Manifestation of Electrolyte Ion Size Effect on Electrochemical Behavior of Poly(ferrocenylsilane) Films

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ABSTRACT: The influences of supporting electrolyte ion size on the cyclic voltammetric (CV) behavior of high-molecular-weight poly(ferrocenylsilane) films in organic solvents were investigated. Three supporting electrolytes with various ion sizes were tested. Electrolyte anions, as counter ions, take part in charge neutrality in the films, so that the size of anion affects the CV behavior of the films remarkably. The large anions are difficult to penetrate into the films, the resistances of the large ions migrating in films are more, the rates of the electroactive species diffusing in the films are slow, and the CV behavior of the polymer films exhibit irreversible features. The electrolyte cations do not take part in charge neutrality in the films, so that the size of cation does not actually affect the CV behavior of the films. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 515–523, 2006

Key words: poly(ferrocenylsilane); polyferrocenyldimethylsilane; films; ion size effect; electrochemical active polymer; electrochemistry; cyclic voltammetry

INTRODUCTION

The high-molecular-weight organometallic polymers which contain ferrocene in main chain are a kind of novel functional polymer material.[1–3] A great deal of research attention has been focused on these novel materials because of their electric, optical, and magnetic activities in the past decade. They have extensive potential applications; can be used as electrochemical sensors,[4,5] electrochromic and thermochromic material,[6] protective charge dissipation coating,[7] and magnetic polymer and magnetic ceramic precursors.[8–11] Therefore, the electrochemical studies on this kind of polymer are an important foundation to application. In previous articles,[12–14] we have reported that various supporting electrolytes, electrolyte concentration, temperature, film thickness, and various organic solvents have noticeable influences on the cyclic voltammetric (CV) behavior of poly(ferrocenylsilane) (PFS) films in aqueous and various organic solutions.

The electrochemical studies on the PFS films have demonstrated that electrolyte ions penetrating into the films plays an important role in electrochemical processes. The oxidation products of the PFS, that is, poly(ferrocenium) cations, need the electrolyte anions as counter ions, to migrate into and out of the films for charge neutrality. Therefore, in organic solvents, the solvent-swelling of the polymer films and the dissociation of electrolytes, which decide the resistances of electrolyte ions penetrating into the films and the rates of mass transfer in the films, are major influencing factors on the electrochemical processes. Previous studies[14] have found that in some suitable polar organic solvents the PFS films are swollen properly, the electrolytes dissociate completely, the electrolyte ions penetrate into and out of the films easily, the resistances of mass transfer and diffusion in the films are small, the active centers in the polymer interact sufficiently, the charge exchange on electrode interface is efficient, and the CV waves of the PFS exhibit distinguishable double peaks and reversible CV process features. When there is a decrease in the polarity of organic solvents, the solvent-swelling of the PFS films, the dissociation of the electrolyte, the rates of penetration, diffusion of the electrolytes, and the efficiency of charge exchange on electrode interface are reduced, and the CV waves of the PFS film exhibit irreversible process features. On the basis of same mechanism of electrochemical process, we can estimate that the ion size of electrolyte should have distinguishable influence on the electrochemical behavior of the PFS films. In this article, we report the CV behavior of the PFS films in six organic solu-
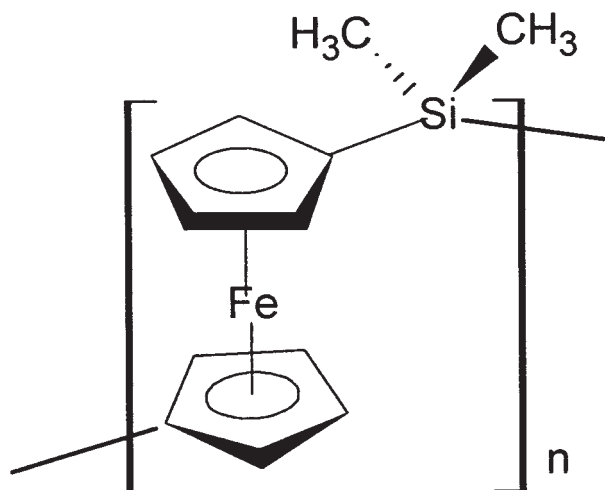
Scheme 1. Structure of PFDMS.

tions, and three supporting electrolytes with different size ions are compared.

EXPERIMENTAL

Structure of PFS

The investigated PFS was polyferrocenyldimethylsilane (PFDMS), and its structure is shown in Scheme 1. The synthesis and characterization of the PFDMS have been reported in previous article.[12] Its molecular weight and molecular weight fraction were $M_w = 1.14 \times 10^5$ g mol^{-1}, $M_n = 2.51 \times 10^4$ g mol^{-1}, and PDI $(M_w/M_n) = 4.54$.

Instruments and reagents

The CV measurements were carried out with a CHI-630A electrochemical analyzer (CH Instruments, Austin, Texas), in an undivided three-electrode cell. All electrodes were from CH Instruments. A platinum wire counter electrode and an Ag/AgCl (3M KCl) reference electrode were used. The working electrode was a Teflon-shrouded and polymer films coated glassy carbon disk electrode (3 mm diameter, 0.071 cm^2 geometric area). The electrode potentials in this article were relative to the Ag/AgCl (3M KCl) reference electrode. The glass carbon electrode surface was hand-polished to a mirror finish before using with 0.05 μm Al$_2$O$_3$ paste on felt, washed by ultrasonication in double-distilled water, and then dried moderately under an infrared lamp. Five-microliter of THF solution of polymer (containing 8.2×10^{-3} mol L^{-1} in ferrocene units) was dropped onto the glassy carbon disk electrode, and then the solvent was evaporated moderately under an infrared lamp to form the film electrode, and the coverage of the film was 5.8×10^{-7} mol cm^{-2} (in ferrocene units).

