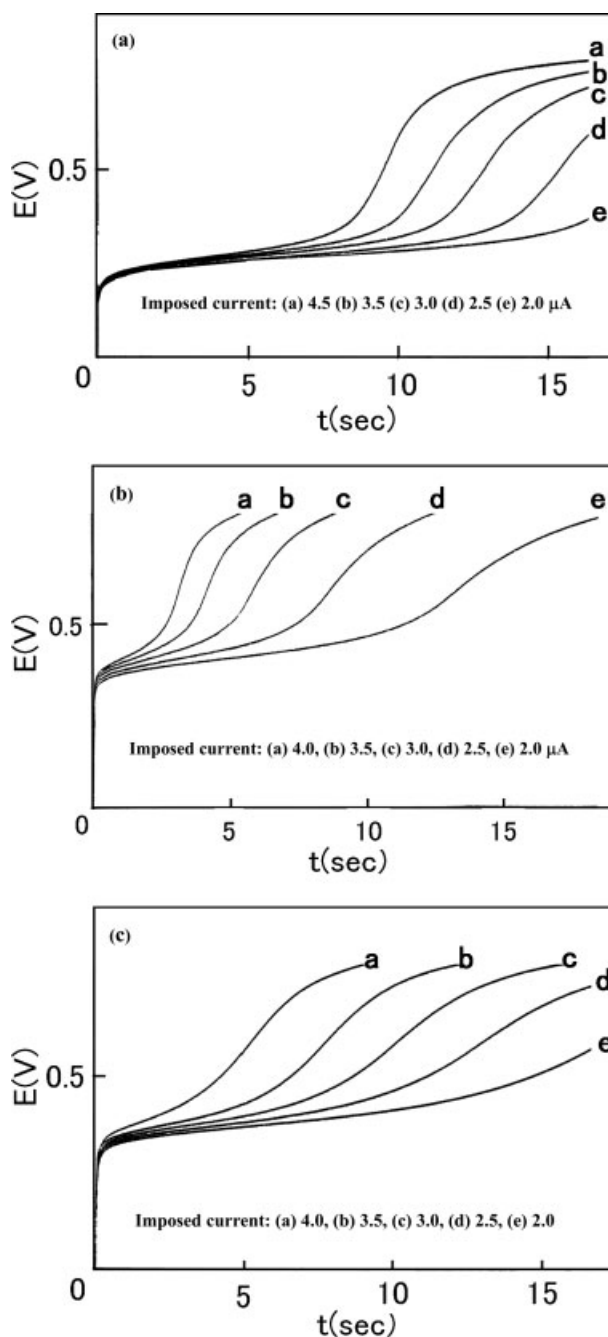
Figure 4 Chronopotentiograms of (a) bare-Au electrode, (b) CEM/50 wt % (c), and AEM/50 wt % polymer gel membranes coated onto Au electrode in contact with 1 mM FcMA at different imposed current.

