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Electrolyte Effects on Electrochemical Properties of Osmium Complex Polymer Modified Electrodes

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The electrolyte effects on the electrochemical behaviors of osmium complex polymer modified electrodes were investigated by a comparison between two osmium complexes, $[Os(bpy)_2(PVI)_{10}Cl]Cl$ ($Os\text{-}PVI_{10}$) and $[Os(bpy)_2(PVP)_{10}Cl]Cl$ ($Os\text{-}PVP_{10}$). The electrode process at $Os\text{-}PVI_{10}$ modified electrodes is reaction-controlled, while a diffusion-controlled electrode process exists at $Os\text{-}PVP_{10}$ modified electrodes. Both the cation and anion in supporting electrolytes strongly affect their electrochemical behaviors, such as the redox potential, wave shape and peak current. These phenomena are attributed to a change in the film structure and polymer swelling in various supporting electrolytes. The influence of electrolyte anions on the electrochemical behaviors is related to their hydrophobicity. The electrode process of $Os\text{-}PVP_{10}$ depends on the pH value of solutions, exhibiting different electron transfer mechanisms.

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Chemical and biosensors based on chemically modified electrodes, particularly polymer modified electrodes, have become an important field of study.[1-3] A modification of the electrode surface greatly improves the chemical, optical and electrical characteristics, leading to many applications as chemical sensors, electrochromic devices, electronic devices and energy storage as well as corrosion protection.[4] $[Os(bpy)_2(PVI)_{10}Cl]Cl$ and $[Os(bpy)_2(PVP)_{10}Cl]Cl$, where bpy is 2,2′-bipyridyl, PVI is poly(*N*-vinylimidazole), and PVP is poly(4-vinylpyridine), are two typical electron transfer mediators with a near-ideal electrochemical behavior,[5] which have been extensively used for the preparation of electrochemical enzyme sensors.[6-11] Modified electrodes based on these polymers show high electrochemical activity and can catalyze those reactions that are difficult for direct electron transfer, such as the electrochemical oxidations of epinephrine and dopamine,[6] ascorbic acid[7] and glucose.[8] After further cross-linking with enzymes, these modified electrodes have been designed for the determination of enzyme activity or their substrates[9,10] and as immunosensors.[11] However, the electrochemical behaviors of these metallopolymers are dependent on many factors, including the pH of the supporting electrolyte, electrolyte species, and solvent. Some of their influences, such as electrolyte species and solvents have been extensively reported by Vos, Forster and Hillman.[1–3,12–15] Vos and Forster studied the effects of the Cl^- and ClO_4^- concentrations and the time scale of electrochemical methods on the homogeneous and heterogeneous charge transfer dynamics of $Os\text{-}PVP_n$ ($n = 1 - 25$)[12] and the difference of SO_4^{2-} and ClO_4^- at $Os\text{-}PVP_{10}$.[13] In order to better understand and exert greater control over the transport properties of the electroactive polymers, the present work further compared the electrochemical behaviors of $Os\text{-}PVP_{10}$ and $Os\text{-}PVI_{10}$ modified electrodes under the same solution environments, and exhaustively studied the effects of the pH, electrolyte cations and anions on these properties by using cyclic voltammetry.

The film structure has a profound effect on the properties of polymer modified electrodes, because it influences both the transport rate of mobile species through a film and the local environment within which it undergoes a mediated charge transfer reaction with polymer-bond redox sites.[15] As generally accepted, the charge transport in such redox polymers undergoes an electron hopping or self-exchange process, accompanying the motion of charge-compensating counterions, solvent and polymer chain segments. The charge transport rate through the film depends on these factors.[16] Because high-redox site concentration results in a fast-electron self-exchange rate, the charge transport within the redox polymer modified electrodes is rapid.[17,18] On the other hand, the charge transport is related to the motion of counterions in polymer film for the requirement of electroneutrality. In other words, ion transport, rather than electron self-exchange, would become the rate-limiting factor of charge transport at an electroactive polymer-modified electrode with a high redox site concentration.[12,19,20] To further probe the relationship between the film structure of redox polymers and the electrode process, we selected two typical electroactive polymers with similar composition and structure to study solvent swelling and the effects of electrolyte type and concentration on the film structure and to examine the relative contributions from the charge transport, conterion diffusion in the electrode process.