The electrochemical quartz crystal balance (EQCM) measurements were carried out with a CHI-400A electrochemical quartz crystal microbalance (CH Instruments). A quartz crystal plate with gold electrodes (diameter, 0.5 cm) sprayed on either sides served as working electrode. The surface area of gold electrode was 0.196 cm^2. The apparent oscillation frequency of the AT-cut quartz crystal was 7.99 MHz. The system calibration constant was obtained as 0.739 Hz ng^{-1}, that is, the mass change was 1.35 ng for 1-Hz frequency change. The gold film quartz electrode surface was washed before it was used with H$_2$SO$_4$: 30%H$_2$O$_2$ $(V/V = 3:1)$, double-distilled water and ethanol, and then dried moderately under an infrared lamp. THF solution (4-μL) of polymer (containing 4.1×10^{-3} mol L^{-1} in ferrocene units) was dropped onto gold disk electrode, and then the solvent was evaporated moderately under an infrared lamp to form the film electrode, and the coverage of the film was 1.65×10^{-8} mol cm^{-2}(in ferrocene units).

All solvents and chemical reagents were purchased from commercial sources, and all were analytical- or pure-grades. The water was double-distilled. The concentration of all test electrolyte solutions was 0.05M. The solutions were filtered with 0.45 μm microbore filter before use. The electrochemical measurements were carried out at 25°C.

iR drop compensation

Because the ohmic potential (iR) drops of organic solutions are considerable, especially in less-polar solutions. So that, the iR drops of the solutions were measured and auto-compensated with CHI instruments in the electrochemical measurements.

RESULTS AND DISCUSSION

To investigate the influence of electrolyte ion size on the CV behavior of the PFS film, three typical electrolyte, that is, sodium tetraphenylborate (NaBPh$_4$, with large anion), tetrabutylammonium perchlorate (Bu$_4$NClO$_4$, with large cation), and tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$, with large cation) were selected as supporting electrolytes. The CV measurements were carried out in acenitrile, acetone, methanol, ethanol, isopropanol, and n-butanol solutions because these large ion electrolytes were difficult to dissolve in water. The corresponding lithium perchlorate (LiClO$_4$) solutions were selected as contrastive system. In previous researches,[12–14] the LiClO$_4$ was found to be the best supporting electrolyte, and in its solutions the stable and repeatable CV waves could be obtained.

The experiment results exhibited that when the large volume ion electrolytes NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ were used as supporting electrolytes, the CV

currents i_p of the PFDMS films attenuated gradually in acenitrile or acetone solutions, as shown in Figures 1 and 2. Whereas, the stable and repeatable CV waves could be obtained in methanol, ethanol, isopropanol, and *n*-butanol solutions, as shown in Figures 3–6, respectively. In previous research,[14] it was found that when LiClO$_4$ was used as supporting electrolyte, the CV i_p of the PFDMS films also attenuated gradually in some polar organic solvents, such as acenitrile, ethyl acetate, and nitromethane solutions, but the stable and repeatable CV waves could be obtained in acetone solution. The attenuation of CV i_p of PFS films in these polar organic solvents has been proved to be the result of the polymer films dissolving gradually due to over swelling of films. The CV i_p of the PFDMS films attenuated gradually in large ion electrolyte acetone solutions indicating that the large volume electrolyte solutions had higher affinity with the PFDMS films, which would lead the PFS films to swell much more in these organic solutions.

As shown in Figures 1–6, when NaBPh$_4$ (with large anion) was used as supporting electrolyte, the CV responses of the PFDMS films were very weak in all tested organic solutions, and reduced with decrease in the polarity of the solvents. The CV wave shapes of the PFDMS film were abnormal and asymmetric ones in various organic solutions besides in acenitrile solution. This phenomena revealed that it was difficult for the large size anions to penetrate into the PFS films and to support the CV process of the PFS films. The transfer and diffusion resistances of electroactive species in the films would be very large due to the absence of anions in the films, which was unfavorable to the charge balance and mass transfer efficiency in the films, so that the CV waves of the PFDMS films exhibited very small CV i_p and irreversible CV features. In NaBPh$_4$ acenitrile and acetone solutions, the CV waves of the PFDMS film had relatively better shapes and certain currents demonstrated that the film was highly swollen in these solutions, and the large anions could penetrate into this swollen film.

