Study on the Electrochemical Behavior of Poly(ferrocenylsilane) Films

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The electrochemical behavior of polyferrocenyldimethylsilane (PFDMS) films and polyferrocenylmethyl-phenylsilane (PFMPS) films deposited on a glassy carbon electrode in 1.0 M aqueous $LiClO_4$ was investigated by means of cyclic voltammetry (CV). The influences of supporting electrolyte concentration, temperature, film thickness, and the molecular structure of the polymer on the electrode process are discussed. In 1.0 M aqueous $LiClO_4$, the electrochemical processes of two polymer films on glassy carbon electrodes were complex and have a low rate of electron transport and mass diffusion. At routine sweep rates, quasi-reversible or irreversible CV processes of the films were observed, but at slow sweep rates, nearly reversible CV waves were recorded. Below 0.05 M, the concentration of the supporting electrolyte had a considerable effect on the CV behavior of the film, especially on the oxidation wave, that is, the kinetics of film oxidation was limited by the counterion flow into the polymer phase. Elevated temperature increased the rate of the electrode process and improved the reversibility of the film electrode process. The diffusion rate of the active species in the film electrode process was reduced with the film thickness. Furthermore, the molecular structure of the polymer had a notable influence on the electrochemical behavior of the films. The phenyl groups in PFMPS hobbled the chain mobility in the polymer and restricted the surface charge transfer and the active species diffusion so that the kinetic parameters of the PFMPS films, especially the surface transfer coefficient αn_α, were found to be smaller than those corresponding to the PFDMS films. The shapes of the CV peaks of the PFMPS films were broader, the peak potentials for both cathodic and anodic peaks were more positive, and the peak separation ΔE_p was larger.

1. Introduction

Over the past decade significant research interest has been given to the high molecular weight organometallic polymer systems which contain transition metals in the main chain, because of their useful physical and chemical properties, including electronic, electrochemical, and magnetic ones.[1−3] For example, all synthesized poly(ferrocenophanes) exhibit electrochemical activity.[4−8] Electrochemical studies of organometallic polymers will help us understand the redox properties of these novel functional polymer materials, the mechanism of the electrode process, and the factors that affect charge transfer. These studies are important in developing potential applications for modified electrodes, electrochemical sensors, and nonlinear optical devices. Since the 1980s, ferrocenyl derivatives and polymers containing ferrocene as pendant groups have been used in chemically modified electrodes, and the electrode processes of these chemically modified electrodes have been investigated extensively.[9−13] However, to our knowledge, only a few detailed electrochemical studies have been reported for the films of high molecular weight poly(ferrocenylsilanes) in which ferrocenyl and silanyl link alternately as main chains rather than as pendant groups.[14] In previous papers,[16,17] we have reported that the various supporting electrolytes have a remarkable influence on the electrochemical behavior and stabilization of the poly-(ferrocenylsilane) films. In this paper, we report the electrochemical properties of polyferrocenyldimethylsilane (PFDMS) films and polyferrocenylmethylphenylsilane (PFMPS) films

deposited on a glassy carbon electrode in aqueous $LiClO_4$. In this electrolyte solution, quasi-reversible or nearly irreversible redox processes were observed for both films. The influences of supporting electrolyte concentration, temperature, and film thickness on the electrode process and the electrochemical mechanism of the film are discussed.

2. Experimental Section

2.1. Instruments and Reagents. The cyclic voltammetry (CV) measurements were carried out with a CHI-630A electrochemical analyzer (CH Instruments, Inc., Austin, Texas), in an undivided three-electrode cell. All electrodes were from CH Instruments. A platinum wire counter electrode and a Ag/AgCl (3 M KCl) reference electrode were used. The working electrode was a Teflon-shrouded glassy carbon disk electrode (3 mm diameter, geometric area 0.071 cm^2), which was polished to a mirror finish with 0.05 μm Al_2O_3 paste on felt, cleaned by ultrasonication successively in 0.1 M NaOH, 1:1 HNO_3, anhydrous ethyl alcohol, and double distilled water, and then dried and used for electrochemical measurements. The electrical conductivity was measured with a DDS-11A electrical conductivity meter (Shanghai Analytical Instruments, Shanghai). All chemicals were purchased from commercial sources and were of analytical or pure grades. Double-distilled water was employed. The solutions were filtered with 0.45 μm microbore filter and purged for 15 min with prepurified nitrogen before use. The electrochemical measurements were carried out at 25 °C, except in the test of temperature influence.

2.2. Synthesis and Characterization of Poly(ferrocenyl-silanes). Poly(ferrocenylsilanes) were synthesized according to

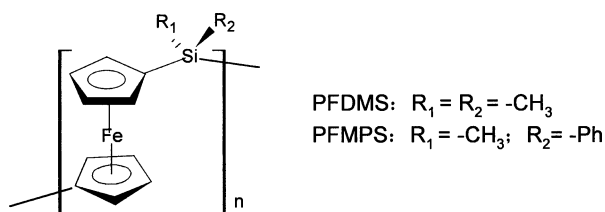* Corresponding author. Phone: +86-571-87953200. Fax: +86-571-87952400. E-mail: opl_wl@dial.zju.edu.cn.

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Figure 1. Structure of poly(ferrocenylsilane).