Experimental

Apparatus and materials

A BAS-100B electrochemical analyzer (BAS, USA) and a conventional three-electrode system, with a saturated calomel electrode (SCE), relative to which all potentials are quoted, a platinum wire and an osmium complex polymer modified glassy carbon electrode as reference, counter and working electrode,

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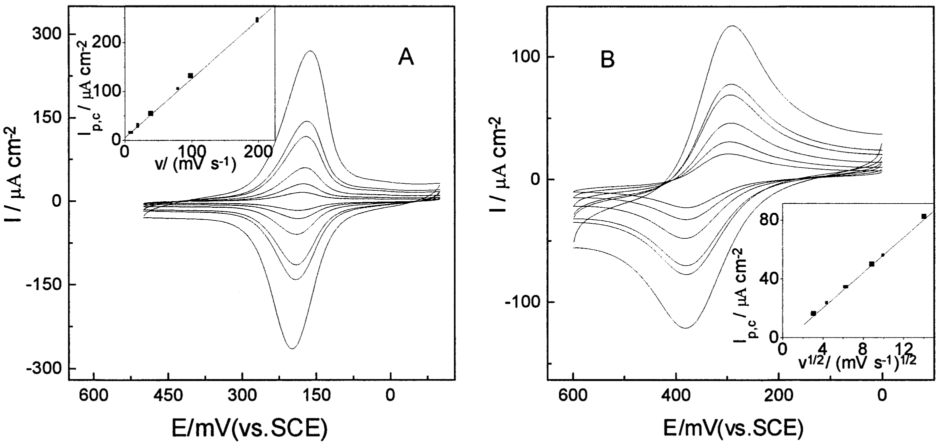

Fig. 1 Cyclic voltammograms of Os-PVI$_{10}$ (A) and Os-PVP$_{10}$ (B) modified electrodes in pH 7.0 PBS at 10, 20, 40, 80, 100, and 200 mV s^{-1} (from the lowest to the highest peak currents). Inset: dependence of the cathodic peak current density on the scan rate.

were used for electrochemical experiments. All measurements were carried out at room temperature without deaeration. Os-PVI$_{10}$ and Os-PVP$_{10}$ were synthesized and characterized according to the literature.[21] Phosphate buffer solutions (PBS), 0.1 M, with various pHs were prepared by mixing stock solutions of NaH_2PO_4 and NaOH, and were adjusted to a certain pH with 0.1 M H_3PO_4 and NaOH. All other chemicals were of analytical grade, and all solutions were prepared with doubly distilled water.

Osmium complex polymer modified glassy carbon electrodes

Prior to a modification, the glassy carbon electrodes were polished successively with 0.3 μm and 0.05 μm Al_2O_3 slurry on microcloth pads (Buehler) to a "mirrorlike" finish, and then rinsed with distilled water. The modified electrodes were prepared by dropping 5 μL Os-PVI$_{10}$ or Os-PVP$_{10}$ ethanol solution on their surface with subsequent drying at room temperature. The surface coverage of the electroactive centers within the Os-PVI$_{10}$ and Os-PVP$_{10}$ films was $(1.5 \pm 0.3) \times 10^{-9}$ and $(1.6 \pm 0.2) \times 10^{-9}$ mol cm^{-2}, respectively, estimated from the area under the anodic peak of cyclic voltammograms in pH 7.0 PBS at 10 mV s^{-1}. In studies where the electrolyte was changed, all of the experiments were carried out with fresh coating.