When Bu$_4$NClO$_4$ and Bu$_4$NBF$_4$ (with large cation) were used as supporting electrolytes, the CV wave shapes, peak potential E_p and i_p of the PFDMS film were similar to the cases of the LiClO$_4$ used as supporting electrolyte, which indicated that the size of cation had small influence on the CV process of the PFS film, that is, the electrolyte cations did not take part in the electrochemical process of the film. Comparing Bu$_4$NClO$_4$ with Bu$_4$NBF$_4$, when the Bu$_4$NBF$_4$ was used as supporting electrolyte, the CV peak shapes were better, the CV i_p were larger, and the varieties of E_p were smaller with changing potential scan rate v. It was consistent with the fact that the size of anion BF$_4^-$ was slightly smaller than anion ClO$_4^-$. Furthermore, as shown in Table I, the resistances of the Bu$_4$NBF$_4$ solutions were smaller than the corre-
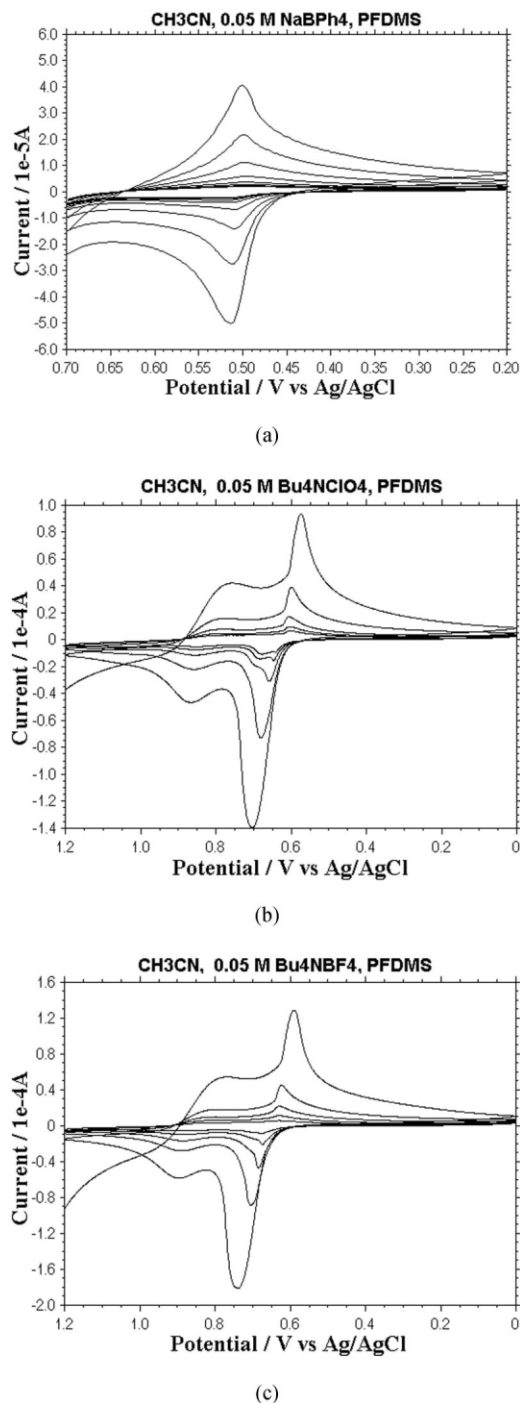

Figure 1 Attenuated cyclic voltammgrams of PFDMS film in acetonitrile NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ solutions. Γ = 5.8 × 10^{-7} mol Fe cm^{-2}; C (electrolyte) = 0.05M; v = 0.10 V/s; at 25 °C.

sponding Bu$_4$NClO$_4$ solutions. It also meant that the dissociation of Bu$_4$NBF$_4$ was slightly higher than Bu$_4$NClO$_4$ in various organic solutions. These two factors show that CV process of the PFDMS films in Bu$_4$NBF$_4$ solutions had the better efficiency of transfer and the better electrochemical reversibility.

When Bu$_4$NClO$_4$ and Bu$_4$NBF$_4$ were used as supporting electrolyte, the solvent effects on the CV be-

havior of the PFDMS films were similar to the that of $LiClO_4$ used as supporting electrolyte. In acenitrile or acetone solutions, the CV waves of the PFDMS films shown as distinguishable double peaks, which suggested that the PFDMS films were swollen in these organic solutions, the configurations of the films were relaxation with bigger holes, the active centers of poly-
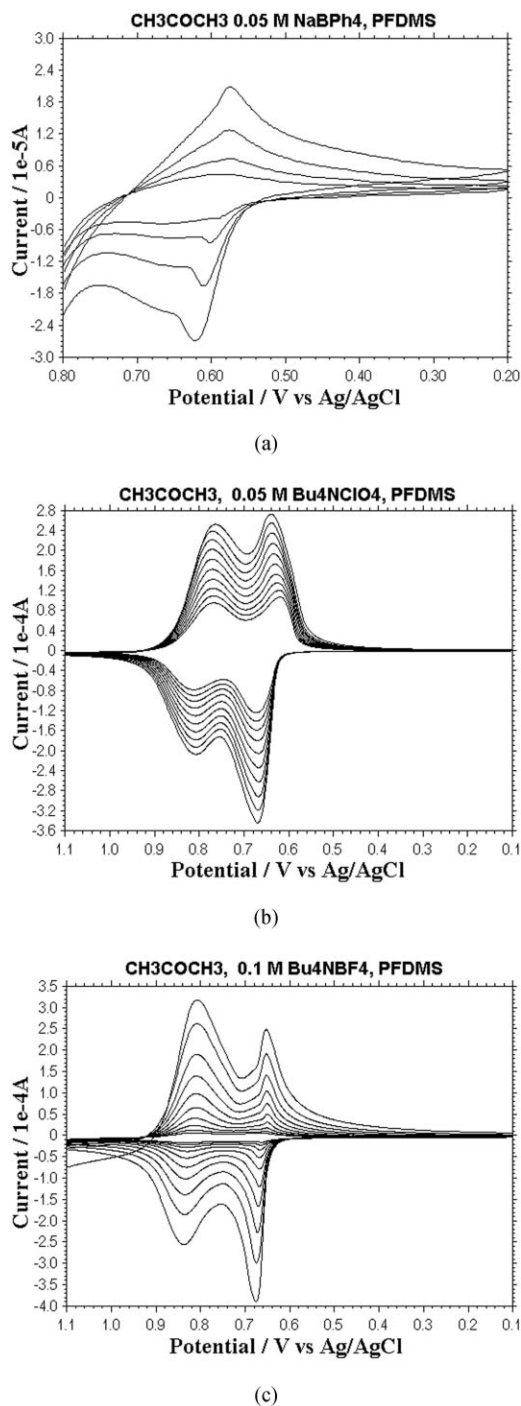