PFDMS: $R_1 = R_2 = -CH_3$

PFMPS: $R_1 = -CH_3$; $R_2 = -Ph$

the literature,[1] their structure being shown in Figure 1. ^{1}H NMR spectra of the polymers were recorded with a 500 MHz AVANCE NMR spectrometer (Model DMX500) in CDCl$_3$, using TMS as the standard. The ^{1}H NMR spectrum of PFDMS showed two resonance peaks for the cyclopentadienyl protons at 4.22 and 4.01 ppm and one resonance peak at 0.44 ppm assigned to the methyl groups attached to silicon. The ^{1}H NMR spectrum of PFMPS showed one resonance peak at 0.64 ppm, assigned to the methyl group attached to silicon, and multiple resonance peaks for the cyclopentadienyl protons at 3.87−4.03 ppm and two resonance peaks at 7.35 and 7.56 ppm, assigned to the phenyl group attached to silicon.

The molecular weight of these polymers was determined by gel permeation chromatography (GPC) with a laser-scattering detector and an Ultrastyragel column with pore sizes of $10^3 \times 10^5$ Å. The eluent was THF at a flow rate of 1.0 mL min^{-1}. A detection wavelength of 632.8 nm and a refraction index increment value for the polymer solutions of dn/dc = 0.20 were used for laser-scattering detection.[18,19] The molecular weight and molecular weight fraction of the PFDMS were $M_w = 1.14 \times 10^5$ g mol^{-1}, $M_n = 2.51 \times 10^4$ g mol^{-1}, PDI (M_w/M_n) = 4.54. The corresponding data for PFMPS were $M_w = 1.12 \times 10^5$ g mol^{-1}, $M_n = 4.96 \times 10^4$ g mol^{-1}, PDI (M_w/M_n) = 2.26.

2.3. Polymer-Film-Coated Electrodes. Poly(ferrocenylsilane)-coated electrodes were prepared by covering the glassy carbon disk electrodes with a solution of poly(ferrocenylsilane) in THF and then allowing the solvent to evaporate at room-temperature.

To estimate the effect of uncompensated ohmic potential, that is, the iR_u drop on the cyclic voltammograms, the iR_u drops of the solutions were measured and autocompensated with the CHI-630A electrochemical analyzer. The results showed that in most cases the ohmic resistances of the solutions were about 30−50 ohm; the compensated cyclic voltammograms and the uncompensated cyclic voltammograms did not exhibit a noticeable difference. This indicated that the ohmic potential iR_u drop effect could be neglected.

3. Results and Discussion

3.1. CV Behavior of the Two Polymer Films. CVs of the polyferrocenyldimethylsilane (PFDMS) films and polyferrocenylmethylphenylsilane (PFMPS) films were investigated in various aqueous supporting electrolytes.[17] The results indicated that different supporting electrolytes exerted a remarkable influence on the electrochemical characteristics of the polymer films. In some electrolyte solutions, stable and reproducible cyclic voltammograms could be recorded, whereas in other solutions CV peak currents decayed gradually, and the rates of attenuation were different in various aqueous electrolyte solutions. We have noticed that no distinguishable deposition and desorption on the film electrodes can be observed. Nguyen's group[14] reported that the reduction in peak currents might be due to loss of electroactivity rather than loss of material from the films. We have found that in aqueous LiClO$_4$, CV peak currents of the PFDMS and PFMPS films increased gradually
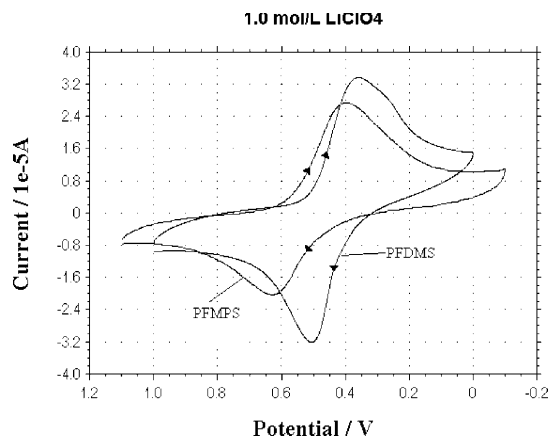

Figure 2. Cyclic voltammograms of PFDMS film and PFMPS film on a glassy carbon electrode. Coverage = 2.8×10^{-6} mol cm^{-2} of ferrocene sites, in aqueous 1.0 M LiClO$_4$, at a scan rate of 40 mV s^{-1}, at 25 °C.

with each successive sweep and then reached a steady state at which stable and reproducible current−potential curves were obtained. Typical cyclic voltammograms of the two poly-(ferrocenylsilane) films on glassy carbon electrodes recorded in 1.0 M aqueous LiClO$_4$ at room-temperature are shown in Figure 2.

The peaks in Figure 2 are broad, and the areas of the oxidation peaks are not equal to those of the corresponding reduction peaks. The peak shapes of the two poly(ferrocenylsilane) films are different. Compared to the cyclic voltammogram of the PFDMS film, the peak potentials of the PFMPS film are more positive, the peak-to-peak separation, ΔE_P, of the PFMPS film is larger, the peaks of the PFMPS film are broader, and the peak currents of the PFMPS film are smaller. It is noticeable that the structure of the polymer, especially the steric configuration, has an influence on the electron transport characteristics of the film. A possible explanation is that the phenyl groups in the PFMPS molecule are bulky and cumber the rotation of the polymer chains, making the charge transfer between the neighboring active sites in the PFMPS molecule much more difficult than in the PFDMS molecule. As a result, the redox potentials of the PFMPS film are increased, and ΔE_p of the PFMPS films are enlarged. We have noticed that the reduction peak current value (i_{pc}) is larger than the oxidation one (i_{pa}) for the PFMPS film, and i_{pa} is larger than i_{pc} for the PFDMS film. Maybe the electronic property of the phenyl group in the PFMPS, the conjugation effect of the phenyl group, is favorable to the reduction process.