Results and Discussion

Electrochemical activity of osmium complex polymers

Cyclic voltammograms of two modified electrodes in pH 7.0 PBS at various scan rates are shown in Fig.1. They exhibit a couple of redox peaks with an average formal potential of +181 mV and +338 mV, respectively.[14,19] There is a linear relationship between the peak current of Os-PVI$_{10}$ and the scan rate when less than 200 mV s^{-1}. The cyclic voltammograms of an Os-PVI$_{10}$ modified electrode give a very small peak-to-peak separation, ΔE_p (for example, 8 mV at 10 mV s^{-1}), indicating that the electrode reaction is typical of a reversible process involving a confined reactant.[19] To the contrary, at an Os-PVP$_{10}$ modified electrode, the peak-to-peak separation is much larger, which is around 81 mV at a scan rate of 10 to 200 mV s^{-1}. The peak current of Os-PVP$_{10}$ is proportional to the square root of the scan rate. The presence of diffusion tailing, the non-zero ΔE_p and the relation between the peak current and the scan rate are indicative of a diffusion-controlled electrochemical response.[3] This is different from that of Os-PVP$_{10}$ cross-linked with organic molecules at which the effect of a potential sweep rate on the peak currents was found to be linear.[22] Here, surface-electron transfer or the electron self-exchange rate is rather fast. The diffusional charge transport contains the ion transport or segmental polymer chain motion within the polymer.[2,3] The motion of counterions in the film is for the requirement of electroneutrality. Rapid electron transfer is generally favored by a high redox site concentration.[19] Thus, the film structure of the Os-PVP$_{10}$ polymer is compact, while the Os-PVI$_{10}$ polymer is relatively swollen and porous.[3,14,23]

Effect of chloride anion

At an Os-PVI$_{10}$ modified electrode, the addition of NaCl to 0.1 M PBS increases slightly the current of the cyclic voltammogram (Fig. 2A). The peak-to-peak separation becomes smaller upon an addition of NaCl up to the concentration of 1.0 M (ΔE_p changes from 33 mV to 14 mV). Here, liquid junction effects due to a change in the NaCl concentration can be neglected,[24] and the impact of an ohmic drop on these experiments performed in 0.1 M PBS is very small. When the concentration of NaCl increases from 0 to 2.5 M, the $E^{0\prime}$ shifts negatively by about 25 mV according to the equations $E_{pa} = 163 - 23\log c$ (mV) ($R = 0.999$) and $E_{pc} = 147 - 16 \log c$ (mV) ($R = 0.983$). These changes result from the permeation of some Cl^- anions as counterions.

At an Os-PVP$_{10}$ modified electrode, $E^{0\prime}$ also shifts negatively for about 55 mV according to the equations of $E_{pa} = 330 - 39 \times \log c$ (mV) ($R = 0.999$) and $E_{pc} = 240 - 35\log c$ (mV) ($R = 0.999$), and the peak current increases greatly (Fig. 2B). Thus, the oxidation of an Os$^{II/III}$ redox couple is easier after Cl^- anions are added into the solution. The change in the ΔE_p value (only 11 mV, from 98 mV to 87 mV) is less than that for an Os-PVI$_{10}$ film. The electrode process is also controlled by the diffusion of counterions for electroneutrality. The larger change in the $E^{0\prime}$ value and the peak current of Os-PVP$_{10}$ rather than Os-PVI$_{10}$ upon the addition of NaCl indicates that the effect of chloride anion as a counter anion on the diffusion-controlled electrode process is larger than that on the surface-controlled electrode process. Because the film of Os-PVI$_{10}$ is porous, phosphate anions can also permeate into the film during the electrochemical process. However, because the Os-PVP$_{10}$ film is dense, it is more difficult for phosphate anions to permeate