(a)

(b)

(c)

Figure 2 Attenuated cyclic voltammgrams of PFDMS film in acetone NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ solutions. Γ = 5.8 × 10^{-7} mol Fe cm^{-2}; C (electrolyte) = 0.05M; v = 0.10 V/s; at 25°C.

(a)

(b)

(c)

Figure 3 Cyclic voltammgrams of PFDMS films in methanol NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ solutions at different scan rates. Γ = 5.8 × 10^{-7} mol Fe cm^{-2}; C (electrolyte) = 0.05M; at 25°C; v from inside to outside 20, 40, 60, 80, and 100 mV/s.

mer molecules in the films interacted obviously, and the CV processes were stepwise redox processes.[6,15] But the double peaks of the CV waves changed into single broad peaks or tailing peaks with reduce in the polarity of the solvents. In methanol solutions, the CV waves were double peaks at low scan rate v, and were
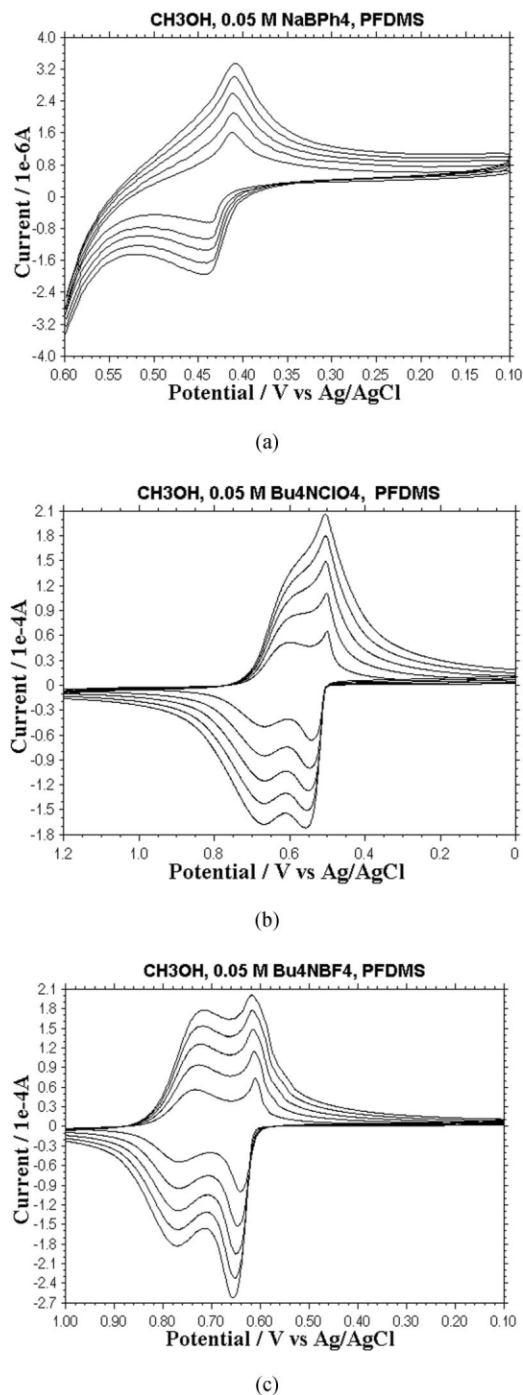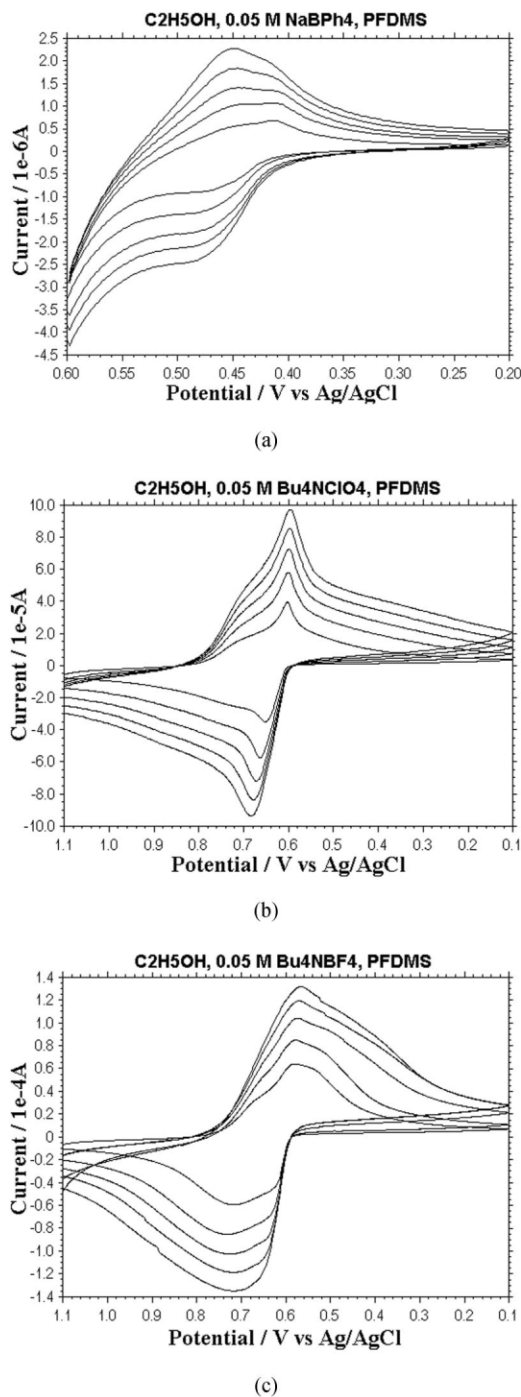
(a)