case of FcMA, FcDM, and FcCA redox substances in contact with bare Au-electrode, the membrane behaves like reversible one. The neutral charged FcDM species penetrate easily through AEM and CEM polymer gel membrane because of its neutral charge made the value of n less than unity. Accordingly, the RT/nF value became larger than 59 mV, so the polymer membrane property deviated from reversibility.
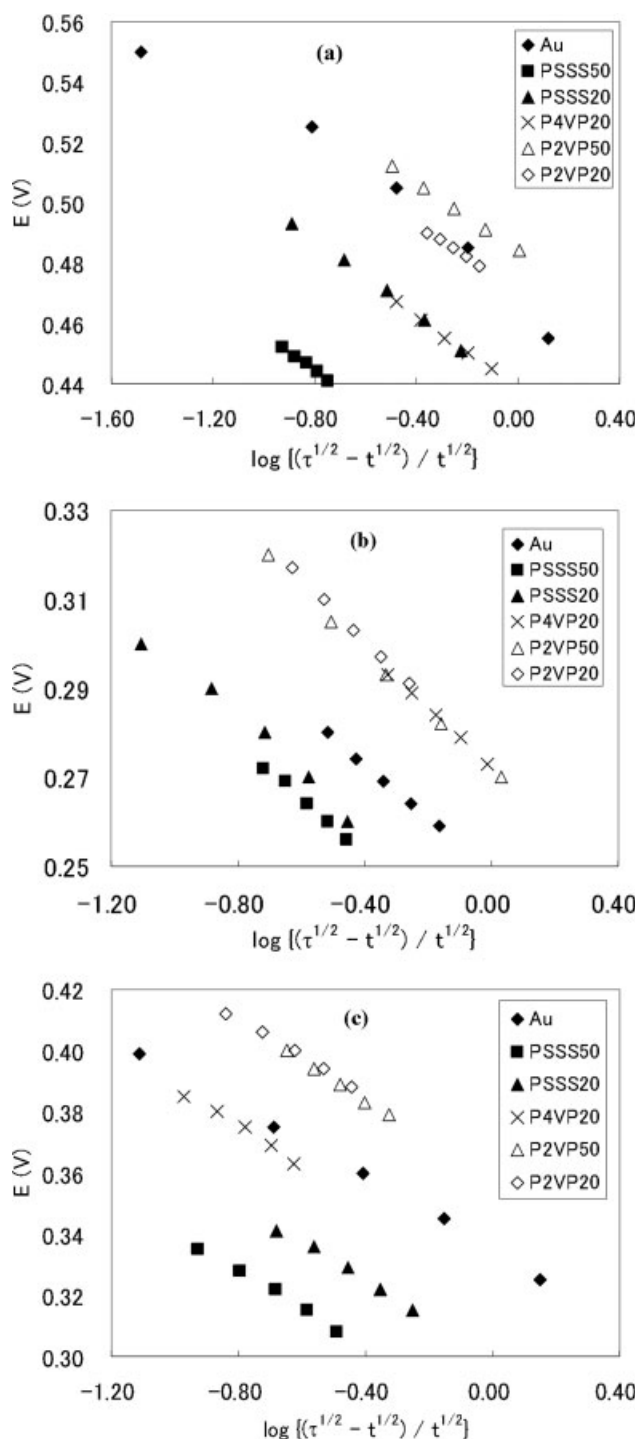
Figure 5 Potential, E vs. log $(\tau^{1/2} - t^{1/2})/t^{1/2}$ plots obtained from Chronopotentiograms in the presence of 1 mM (a) FcMA, (b) FcDM, and (c) FcCA, respectively.

Concentration of redox substances in polymer membranes

To estimate the concentrations of redox substance in polymer gel membrane, CA were used. The slope of I_P vs. $v^{1/2}$ was depended on supporting electrolyte concentration, KCl. The slope was also depended on the product of concentration and diffusion coeffi-

TABLE III
Potential Gradient (mV)

Reagent	FcMA	FcDM	FcCA
Charge	+	0	−
Au	59.3	59.3	58.5
PSSS/CEM-50	60.0	60.0	61.3
PSSS/AEM-20	61.8	63.7	60.2
P4VP/AEM-20	59.0	61.5	60.8
P2VP/AEM-50	56.1	58.6	60.0
P2VP/AEM-20	61.6	66.0	60.7

cient.[16–18] A $dI_p/dv^{1/2}$ is direct proportional to $D \times C$, where D is the diffusion coefficient and C is the concentration of the redox substances in the membrane. The obtained coulomb number, Q consists of the electrode reaction of redox substance, coulomb number of capacitive current, Q_c and background.[16,17] To determine the redox concentration in the membrane, the coulomb number of capacitive current and background current must be subtracted. The latter two values were determined by measuring CA in the solution containing KCl without redox substances. The concentration of redox substances were calculated from the following eq. (3)