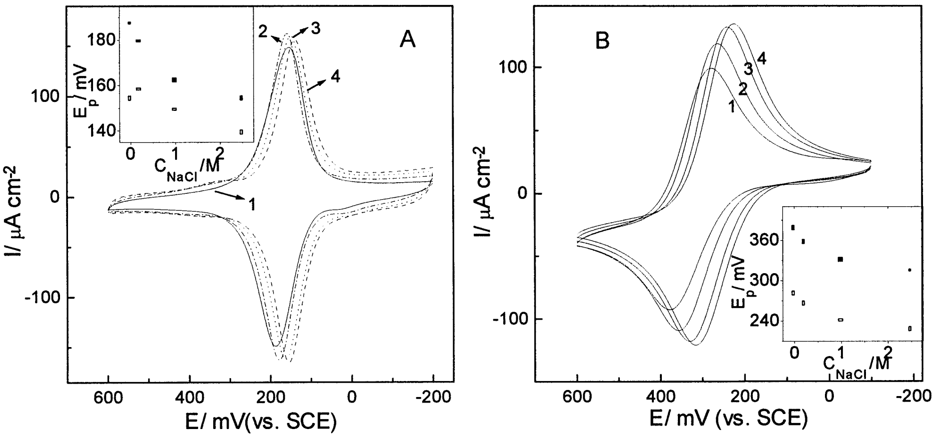

Fig. 2 Cyclic voltammograms of Os-PVI$_{10}$ (A) and Os-PVP$_{10}$ (B) modified electrodes in pH 7.0 PBS containing (1) 0, (2) 0.2, (3) 1.0 and (4) 2.5 M NaCl at 100 mV s^{-1}. Inset: plots of E_{pa} (■) and E_{pc} (□) *vs.* c_{NaCl}.

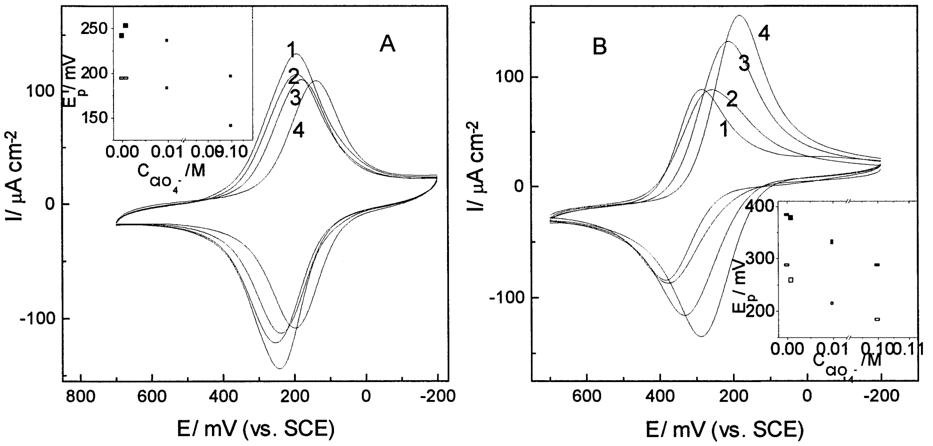

Fig. 3 Cyclic voltammograms of Os-PVI$_{10}$ (A) and Os-PVP$_{10}$ (B) modified electrodes in PBS 7.0 containing (1) 0, (2) 0.001, (3) 0.01 and (4) 0.1 M NaClO$_4$ at 100 mV s^{-1}. Inset: E_{pa} (■) and E_{pc} (□) *vs.* c_{NaClO4}.

into the film, which is also one of the factors making the $E^{0\prime}$ value of Os-PVP$_{10}$ film more positive and the oxidation of an Os$^{II/III}$ redox couple more difficult. Thus, the effect of chloride anion on the redox behaviors of Os-PVP$_{10}$ is larger than that of Os-PVI$_{10}$.