3.2. Influence of Scan Rate. In aqueous LiClO$_4$, it was found that the CV peak current values i_p of the PFDMS and PFMPS films were proportional to the square root of the scan rate ($v^{1/2}$) over a wide scan rate range. Furthermore, the increase of the reduction peak currents i_{pc} with increasing potential scan rate was faster than that of the oxidation currents i_{pa}. The linear range of the linear equation for the PFDMS films was much wider than that of the linear equation for the PFMPS films. The results of the linear correlation between i_p and $v^{1/2}$ are listed in Table 1. These relationships indicate that at room-temperature the charge transport through the films obeys Fick's Law. The electrode processes of the films are diffusion controlled.[20]

Wave shapes are sensitive to the scan rate and become more distorted at higher scan rates. The potentials of the reduction peaks shifted toward more negative potentials, and the potentials of the oxidation peaks shifted toward more positive potentials; thus, the peak-to-peak separation ΔE_p increased with increasing

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TABLE 1: Relationships between the Peak Currents, Peak Potentials, and the Potential Scan Rates of Two Films

| temp °C	film	thickness (mol Fe cm⁻²)	rate range v(V s⁻¹)	linear equation	correlation coefficient r
25	PFDMS	2.8×10^{-6}	0.02–2.0	$i_{pa}(\mu A) = -5.694 - 147.96v^{1/2}$	−0.9993
			0.1–2.0	$\ln -i_{pa}(A) = -11.173 + 18.213(E_p - E^{0\prime})$	0.9913
			0.02–2.0	$i_{pc}(\mu A) = -1.507 + 159.19v^{1/2}$	0.9994
			0.1–2.0	$\ln i_{pc}(A) = -11.666 - 19.80(E_p - E^{0\prime})$	0.9954
	PFMPS	2.8×10^{-6}	0.04–1.0	$i_{pa}(\mu A) = -3.927 - 86.31v^{1/2}$	−0.9999
			0.1–1.0	$\ln -i_{pa}(A) = -11.996 + 10.68(E_p - E^{0\prime})$	0.9891
			0.04–1.0	$i_{pc}(\mu A) = -2.139 + 129.03v^{1/2}$	0.9992
			0.1–1.0	$\ln i_{pc}(A) = -11.830 - 11.383(E_p - E^{0\prime})$	0.9840
	PFDMS	2.8×10^{-8}	0.006–1.0	$i_{pa}(\mu A) = 13.676 - 112.75v^{1/2}$	−0.9907
			0.006–1.0	$i_{pc}(\mu A) = -10.651 + 86.66v^{1/2}$	0.9907
	PFMPS	2.8×10^{-8}	0.04–2.0	$i_{pa}(\mu A) = 28.459 - 145.88v^{1/2}$	−0.9926
			0.04–2.0	$i_{pc}(\mu A) = -22.441 + 109.77v^{1/2}$	0.9917
50	PFDMS	2.8×10^{-6}	0.02–2.0	$i_{pa}(\mu A) = -50.393 - 482.72v^{1/2}$	−0.9997
			0.1–2.0	$\ln -i_{pa}(A) = -9.599 + 20.207(E_p - E^{0\prime})$	0.9828
			0.02–2.0	$i_{pc}(\mu A) = 22.483 + 536.55v^{1/2}$	0.9993
			0.1–2.0	$\ln i_{pc}(A) = -9.769 - 22.277(E_p - E^{0\prime})$	0.9805
	PFMPS	2.8×10^{-6}	0.04–1.0	$i_{pa}(\mu A) = -28.413 - 167.87v^{1/2}$	0.9998
			0.1–1.0	$\ln -i_{pa}(A) = -10.669 + 13.361(E_p - E^{0\prime})$	0.9945
			0.04–1.0	$i_{pc}(\mu A) = -25.107 + 243.48v^{1/2}$	−0.9966
			0.1–1.0	$\ln i_{pc}(A) = -10.483 - 13.967(E_p - E^{0\prime})$	0.9904
	PFDMS	2.8×10^{-8}	0.006–1.0	$i_{pa}(\mu A) = 30.0707 - 171.56v^{1/2}$	−0.9929
			0.006–1.0	$i_{pc}(\mu A) = -23.755 + 137.90v^{1/2}$	0.9957
	PFMPS	2.8×10^{-8}	0.04–2.0	$i_{pa}(\mu A) = 38.098 - 188.54v^{1/2}$	−0.9925
			0.04–2.0	$i_{pc}(\mu A) = -28.844 + 132.79v^{1/2}$	0.9891
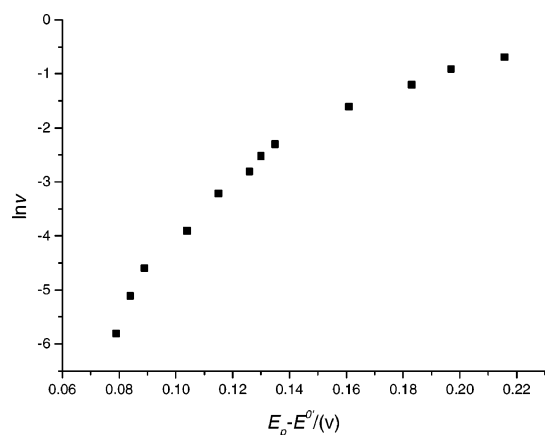
Figure 3. Peak potential of the PFDMS film vs the potential scan rate. Coverage = 2.8×10^{-6} mol Fe cm⁻², in aqueous 1.0 M LiClO₄, at 25 °C.

scan rate. Compared with the oxidation peaks, the reduction peaks were widened and shifted negatively much more so that the apparent formal potential $E^{0\prime}$, where $E^{0\prime} = (E_{pc} + E_{pa})/2$, shifted to slightly more negative potentials with increasing scan rate.