$$C_{in} = Q/(F \times V_{memb}) \qquad (3)$$

Where F, the Faraday constant (C/mol), and V_{memb} (cm^3) the membrane volume which is obtained from the amount of the membrane substance. The concentration of redox substances in the CEM and AEM were calculated, and provided in Table IV. The concentrations of the positive charged FcMA redox substance in the AEM were approximately close to zero. Table IV shows that the concentration of positive charged species FcMA in the CEM/50 wt % polymer gel membrane was larger than that of CEM/20 wt % polymer gel membrane even though the ion exchange site (SO$_3^-$) was the same in both membranes. This may attributed to the large number of (SO$_3^-$) ion exchange sites in CEM/50 wt % compared with CEM/20 wt % made the diffusion of FcMA in the cationic exchange polymer membrane (CEM/50 wt %) larger than that of CEM/20 wt %. The higher concentration value of neutral species FcDM in the AEM/50 wt % compared with that of CEM/50 wt % polymer membrane was observed. The similar concentration

TABLE IV
Concentration in the Membrane(mM)

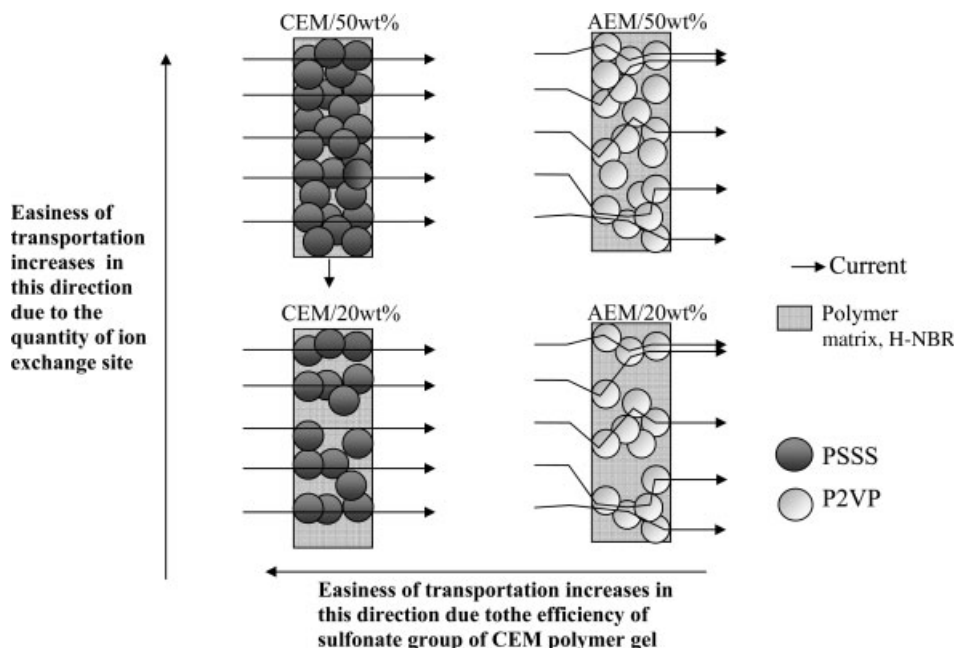| Reagent	FcMA	FcDM	FcCA
Charge	+	0	−
PSSS/CEM-50	1.5	0.3	0.3
PSSS/AEM-20	0.3	0.2	0.2
P4VP/AEM-20	0	0.2	0.1
P2VP/AEM-50	0	0.5	0.8
P2VP/AEM-20	0	0.2	0.1

Figure 6 Schematic representation of ionic transport behavior for cationic exchange polymer membrane, PSSS (CEM), and anionic exchange polymer membrane, P2VP (AEM) mixed with polymer matrix H-NBR.

value of FcDM in both CEM/20 wt %, and AEM/20 wt % polymer membranes was recorded. The higher concentration value of negatively charged FcCA in the AEM/50 wt % compared with that of CEM/50 wt % was monitored. This explains that the interaction force between N^+—CH_3Cl group of P2VP polymer and the negative charge of FcCA species led to the increase of FcCA concentration in the AEM (AEM/50 wt %).