Effect of ClO_4^- anion

Similarly, the effects of ClO_4^- anion on the electrochemical behaviors of two electroactive polymers are shown in Fig. 3. With increasing ClO_4^- concentration in 0.1 M pH 7.0 PBS, the formal potentials ($E^{0\prime}$s) at two modified electrodes shift in a negative direction. The changes in the peak potentials follow the equations $E_{pa} = 172 - 28\log c$ (mV) ($R = 0.975$) and $E_{pc} = 119 - 26\log c$ (mV) ($R = 0.954$) for Os-PVI$_{10}$ and $E_{pa} = 242 - 45 \times \log c$ (mV) ($R = 0.999$) and $E_{pc} = 143 - 37\log c$ (mV) ($R = 0.995$) for Os-PVP$_{10}$. The appearance is similar to that when the Cl^- anion concentration increases. The slopes and the change in their $E^{0\prime}$ values upon the addition of ClO_4^- anion are larger than upon the addition of Cl^- anion. When the concentration of ClO_4^- increases from 0 to only 0.1 M, the $E^{0\prime}$s of Os-PVI$_{10}$ and Os-PVP$_{10}$ shift negatively for about 50 mV and 95 mV, respectively. Thus, the ClO_4^- anion is a better counterion for the Os$^{II/III}$ redox couple. This phenomenon can be explained using the hydrophobicity of two kinds of anion. Because the hydrophobicity of ClO_4^- anion is stronger, it has been identified as forming compact polymer films due to "dehydrating" and "cross-linking" properties.[14,15,23,25] The ClO_4^- anion possesses a stronger ability of permeation and motion than the Cl^- anion into the film as a counterion in the process of an electrode reaction, resulting in a larger change in the $E^{0\prime}$ value of the Os$^{II/III}$ redox couple. The larger shift of $E^{0\prime}$ at the Os-PVP$_{10}$ electrode is due to the more compact structure.[3] Because the compact structure of Os-PVP$_{10}$ polymer makes the permeation of other anions with lower hydrophobicity more difficult, the effect of the ClO_4^- concentration on the redox behaviors of Os-PVP$_{10}$ is greater.

The changes in the peak currents of two polymers are different. At an Os-PVI$_{10}$ modified electrode, with increasing ClO_4^- concentration, the peak current decreases and then trends to a constant value, while the peak current increases at an Os-PVP$_{10}$ modified electrode. The increase is due to the fact that the permeability of ClO_4^- is stronger than phosphate anions, and thus its diffusion rate faster. Upon the addition of ClO_4^-, it becomes the major role of the counterion to maintain electroneutrality. The effect of the ClO_4^- concentration on the charge-transport rate of Os-PVI$_{10}$ polymer is complex. The Os-

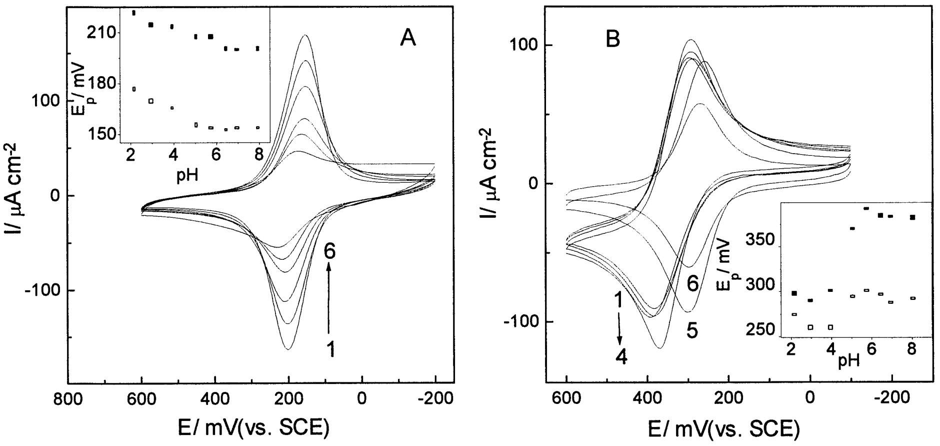

Fig. 4 Cyclic voltammograms of Os-PVI$_{10}$ (A) and Os-PVP$_{10}$ (B) modified electrodes in pH (1) 8.1, (2) 6.5, (3) 5.8, (4) 5.1, (5) 4.0 and (6) 2.2 PBS containing 0.1 M NaCl at 100 mV s^{-1}. Inset: plots of E_{pa} (■) and E_{pc} (□) *vs*. pH.