(b)

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Figure 4 Cyclic voltammgrams of PFDMS films in ethanol NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ solutions at different scan rates. $\Gamma = 5.8 \times 10^{-7}$ mol Fe cm^{-2}; C (electrolyte) = 0.05M; at 25°C; v from inside to outside 20, 40, 60, 80, and 100 mV/s.

tailing peaks at high v. In ethanol, isopropanol, and *n*-butanol solutions, all the CV waves were single broad peaks. These phenomena indicated that the swelling of the PFDMS films was decreased, and the interaction of the active centers was reduced with decrease in the polarity of the solvents.

The properties of solvents should have significant influence on the reversibility of the CV process of the

PFDMS film. In Bu$_4$NClO$_4$ and Bu$_4$NBF$_4$ methanol solutions, the oxidation peak-reduction peak potential separation ΔE_p were small, and peak potenial E_p did not change with changing v, the CV waves expressed the reversible CV process features. With decrease in the polarity of the solvents, the CV i_p reduced, the

(a)

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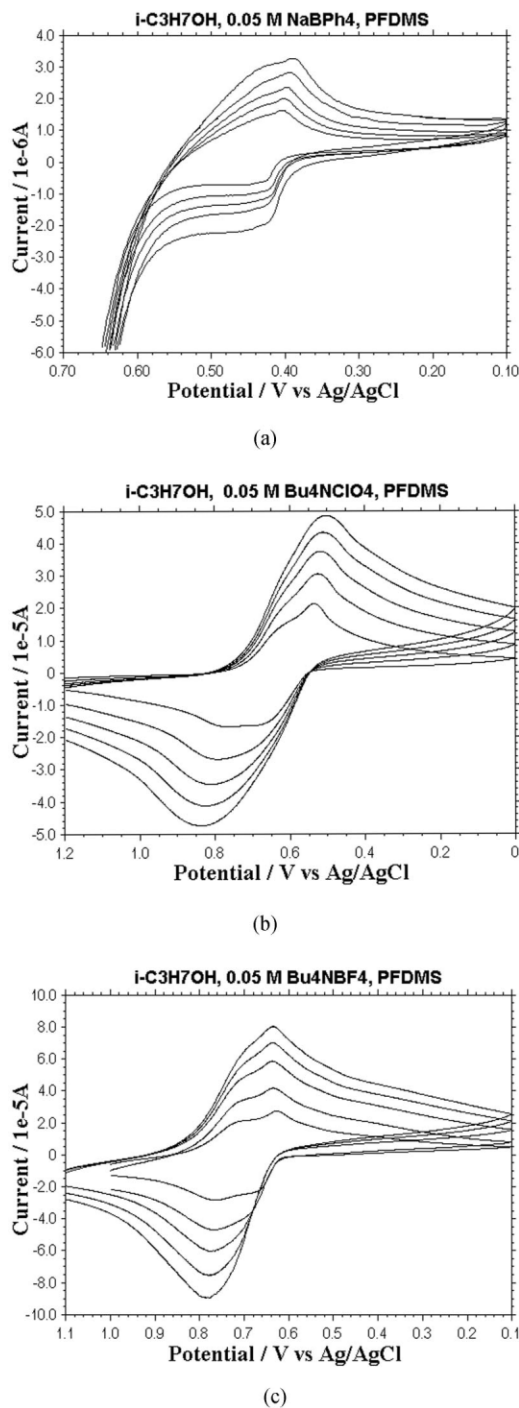
Figure 5 Cyclic voltammgrams of PFDMS films in *i*-propanol NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ solutions at different scan rates. $\Gamma = 5.8 \times 10^{-7}$ mol Fe cm^{-2}; C (electrolyte) = 0.05M; at 25°C; v from inside to outside 20, 40, 60, 80, and 100 mV/s.
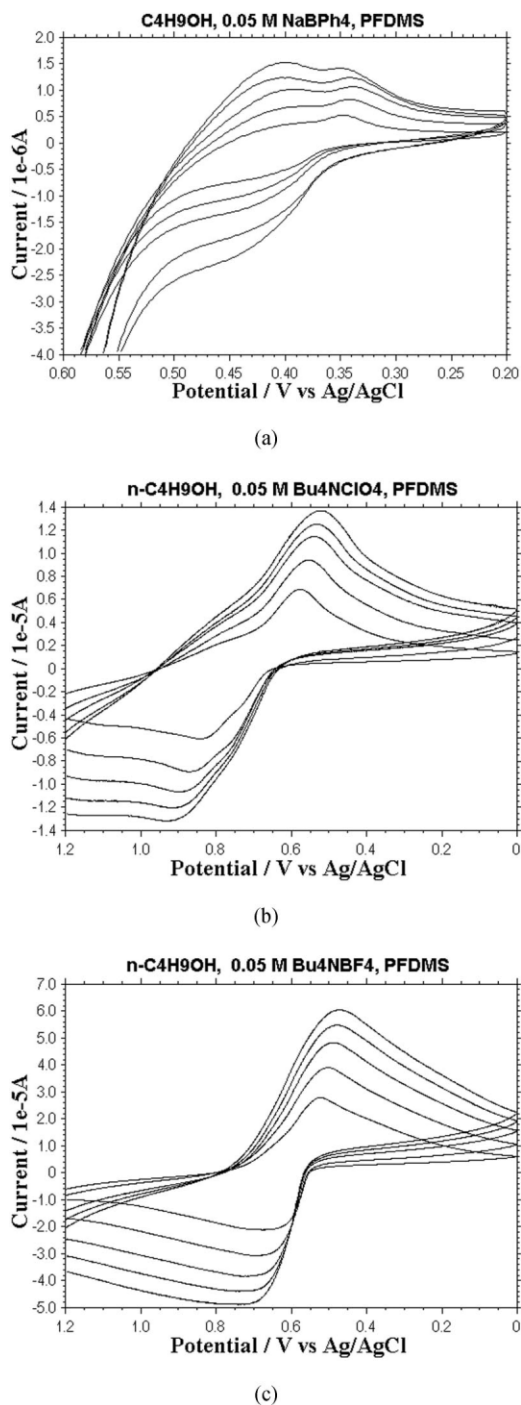
(a)