The relationship between the peak potential $(E_p - E^{0\prime})$ and the logarithm of potential scan rate $\ln v$ of the PFDMS film is shown in Figure 3. The PFMPS film exhibited similar trends. The peak potentials of the two films shifted with increasing potential scan rate, but the relationship was nonlinear. At slow scan rates, there were more symmetrical and narrower peak shapes and the variability of peak potential with potential scan rate changed slightly. Along with the potential scan rate increase, the peak shapes broadened and the variability of peak potential with scan rate increased. According to the theory of CV, [20] in a reversible electrode process, the peak potential E_p is independent of scan rate. At the same time, in a totally irreversible process there is a linear relationship between the peak potential and the logarithm of the scan rate. The above experimental results indicated that the electrochemical processes of poly-(ferrocenylsilane) films on glassy carbon electrodes were complex. These processes were neither simply reversible nor totally irreversible ones. It was apparent that the rates of electron transport through the film and transfer between the film and the electrode were slow. Although the electrode processes were diffusion controlled, the rates of charge transport and the electrode reaction were rather slow. Because of the slow rates of charge transport, when the potential was scanned at a low rate, the electrode reaction could reach completion, and the CV exhibited nearly reversible features. But when potential was scanned at higher rates, the electrode reaction could not reach completion in time; hence, the CV exhibited quasi-reversible or irreversible features, and this electrode process was controlled by both the electrode reaction and mass diffusion.

3.3. Influence of the Concentration of the Electrolyte. The influence of LiClO₄ concentration in the supporting electrolyte on the CV process was also investigated. The tested concentration range was 0.0063–2.0 M. The results are shown in Figure 4. At concentrations greater than 0.5 M, the electrolyte concentration had no more influence on peak currents and peak potentials, in a wide concentration range (Figure 4, parts a and b). But at low concentrations, the peak currents i_p of both films increased with increasing concentration. When the concentration was about 0.05 M, the peak currents reached their maximum and then decayed and gradually became stable. Similarly, in the low-concentration region, with increasing concentration the oxidation peak moved to lower potentials, while the reduction peak moved to higher potentials; thus, the peak-to-peak separation ΔE_P decreased and then stabilized gradually. Moreover, the values for i_{pa} and E_{pa} changed with electrolyte concentration much more than those corresponding to the reduction peaks; hence, the influence of electrolyte concentration on the oxidation process was more significant.

In our studies, we have also found that the CV waves of polyferrocenylsilane films in aqueous solutions were different from those in some organic solutions. For example, in methyl alcohol, ethyl alcohol, and acetone electrolyte solutions, the CV waves of the PFDMS and PFMPS films showed two couples of well-resolved reversible or nearly reversible waves, similar to the cyclic voltammograms of the polymer solutions, with lower oxidation potential, smaller peak-to-peak separations ΔE_P,
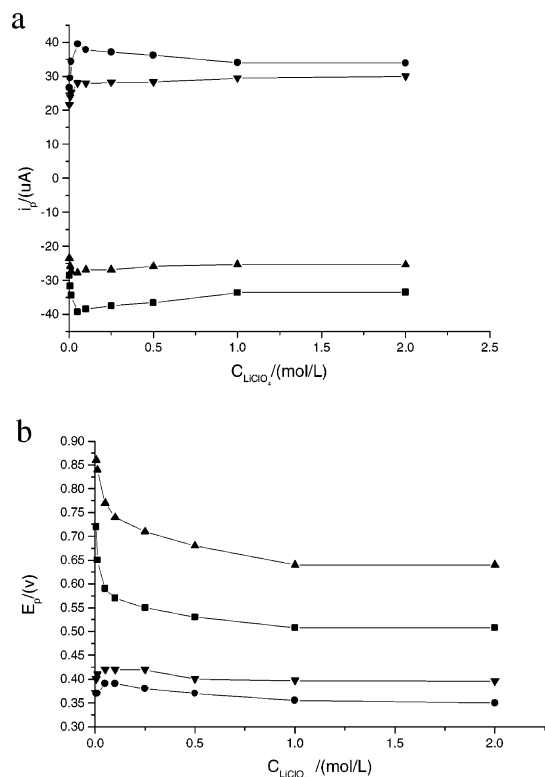
Figure 4. Influences of LiClO$_4$ concentration on i_p and E_p of two films. Coverage = 2.8 × 10^{-6} mol Fe cm^{-2}, potential scan rate v = 0.04 V s^{-1}, at 25 °C. (a) Influence of LiClO$_4$ concentration on i_p of two films; ■ i_{pa} (PFDMS), ● i_{pc} (PFDMS), ▲ i_{pa} (PFMPS), ▼ i_{pc} (PFMPS); (b) Influence of LiClO$_4$ concentration on E_p of two films; ■ E_{pa} (PFDMS), ● E_{pc} (PFDMS), ▲ E_{pa} (PFMPS), ▼ E_{pc} (PFMPS).

larger peak currents, and smaller variability of potential with scan rate, that is, better reversibility, than those in corresponding aqueous electrolyte solutions.