Transport through membranes

To explain the transport behavior of redox substances inside the AEM and CEM polymer gel membranes, we represent CEM and AEM polymer gel membrane schematically in Figure 6. However, AEM and CEM contains different volume fractions from polymer gels with respect to membrane matrix, H-NBR, the ion exchange capacity, IEC of polymer gel membranes AEM and CEM are almost identical.[15] Figure 6 shows that the quantities of ion exchange site (the concentrations of the SO_3^- groups in PSSS polymer, i.e larger wt %) in the CEM membrane (50 wt %) were more than that of CEM polymer gel membrane (20 wt %). However, the quantities of ion exchange sites of SO_3^- groups of PSSS polymer in the CEM/50 wt %, and N^+—CH_3Cl— functional groups of P2VP polymer in the AEM/50 wt % are equal, i.e. same wt %, the higher values of diffusion coefficients of FcMA species and FcDM in the CEM/50 wt % polymer membrane compared with that of AEM/50 wt %, and CEM/20 wt % polymer membranes were observed. This explains that the SO_3^- groups of PSSS polymer in

the CEM membrane enhanced the transport properties of CEM polymer gel membrane compared with that of P2VP polymer in the AEM/50 wt % membrane. In contrast, the transport properties of polymer gel membrane AEM/50 in contact with negatively charged FcCA species increased with respect to CEM/50 and AEM/20. When the volume fraction of polymer gel becomes small with respect to H-NBR polymer matrix (e.g. 20 wt % AEM, and CEM/20 wt % cases), the diffusion of redox substance were suppressed by polymer matrix, H-NBR. In other words, the presence of SO_3^- groups in CEM polymer gel membrane increase its performance toward redox ions. It can be said that the transport properties and performance of polymer gel membranes depend on the content of polymer gel, i.e. anionic exchange polymer sites or cationic polymer exchange site, and the quantity of functional groups in the polymer, i.e. 50 wt %, and 20 wt %. So, the transport properties of CEM/50 wt % and CEM/20 wt % polymer gel membranes are increased when compared with AEM/50 wt % and AEM/20 wt % polymer gel membranes because of existence of SO_3^- ion exchange site of PSSS in CEM membrane.

CONCLUSION

The CV, CP, and CA techniques were used to calculate the diffusion coefficients and concentration of FcMA, FcDM, and FcCA in the two newly designed polymeric gel membrane CEM and AEM. It was found that the diffusion coefficients of FcMA and FcDM in the presence of CEM (CEM/50 wt %)

showed higher values than that of anionic exchange membrane AEM/50 and AEM/20 wt % values. These results were attributed to the interaction between SO_3^- groups of the catioic exchange membrane AEM/50 and AEM/20 wt % values. These results were attributed to the interaction between SO_3^- groups of the cationic polymer gel in CEM membrane and positively charged species FcMA happened. The diffusion coefficients of positively charged FcMA in the presence of anionic exchange membrane (AEM/50 and AEM/20 wt %) were not remarkably observed. This explains that the repulsion force between positively charged N^+—CH_3Cl group of AEM and the positively charged FcMA species occurred. This means that the diffusion of FcMA species was suppressed. The concentration of redox substances in the CEM and AEM were calculated by using chronocoulometry. The concentrations of the redox substance in the AEM were approximately close to zero. The concentrations of FcMA and FcDM within CEM polymer membrane showed higher values than that of AEM polymer membrane values. While, the concentration of negatively charged FcCA within AEM/50 wt % showed higher values than that of CEM/50 wt % and CEM/20 wt % polymer gel membranes values. As a whole in this study, the CEM/50, and CEM/20 wt % polymer gel indicated that the membrane performance are comparable with those of conventional ion exchange polymer membrane of Nafion, and Nafion blended with Collodion.[12] Also, it can be proposed that the polymer gel membranes CEM compared with AEM one, are recommended as an alternative ion exchange polymer membrane.

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