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Figure 6 Cyclic voltammgrams of PFDMS films in *n*-butanol NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ solutions at different scan rates. $\Gamma = 5.8 \times 10^{-7}$ mol Fe cm^{-2}; *C* (electrolyte) = 0.05*M*; at 25°C; *v* from inside to outside 20, 40, 60, 80, and 100 mV/s.

oxidation peak shifted toward positive potentials, the reduction peak shifted toward negative potentials, ΔE_p increased, and E_p changed with increasing *v*, that is, the reversibility of the CV process decreased. The polarity of the solvents exhibited more noticeable effect on the Bu$_4$NClO$_4$ solutions than the Bu$_4$NBF$_4$

solutions. In Bu$_4$NClO$_4$ *n*-butanol solution, E_p noticeable changed with *v*, the oxidation peaks exhibited irregular peak shapes, the CV waves expressed an irreversible CV process feature.

The electrical conductivity of solutions is important to a diffusion-controlled CV process of the redox polymer films. The conductivity of organic solutions depends on the dissociation of electrolytes and the polarity of the solvents. In general, the dissociation of electrolyte decrease, and the resistance of solutions increase with decrease in the dielectric constants of solvents. The resistance of solution also depends on the viscosity of solutions. In general, the ion migration rate decrease, and the resistance of solutions increase with increasing the viscosity of solutions. The dielectric constants, viscosities, and resistances of the tested solutions are listed in Table I. The resistances of the solutions increased clearly with reducing the dielectric constant and increasing the viscosity. The dielectric constants of acenitrile and acetone were smaller than that of water, but the resistances of these solutions were smaller than that of aqueous, this could be related to the small viscosity of the solvents, it also indicated that these large ion electrolytes, NaBPh$_4$, Bu$_4$NClO$_4$, and Bu$_4$NBF$_4$ were dissociated nearly completely in these polar organic solvents. The dielectric constants of the solvents and the dissociation of the electrolytes were decreased with lengthening the carbon chain of the solvent molecules (Table I). The resistances of Bu$_4$NClO$_4$ and Bu$_4$NBF$_4$ methanol, ethanol, isopropanol, and *n*-butanol solutions were larger than those of corresponding LiClO$_4$ solutions. It indicated that the dissociation of large ion electrolytes decreased quickly with decrease in the polarity of solvents. The low dissociation of large size electrolyte decreased the anion activities, and was unfavorable to the charges transfer and ions balance in the films, so that the CV i_p and reversibility of the CV process decreased in these organic solutions. Therefore, the dissociation of the electrolytes also was the major factor of the CV i_p and the reversibility of the CV processes.

The reversibility of the CV process of the PFDMS films was related with the potential scan rates, as shown in Figures 3–6. In methanol, ethanol, isopropanol, and *n*-butanol solutions, at routine scan rates (0.01~0.10 V/s), the CV i_p were proportional to the square root of the scan rate ($v^{1/2}$), which indicated that the CV process of the PFDMS films was diffusion controlled. In methanol and ethanol solutions, at slow *v* (smaller than 0.1 V/s), E_p was changed slightly with changing *v*, but at high *v* (larger than 0.1 V/s), E_p was changed noticeably with changing *v*, the oxidation peaks and reduction peaks shifted positively and negatively, respectively, with increasing *v*. As a result the CV waves of the PFDMS films exhibited as single broad peaks with larger ΔE_p at high *v*. It meant the

TABLE I
Dielectric Constants, Viscosity Factors, and Resistances of Solutions[a]