These results indicate that the solvent swelling of high molecular weight polymer films and the penetration of solvated electrolyte ions play an important role in film electrode processes. As a consequence of incorporation of ions and solvent molecules into the film, swelling of the polymer matrix can take place. The originally neutral polymer film is transformed into a swollen polyelectrolyte gel. Along with increasing electrolyte concentration, the ohmic resistance of the solutions decreases and the ion concentration and the diffusion rate of the electroactive species increase in the film.

In a "good" organic solvent, the film is swollen adequately, and the swollen film is provided with a higher electrolyte permeability, lower diffusion resistivity, and greater rate of charge transfer. Therefore, the cyclic voltammograms of the PFDMS and PFMPS films exhibit quasi-reversible or nearly reversible features in organic electrolyte solutions. But in aqueous electrolyte solutions, the films are poorly solvated and swollen to a low degree, which induces films with a lower electrolyte permeability, higher diffusion resistivity, and lower rate of charge transfer. Therefore, the cyclic voltammograms of the PFDMS and PFMPS films exhibit quasi-reversible or nearly irreversible features in aqueous electrolyte solutions.

When the concentration of electrolyte is increased continually, the ionic shielding of the polyelectrolyte increases and the molecules adopt a more compact configuration, that is, a charged polymer film will also adopt a more compact structure. In addition, at high electrolyte concentration the activity of the solvent is low, and consequently the swelling and permeability of the film are less than that encountered in dilute electrolyte
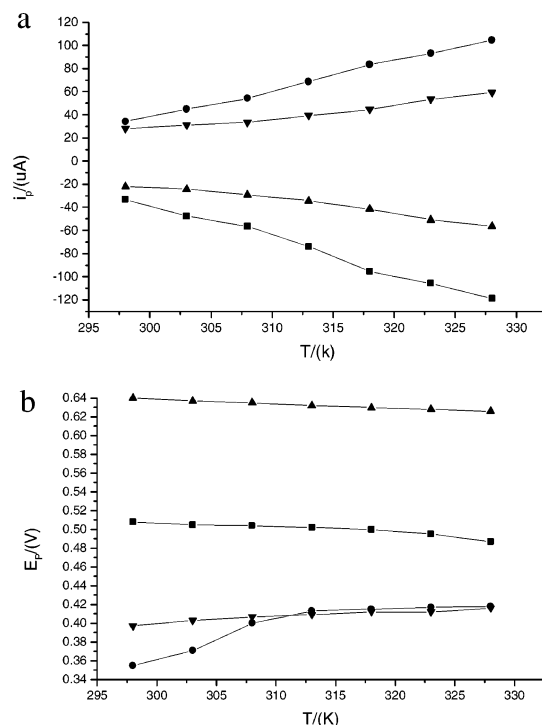

Figure 5. Temperature influence on i_p and E_p of two films. Coverage = 2.8 × 10^{-6} mol Fe cm^{-2}, concentration of electrolyte, C(LiClO$_4$) = 1.0 M, potential scan rate v = 0.04 V s^{-1}. (a) Temperature influence on i_p of two films; ■ i_{pa} (PFDMS), ● i_{pc} (PFDMS), ▲ i_{pa} (PFMPS), ▼ i_{pc} (PFMPS); (b) Temperature influence on E_p of two films; ■ E_{pa} (PFDMS), ● E_{pc} (PFDMS), ▲ E_{pa} (PFMPS), ▼ E_{pc} (PFMPS).

solutions. Thus, the maximum in the peak currents is observed at intermediate supporting electrolyte concentrations.

We believe that the oxidation process in these polymer films is limited by the ionic transport rate. The oxidation product, poly(ferricenium), is ionic, the kinetics of oxidation in these films being limited by counterion flow into and out of the polymer phase (for charge neutrality). Thus, the electrolyte concentration had a notable influence on oxidation peaks.

At the same time, we noticed that the electrolyte concentration gave a more notable effect on peak potentials and peak currents of the PFDMS films relative to PFMPS films. This result indicates that PFDMS films are easier to solvate and swell, and they would be of lower diffusion resistivity and higher electrolyte permeability.