PVI$_{10}$ polymer has a porous structure. The rate-determining step of its electrode reaction is charge transport. Depending on the distance separating the active sites, the motion of polymer chain segments may be required to bridge the interstice separation for charge transport.[16,19] The permeation of ClO_4^- possibly decreases the polymer chain motion, resulting in a change in the peak currents.

Inference of pH

A solution containing 0.1 M NaCl and 0.1 M PBS was used for this study, where 0.1 M NaCl was kept in all electrolyte solutions to avoid the effect of a counterion concentration change due to the phosphoric acid equilibria over the pH range. At an Os-PVI$_{10}$ modified electrode, the changes in the peak potentials follow the equations E_{pa} = 227 – 3.8pH (mV) (R = 0.963) and E_{pc} = 181 – 4.2pH (mV) (R = 0.923) (Fig. 4A). In acidic solutions, the charge current increases, causing the ratio of the Faraday current to the charge current to greatly decrease and the wave shape to become worse. Because these appearances are attributed to a swelling of the polymer in a low-pH solution,[13] more protons permeate into the film. The permeation of protons increases the charge current and makes the film structure looser and the oxidation of Os$^{II/III}$ more difficult, resulting in a great decrease in the redox peak currents of the Os-PVI$_{10}$ polymer. On the other hand, the interaction between protons and electroactive centers with positive charge also reduces the stability of polymers. Some of the electroactive centers are possibly divorced from the complexes. This inference is also supported by the phenomenon that the peak current of the Os-PVI$_{10}$ modified electrode decreases when it is put back into a solution of high pH after scanning in an acidic solution.

At an Os-PVP$_{10}$ modified electrode, some changes are also observed along with a change in the solution pH (Fig. 4B). When pH >5.0, the peak current of an Os$^{II/III}$ redox couple increases with decreasing pH. The formal potential and peak separation remain almost constant. However, when the pH is lower than 5.0, the formal potential shifts toward a more negative value and the peak separation greatly decreases with decreasing pH (from 73 mV to 48 mV for pH 5.1 to 4.0), indicating that the electrode reaction turns from a diffusion-controlled process to a surface-controlled process. All of these changes and a significant increase in the peak current at pH 5.1 are attributed to swelling of the polymer due to the interaction between protons and the Os Os$^{II/III}$ redox couple. The swelling produces a loose structure, which facilitates the mass transport of counterions in the film, and thus the current increases. But, when pH <5.0, the peak currents decrease again. These phenomena are due to protonation of the pendant pyridine in the PVP polymer chain with a pK_a of 3.3 for PVP,[13,21] which results in a further swelling of the polymer and yields a more open porous structure while changing the charge transport mechanism. The porous structure makes the permeation of counterions in the film easier, thus leading to a negative shift of formal potential. The swelling, on the other hand, decreases the surface concentration of Os$^{II/III}$ electroactive sites and the electron self-exchange rate, thus, as seen at Os-PVI$_{10}$, the peak current decreases.

Because the electrochemical responses of Os-PVI$_{10}$ to the pH value of the solution further indicates that the film on the electrode surface is more porous, thus more counterions can permeate into the polymer, and the motion of counterions is also very fast. The electrode process is surface-controlled. With an increase in the proton concentration, the rate of electron self-exchange decreases, resulting in a decrease of the redox peak current. Contrarily, the film of Os-PVP$_{10}$ is denser, showing a diffusion-controlled electrode process. The permeation of protons produces a porous film structure and displays some different electrochemical behaviors from the Os-PVI$_{10}$ film.