	Acenitrile	Acetone	Methanol	Ethanol	Isopropanol	*n-Butanol*	Water
Dielectric constant[16] (25°C)	37.5 (20°C)	20.7	32.63	24.3	18.3	17.1	78.5
Viscosity factors[16] (20°C)	0.340 (25°C)	0.316	0.595	1.17	2.1	3.379 (15°C)	0.894
Solution resistances (Ω)							
(0.05M LiClO$_4$)	3.19×10^2	3.34×10^2	4.89×10^2	1.06×10^3	2.19×10^3	5.13×10^3	5.40×10^2
(0.05M NaBPh$_4$)	3.91×10^2	3.58×10^2	6.44×10^2	1.37×10^3	2.58×10^3	4.44×10^3	–
(0.05M Bu$_4$NClO$_4$)	3.12×10^2	4.93×10^2	7.29×10^2	2.18×10^3	5.88×10^3	1.14×10^4	–
(0.05M Bu$_4$NBF$_4$)	2.90×10^2	3.62×10^2	6.38×10^2	1.95×10^3	5.60×10^3	9.16×10^3	–

[a] Films coverage : 5.8×10^{-7} mol Fe cm^{-2}; supporting electrolyte concentration: 0.05M; temperature: 25°C; resistance of working electrode: 50Ω.

reversibility of the electrochemical process of the films decreased at high v.

As shown in Figures 3–6, the solvents had more effect on the oxidation peaks of the PFDMS films. The varieties of E_{pa} with v were larger than E_{pc} with decrease in the polarity of the solvents, it was consisted with the oxidation mechanism of the films. The dissociation of the electrolytes decreased with reduce in the polarity of the solvents, which was unfavorable to the charges balance and diffusion in the films when in oxidation state. So that in the less-polar solutions, the oxidation peaks changed noticeably bad, the E_{pa} shifted toward the positive potentials, the CV i_{pa} reduced, the CV process expressed as an irreversible ones.

The EQCM is a simple, cost effective, high-resolution mass sensing technique based upon the piezoelectric effect. It can measure the mass change of the electrode surface in situ during the electrochemical process, which is effective to understand the mechanism of the electrochemical process.[17–22] The mass changes of PFDMS film on the electrode surface during the CV processes in Bu$_4$NClO$_4$ and NaBPh$_4$ methanol solutions were measured by EQCM technique. As shown in Figure 7. The oscillation frequency of the quartz crystal plate increased quickly at reduction peak region, which meant that the mass of the film decreased quickly. The other way round, the oscillation frequency decreased quickly at oxidation peak region, which meant that the mass of the film increased quickly. The EQCM behavior of PFDMS film was consistent with our above-mentioned analysis: when the oxidation took place in PFDMS films, the PFS was oxidized to poly(ferrocnium), polycations, which needed electrolyte anions to penetrate into the film for charge balance and conduced the weight of the film increased. By contrary, when reduction took place in the films, the polycations film reduced to neutral state, the electrolyte anions moved out from the films and the weight of the film decreased.

Figure 7 presented that the EQCM mass change of PFDMS film during the CV process in the Bu$_4$NClO$_4$ solution was similar to the case of the LiClO$_4$ used as

supporting electrolyte. According to the mechanism of film electrode, the EQCM mass change (Δm_c) of film should contain mass of anions (Δm_a) of penetrating into film and mass of solvent (Δm_s) of penetrating into film, that is, $\Delta m_c = \Delta m_a + \Delta m_s$. The molar amount of anions penetrating into the film should be equal to the molar amount of ferrocene oxidized during oxidation process, which could be calculated by Faraday law $N = Q/nF$. So, the Δm_a should be equal to the molar weight of anions multiplied the molar amount of fer-
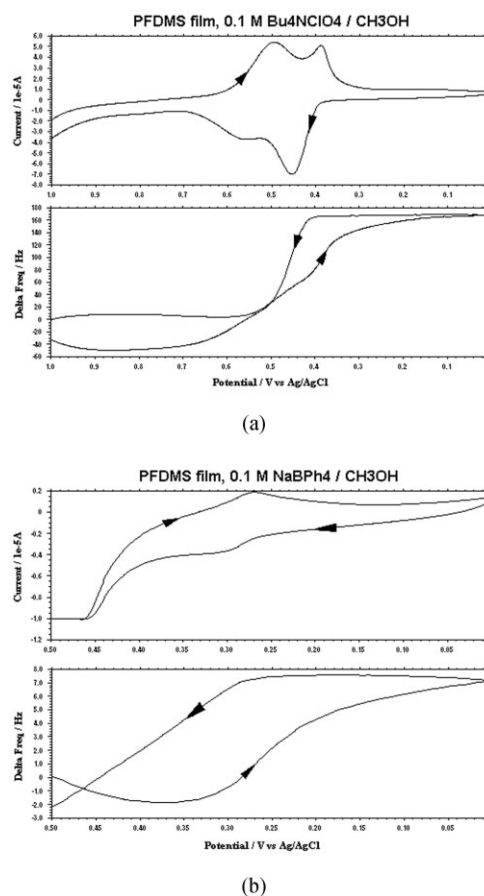

(a)

(b)

Figure 7 The EQCM and CV responses of the PFDMS films in Bu$_4$NClO$_4$ (with large cation) and NaBPh$_4$ (with large anion) methanol solutions at scan rate 60 mV/s.