3.4. Influence of Temperature. The shapes of the CV peaks became sharper with rising temperature. The reduction peaks E_{pc} and oxidation peaks E_{pa} moved to a higher potential value and a lower potential value, respectively. Thus, the peak-to-peak separation ΔE_p decreased with rising temperature; moreover, the reduction peak E_{pc} moved more than the oxidation peak E_{pa}. At elevated temperature the variation of potential with scan rate decreased. Both oxidation and reduction peak current values increased linearly with rising temperature. The oxidation peak currents increased quicker than the reduction peak currents. The peak current values of PFDMS films increased faster than those of PFMPS films. The results are shown in Figure 5, from 25 to 50 °C. The reduction currents of PFDMS and PFMPS films increased 2.7 and 1.9 times, respectively. On their turn, oxidation currents of the PFDMS and PFMPS films increased 3.2 and 2.5 times, respectively. The current increase is likely to be controlled by the electrical conductivity of the solutions, the rate of diffusion, and the rate of electron transport. Therefore, the electrical conductivity of the solutions was measured in this temperature range. Results show that, from 25 to 50 °C, the
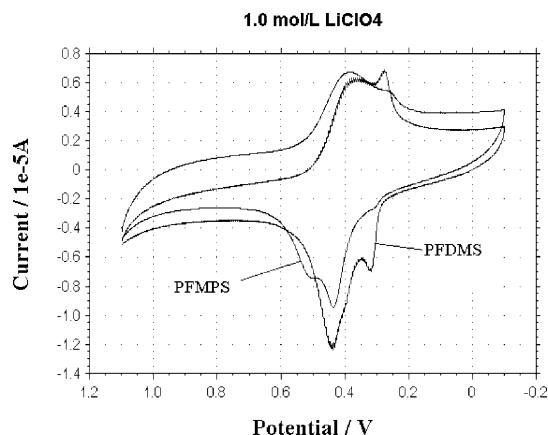
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Figure 6. Cyclic voltammograms of low-coverage films in aqueous LiClO$_4$. Coverage $\sim 2.8 \times 10^{-8}$ mol Fe cm^{-2}, concentration of electrolyte C(LiClO$_4$) = 1.0 M, potential scan rate v = 0.04 V s^{-1}, at 25 °C.

Figure 7. Relationship between the CV peak currents i_{pc} and the coverage of PFDMS film on a GC electrode; 1.0 M aqueous LiClO$_4$, potential scan rate 0.04 V s^{-1}, 25 °C.

electrical conductivity of the solutions increased from 4.8×10^{-3} S cm^{-1} to 6.4×10^{-3} S cm^{-1}, which is equivalent to only 30%. By contrast, the peak currents increased much more. This means that the segmental motions of the polymer chains, the rate of diffusion, and the rate of electron transport increased with rising temperature. Namely, the reversibility of the electrode reaction improved with increasing temperature.

3.5. Effect of Polymer Film Thickness. Film thickness also exerted a major effect on the cyclic voltammograms. At different film thicknesses, there were significant differences in peak shapes, peak currents, and peak potentials. At low apparent coverage, $\sim 2.8 \times 10^{-8}$ mol Fe cm^{-2}, the polymer films in contact with 1.0 M aqueous LiClO$_4$ exhibited two pairs of oxidation–reduction peaks, which were similar to the CV waves of poly(ferrocenylsilane) solutions.[3–6] The double peaks of thin PFDMS films could be seen at variable scan rates, but the double peaks of thin PFMPS films could be seen only at very slow scan rates. At low coverage, the oxidation peaks were sharper than the reduction peaks, and i_{pa} were larger than i_{pc}. Typical cyclic voltammograms of the low-coverage PFDMS films and the PFMPS films on a glassy carbon electrode in aqueous LiClO$_4$ are shown in Figure 6.

As the film thickness increased, however, striking changes occurred; two pairs of peaks became incorporated into a pair of broad peaks, and both the oxidation and the reduction peaks became asymmetrical broad peaks, while ΔE_P increased. E_{pa} values were more sensitive to film thickness; they shifted to positive potentials quickly. This phenomenon is consistent with the viewpoint that electrolyte permeability and diffusion control the oxidation process.

The double peak phenomenon was general in the CVs of poly(ferrocenylsilane) solutions;[3–6] the proposed explanation was that they resulted from the stepwise oxidation of the polymer, where the alternating ferrocene centers attached to the chain were oxidized.[21] For thick films, the rates of diffusion and electron transport were slowed, the electrode potential range of electrode process was enlarged, the potential difference of the stepwise redox process was decreased, and, as a result, the double peaks were incorporated into a broad peak.

At low coverage, the peak currents i_p increased with increasing film thickness, at the same scan rate. But at high coverages, no variation of the peak currents with films thickness was observed. The relationship between i_p and PFDMS film coverage is shown in Figure 7. The PFMPS films showed similar trends. Because i_{pc} increased quicker than i_{pa}, at high coverage i_{pc} was
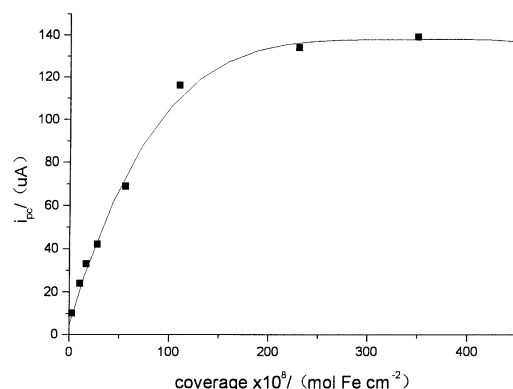
larger than i_{pa}. At low coverage, the electrode surface was covered incompletely and electrolyte penetration and mass diffusion proceeded fast and unhindered, while the amount of electroactive species on the electrode surface increased with increasing thickness. Therefore, as expected, i_p increased with increasing film thickness. When the polymer films were thick enough, the electrode surface was covered completely, and the diffusion layer was broad enough, the concentration of electrochemically active species in the diffusion layer was constant, the peak currents depended on the diffusion rates of electroactive species, and the reaction rate of the electrode processes; hence, i_p was affected by temperature and scan rate and was independent of the thickness of the films so that we recorded constant peak currents.