Responses to Li^+, Na^+, K^+ cations

Figure 5 shows cyclic voltammograms of the Os-PVI$_{10}$ and Os-PVP$_{10}$ modified electrodes in pH 7.0 PBS including 0 or 0.05 M $LiClO_4$, $NaClO_4$ and $KClO_4$, respectively. The shifts of the $E^{0\prime}$s of both polymers mainly result from the addition of ClO_4^- anion. The effects of Li^+, Na^+ and K^+ cations on the peak potentials of the Os$^{II/III}$ redox couple are very small. As observed, upon the addition of protons, the permeation of cations into the film produces more swelling and a porous structure. The effect of cations comes from the change in the film structure. The change sequence of the peak currents of the Os$^{II/III}$ redox couple upon the addition of three cations is $i_{p,Li^+}<i_{p,Na^+}<i_{p,K^+}$. Because the radius of the hydration the K^+ cation is the smallest,[24] it easily permeates into the film. Thus, film swelling is the greatest in the case of K^+ cation, which increases the motion rate of counterions in the polymer film for the requirement of electroneutrality, which results in the largest increase in the peak current for a diffusion-controlled process at the Os-PVP$_{10}$ modified electrode. While at an Os-PVI$_{10}$

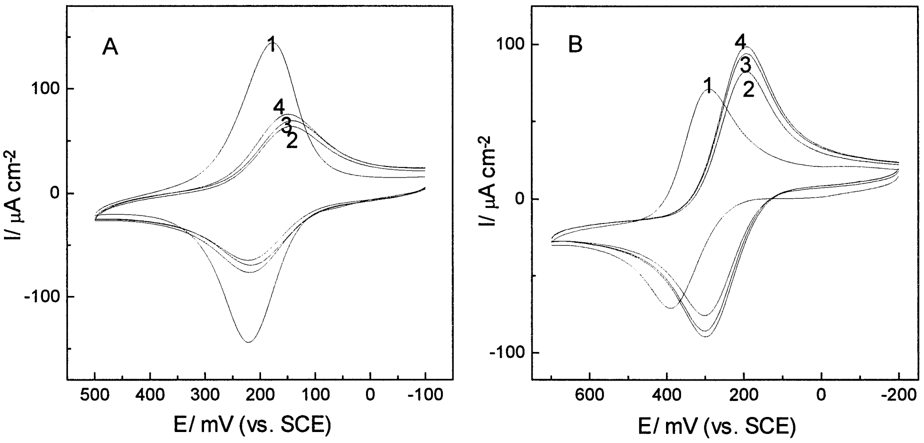

Fig. 5 Cyclic voltammograms of Os-PVI$_{10}$ (A) and Os-PVP$_{10}$ (B) modified electrode in pH 7.0 PBS containing 0 (1) and 0.05 M Li$^+$ (2), Na$^+$ (3), K$^+$ (4) at 100 mV s^{-1}.

electrode modified with a more porous structure, the permeation of cations has little effect on the Faraday current, but increases the charge current as those observed in a study of the pH effect. Similarly, the change in the charge current in the case of the K$^+$ cation is the greatest.

Conclusions

The electrode reactions of an Os$^{II/III}$ redox couple at Os-PVI$_{10}$ and Os-PVP$_{10}$ modified electrodes are typical examples of two different dynamic processes. The interaction between the electrolytes and the polymer has a profound influence on their electrochemical properties. The permeation of electrolyte ions into the film changes the surface status and the transport rates of the charge and counterion. The surface structure of the Os-PVP$_{10}$ modified electrode is dense, and the high concentration of closely packed redox sites favors fast electron self-exchange. Thus the electrode process is diffusion-controlled. Film swelling not only improves its charge-transport properties, but can also change the rate-determining step of the electrochemical process. However, the Os-PVI$_{10}$ modified electrode has a more porous structure and the electrode process is considered to be surface-controlled. Because the swelling of the film increases the osmium-osmium separation, a high electrolyte concentration would be expected to reduce the charge-transport rate, which results in a decrease in the peak current.

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