rocene oxidized during oxidation process. The comprehensive analysis of the mass change of the film and the redox charges, we found that the mass change of the films during the redox process is larger than the weight of the corresponding coulombic ClO_4^-, which meant that there were solvent molecules chaperonage ClO_4^- penetrating into the films, namely ClO_4^- was solvated in methanol, and the calculated results indicated that every ClO_4^- of penetrating into the films chaperonage one methanol molecules. This result supported the opinion that the PFDMS film was solvent swollen in methanol. But when $NaBPh_4$ was used as the supporting electrolyte, the EQCM mass change and the CV i_p of PFDMS film all were very small, and the mass change of reduction process only was $\sim 10^{-8}$ g. It meant that the large anions were difficult to penetrate into the film. The absence of the anions which were necessary for charge balance in the film would conduce the electrochemical reaction hard to keep up, so that, the CV i_p was very small.

According to the CV theory,[23] there is relationship between the peak current and potential scan rate for a diffusion controlled reversible CV process as below:

$$i_p = 0.4463nFA\left(\frac{nF}{RT}\right)^{1/2} D_0^{1/2} C_0^* v^{1/2} \qquad (1)$$

and there are relationships between the peak current, peak potential and potential scan rate for an irreversible process as below:

$$i_p = 0.4958nF(\alpha n_\alpha)^{1/2}\left(\frac{F}{RT}\right)^{1/2} AD_0^{1/2}C_0^* v^{1/2} \qquad (2)$$

$$i_p = 0.227nFAC_0^* k^0 \exp\left[-\left(\frac{\alpha n_\alpha F}{RT}\right)(E_p - E^0)\right] \qquad (3)$$

where i_p is the peak current in A; A is the area of film coverage of the working electrode surface (cm^2); v is the potential scan rate (V s^{-1}); C_0^* is the concentration of the electroactive species in the films (mol cm^{-3}); D_0 is the diffusion coefficient of the electroactive species ($cm^2 s^{-1}$); αn_α is the surface transfer coefficient; k^0 is the standard rate constant (cm s^{-1}); and the remaining terms have the usual significance.

Because the most CV processes in investigated organic solutions were reversible or nearly reversible processes, eq. (1) could be used approximately for reversible process. While at the same time, the CV processes of the PFDMS films in Bu_4ClO_4 isopropanol, Bu_4NClO_4, and Bu_4NBF_4 n-butanol solutions exhibited irreversible features, eqs. (2) and (3) were used for these irreversible processes. Because the swelling degree of the films were different in various organic solvents, the thickness of the films were variational, the concentration of electroactive species in the films

TABLE II
Apparent Diffusion Coefficient ($D_0^{1/2} C_0^*$) $\times 10^9$ of PFDMS in Organic Solutions (25°C)

Solvents	Bu_4NClO_4		Bu_4NBF_4	
	Cathodic peak	Anodic peak	Cathodic peak	Anodic peak
Methanol	41.5	31.3	37.4	48.9
Ethanol	17.5	18.2	20.9	22.7
Isopropanol	10.5[a]	11.9[b]	15.4	17.4
n-Butanol	3.67[c]	3.63[d]	14.9[e]	12.9[f]

[a–f] Deal with as irreversible processes, calculated surface coefficient αn_α were a, 0.50; b, 0.48; c, 0.25; d, 0.28; e, 0.37; f, 0.34, respectively.

C_0^* changed with solvents, so that $(D_0^{1/2}C_0^*)$ was termed as apparent diffusion coefficient. The calculated apparent diffusion coefficient in solutions are listed in Table II.

As shown in Table II. The apparent diffusion coefficient were reduced with decreasing the polarity of the solvents. Comparison with the results of previous paper,[14] the apparent diffusion coefficient of the PFDMS films in Bu_4NClO_4 methanol, ethanol solutions were closed to those in corresponding $LiClO_4$ solutions, but the apparent diffusion coefficient of the films in Bu_4NClO_4 isopropanol, n-butanol solutions, were smaller than those in corresponding $LiClO_4$ solutions. The reasons were same as the above-mentioned analysis, the dissociation of the large ion electrolytes in low-polar solvents were decreased. The apparent diffusion coefficient of the PFDMS films in Bu_4NBF_4 solutions were larger than those in corresponding Bu_4NClO_4 solutions. As the above-mentioned analytic demonstrates, the size of BF_4^- smaller than ClO_4^-, and it had better films penetration and higher migration rate.

CONCLUSIONS

The influences of the supporting electrolyte ion size effect on the CV behavior of high-molecular-weight PFS films in organic solutions were investigated. Three supporting electrolytes with various size ions were tested. Electrolyte anions take part in charges neutrality in the films, so that the size of anions affect the CV behavior of the films remarkably. The large anions were difficulty to penetrate into and out of the films, the migration resistance of the large ions in films are high, the diffusion rates of the electroactive species in the films are low, and the CV behavior of the polymer films exhibit irreversible features. The electrolyte cations do not take part in charges neutrality in the films, so that the size of the cations do not affect the CV behavior of the films on the whole.

Because the large volume electrolytes have higher affinity with the PFDMS films, the films are swollen

highly in the large volume supporting electrolytes solutions. The dissociation of large volume electrolytes are decreased with reducing the polarity of the solvents, which is unfavorable to the charges transfer and balance in the films, so that the reversibility of the CV processes of the PFDMS films in large volume electrolytes and low-polar solutions are decreased.

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