At low coverage, for example, $\sim 2.8 \times 10^{-8}$ mol cm^{-1}, the peak currents of both films were directly proportional to the scan rate, v, rather than to the square root of the scan rate, $v^{1/2}$, as experienced at high coverage. Peak potentials shifted slightly with increasing potential scan rate. The anodic and cathodic peaks were separated by small ΔE_P, about 40–50 mV for the PFDMS films. These CV features indicated that there were faster rates of the electrode processes, and the electrode processes of the film approached reversibility at low coverage. The electrochemical behavior of the ultrathin films was similar to that of monolayer films, in which the redox centers are surface confined. These results indicated that increasing the film thickness hindered diffusion and electron transport and slowed them down, and the film electrode processes became quasi-reversible or irreversible. This difference arises from the fact that in the case of the monolayer film there is no diffusion of electroactive material to the electrode since it is all confined at the electrode surface, and the voltammogram shown is for an electrochemically reversible system.[11]

Neutral site redox polymer films usually require several CV scans before a steady current–potential pattern can be acquired. Such a "break-in" pattern was observed for both the PFDMS and the PFMPS films, in aqueous solutions. The number of cycles required for this process depends on the film thickness, scan rate, temperature, and the nature of the supporting electrolyte. The low-coverage films needed only a few CV scans to reach steady state, while the thicker films needed several additional scans before a steady-state response was developed, for example, PFDMS films with coverage = 2.8×10^{-6} mol Fe cm^{-2} needed about 20 cyclic scans. These results supported the viewpoint that the film solvation and electrolyte penetration significantly affect the electrode processes of the film.

The "break-in" phenomenon of the poly(ferrocenylsilane) films can be viewed as follows: a virgin film has low ambient

TABLE 2: Kinetic Parameters of the Electrode Process for Two Films in 1.0 M Aqueous LiClO₄

temp °C	film	thickness (mol Fe cm⁻²)	peak type	αn_α	$D_{app} \times 10^{11}$ (cm² s⁻¹)	$k^0 \times 10^6$ (cm s⁻¹)
25	PFDMS	2.8×10^{-6}	oxidation peak	0.47	1.33	3.24
			reduction peak	0.51	1.42	1.98
	PFMPS	2.8×10^{-6}	oxidation peak	0.27	0.79	1.42
			reduction peak	0.29	1.64	1.68
50	PFDMS	2.8×10^{-6}	oxidation peak	0.56	12.9	15.6
			reduction peak	0.62	14.4	13.2
	PFMPS	2.8×10^{-6}	oxidation peak	0.37	2.36	5.36
			reduction peak	0.39	4.72	6.46

internal electrolyte concentration (and thus large ohmic resistance); oxidation of a few sites to ferrocenium draws counterions into the film, swells the film, and quickly lowers the film resistance. A fully oxidized and swollen film has a concentrated ferrocenium perchlorate polyelectrolyte solution and has a much lower ohmic resistance than virgin films. Along with decreasing film thickness, swelling of films by solvent and counterion penetration become quicker until equilibrium is reached. In the steady state, as described above, the films exhibit remarkable electrochemical stability and unchanged response over many hundreds of cycles.

3.6. Kinetic Parameters of the Film Electrode Process. According to CV theory,[20] there are relationships between the peak potential, peak current, and potential scan rate for an irreversible process as shown below:

$$i_p = 0.4958 nF(\alpha n_\alpha)^{1/2}\left(\frac{F}{RT}\right)^{1/2} A D_0^{1/2} C_0^* v^{1/2} \quad (1)$$

$$i_p = 0.227 nFAC_0^* k^0 \exp\left[-\left(\frac{\alpha n_\alpha F}{RT}\right)(E_p - E^{0\prime})\right] \quad (2)$$

where i_p is the peak current in A; A is the area of film coverage of the electrode surface in cm²; v is the potential scan rate in V s⁻¹; C_0^* is the concentration of the electroactive species in the films in mol cm⁻²; αn_α is the surface transfer coefficient; D_0 is the diffusion coefficient of the electroactive species in cm² s⁻¹; k^0 is the standard rate constant in cm s⁻¹; and the remaining terms have the usual significance.

We used the above equations to deal with the experimental data. Because the concentration of ferrocene sites in the film, C_0^*, cannot be measured accurately, we assumed an approximate film thickness $d = 10\ \mu m$ and obtained $C_0^* = $ coverage/d mol/cm². Equation 2 and Figure 3 indicated that the surface transfer coefficient αn_α and standard rate constant k^0 of the films would depend on the potential scan rates in practice. The values of αn_α and k^0 decreased with increasing scan rate. We took the segment of sufficiently high potential scan rate 0.1–1.0 V s⁻¹, where an approximate linear relationship between peak potential E_p and the logarithm of the scan rate $\ln v$ was attained, namely, the irreversible region, to calculate the kinetic parameters. First, the αn_α and k^0 values were calculated using eq 2, then D was calculated from eq 1, and the calculated diffusion coefficient D was termed the apparent diffusion coefficient D_{app}. The values of the calculated αn_α, D_{app}, and k^0 are listed in Table 2.

The obtained kinetic parameters, the surface transfer coefficient αn_α, the apparent diffusion coefficient D_{app}, and the standard rate constant k^0 of the films were extraordinarily small; even a 10-fold uncertainty in C_0^* would not affect this statement. They were smaller than the parameters obtained from the same polymers in solution. For example, D_{app} of the PFDMS in CH_2Cl_2 solution was of about 10^{-6} cm² s⁻¹.[15] These results indicated that the diffusion rates of the electroactive species and the rate of charge transport between the films and the

TABLE 3: Apparent Activation Energy E_a and Preexponential Factor A for a Diffusion-Controlled Process

film	process	$E_a (D_{app})$ (kJ mol⁻¹)	$A (D_{app})$ cm² s⁻¹	$E_a (k^0)$ (kJ mol⁻¹)	$A (k^0)$ cm s⁻¹
PFDMS	anodic	72.3	64.8	51.8	3.89×10^3
	cathodic	72.1	63.6	62.0	1.54×10^5
PFMPS	anodic	28.4	9.37×10^{-7}	26.5	1.05×10^{-1}
	cathodic	27.6	1.39×10^{-6}	20.7	1.46×10^{-2}

electrode were slow, because the poorly solvent-swollen high molecular weight polymer thick film hindered the mass diffusion and the interaction of active sites. It was the reason for the electrode processes to be irreversible at high scan rates.

Because the αn_α and D_{app} for cathodic peaks were larger than those for anodic peaks, the slopes of the linear equation were greater, as shown in Table 1. As a result, at routine potential scan rates, i_{pc} were larger than i_{pa}, but at very low scan rates, i_{pa} can be larger than i_{pc}.

In general, the αn_α expresses the electrode surface electron exchange efficiency, that is, the reversibility of the electrode process; αn_α affects the peak potentials and the symmetry of the curves. Along with the αn_α decrease, the cathodic peak shifts cathodically, the anodic peak shifts anodically, the peaks broaden, and the peak heights decrease. The rather small αn_α and k^0 values revealed that the low rates of charge transport and low electron exchange efficiency at the electrode surface might be the major factors responsible for the low electrode reaction rate. Upon comparing the kinetic parameters of the two films, we noticed that most values for the PFMPS films were smaller than those corresponding to the PFDMS films; especially, the αn_α of the PFMPS films was significantly smaller. These small kinetic parameters indicate that the slower charge transport rates between the films and electrodes, and the lower electron exchange efficiency on electrodes surface, were major factors that caused the lower film electrodes reaction rates and decreased reversibility of the PFMPS film electrode processes.

With rising temperature, all three kinetic parameters, αn_α, D_{app}, and k^0 increased, and the kinetic parameters of the PFDMS films increased faster than those of the PFMPS films. According to the Arrhenius equation

$$k^0 = A_k \exp\left(\frac{E_a(k^0)}{RT}\right) \quad (3)$$

$$D_{app} = A_D \exp\left(\frac{E_a(D_{app})}{RT}\right) \quad (4)$$

We can obtain the apparent activation energy, E_a, and the preexponential factor, A, for mass-diffusion-controlled process; the results are listed in Table 3.

By comparing the obtained data, one can find that the differences of the kinetic parameters between the two films, no matter what the magnitudes of D_{app} or k^0 would be, are mainly caused by the preexponential factor A, rather than the apparent

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activation energy E_a. This result is consistent with the viewpoint that the molecular structure of the polymer exerts a major effect on the kinetic characteristics, because of the preexponential factor A, mainly determined by the molecular configuration.

4. Conclusions

The CVs of two kinds of poly(ferrocenylsilane) films, PFDMS and PFMPS, on glassy carbon disk electrodes in aqueous LiClO$_4$ were recorded. The major influence factors, namely, the concentration of supporting electrolyte, temperature, film thickness, and the mechanism of the film electrode process, were investigated. Kinetic parameters of the electrode processes were calculated. The results indicate that the electrochemical processes of poly(ferrocenylsilane) films on glassy carbon electrodes are complex. The rate of electron transport through films and transport between films and electrodes are rather slow. At routine potential scan rates, the CV is quasi-reversible or irreversible. At low scan rates, the CV is nearly reversible.

The mechanism controlling the migration of electrochemical charge through the redox polymer films is also of interest. The experimental results demonstrate that the concentration of supporting electrolyte and thickness of the films exert a more notable influence on the oxidation peaks than on the reduction peaks (at low concentrations and at low coverages). This means that the flow of counterions into and out of the solvent-swollen poly(ferrocenylsilane) films is the rate-controlling process. Oxidation and reduction of fixed electroactive sites generated charged sites in the polymer film, for maintaining charge neutrality.

The kinetic parameters of the two films, the surface transfer coefficient αn_α, the apparent diffusion coefficient D_{app}, and the standard rate constant k^0, are extremely small, that is, smaller than those obtained for the same polymer in the bulk phase. This result indicates that the diffusion rates of active species and the rates of charge transport between the films and the electrodes are slow. It is because the poorly swollen thick polymer films hinder the mass diffusion and the interaction of the active sites that the electrode process is quasi-reversible or irreversible.

The phenyl groups in the PFMPS molecules hobble the mobile chains of the polymer. This molecular steric configuration limits the rate of mass diffusion and interaction of the electroactive sites in the PFMPS films so that their kinetic parameters, especially αn_α, are smaller than those of the PFDMS films. Therefore, the shapes of the voltammetric peaks of the PFMPS films are broader, both the cathodic and anodic peak

potentials are more positive, and the peak-to-peak separation ΔE_p is larger than the corresponding parameters of the PFDMS films.

We have found that the differences of the kinetic parameters between the two films, regardless of the D_{app} or k^0, were mainly caused by the preexponential factor A, rather than by the apparent activation energy E_a. This result is consistent with the viewpoint that the molecular structure of the polymer exerts a major effect on the kinetic characteristics of these electroactive films.

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