Adsorption and desorption of complex metal ions in polyviologen or its polyion complexes with poly(sulphonate)s by the control of a given potential

Masayuki Kato, Naoto Oki, Hiroyuki Ohno and Eishun Tsuchida*
Department of Polymer Chemistry, Waseda University, Tokyo 160, *Japan*

and Noboru Oyama
Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology, Tokyo 184, *Japan*

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Complex anions and a complex cation were concentrated electrostatically in the domain of polyviologen by the control of a given potential. Pyrolytic graphite electrodes were coated with polyviologen or the polyion complex of polyviologen with poly(sulphonic acid) for the concentration of complex anions or the complex cation, respectively. In an aqueous solution in which $Mo(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$ coexisted, the polyviologen-coated electrode predominantly concentrated $Mo(CN)_8^{4-}$. Furthermore, the $Mo(CN)_8^{4-}$ incorporated in the film was desorbed by reducing the charge density of polyviologen. The desorption rate was proportional to the charge density of polyviologen which depended on a given potential. On the other hand. $Ru(NH_3)_6^{3+}$ was adsorbed in the domain of the polyion complex of polyviologen with poly(sulphonic acid) and it was desorbed completely in a few seconds by reducing the overall charge density of the polyion complex. Generally, reversible adsorption–desorption of multivalent ions could be performed by changing the given potential if redox-active sites were fixed or chemically bonded in the polymer matrix. Redox-active polymers were stabilized by polyion complex formation with oppositely charged polyelectrolytes.

Keywords Polyion complex; polyviologen; reversible redox system; selective ion concentration

INTRODUCTION

In the conventional techniques for ion concentration, there are many problems, for example troublesome procedures,difficulty in treatment of large quantities, etc. It is well known that polyelectrolytes can interact with several micro-ions and that the interaction force gets larger with increase of valency of the micro-ions. The ion concentration process would be available if the adsorption and desorption of ions could be controlled reversibly by a given potential. Recently, an electric-field-regulated redox system was used for the concentration of multivalent ions[1]. A carbon electrode coated with polypyridine or poly(benzyl ammonium) could concentrate $IrCl_6^{3-}$ or $Mo(CN)_8^{4-}$ from a very dilute aqueous system. This knowledge is applicable to several ion sensors. Here, selective concentration and reversible adsorption–desorption of multivalent complex ions were investigated by changing the charge density on the coated polyviologen or its polyion complex with poly(sulphonate).

EXPERIMENTAL

Materials

Poly(xylylviologen) (PXV) was prepared from xylylene dibromide (*o*-, *m*-, *p*-) and 4,4′-bipyridine by the successive Menshutkin reaction in *N*,*N*-dimethylformamide (DMF) at 60°C for 72 h. PXV was obtained as a precipitate in DMF solution after polymerization. The precipitate was filtered and washed with dry acetone on a glass filter. PXV was obtained as a yellow powder after drying *in vacuo*. The intrinsic viscosity of PXV (*meta* derivative) was 3.9×10^{-2} dl g^{-1} (in 0.5 M KBr aqueous solution at 25°C) and gave an average molecular weight of about 8×10^3.[2] As *o*- and *p*-PXV showed less solubility in water, *m*-PXV was used throughout the experiments. Poly(*p*-styrenesulphonate sodium salt) (PSS) was prepared by radical polymerization of the corresponding monomer[3]. *p*-Styrenesulphonic acid (Seimi Kagaku Co., Ltd) (5.00 g) was dissolved in 25 ml of degassed pure water and the temperature was kept at 60°C for 5 h after adding 0.061 g of potassium persulphate (Tokyo Kasei Co., Ltd) as a radical initiator. The polymer solution obtained was poured slowly into an excess of dry acetone. A white precipitate of PSS was collected on a glass filter and washed with dry acetone. PSS was used after complete drying under reduced pressure. The average molecular weight of PSS was 5×10^4.

'Nafion' membrane 125 (E. I. du Pont de Nemours and Co.) of perfluorosulphonic acid was boiled in 0.20 M NaOH solution for 30 min, and washed with distilled water several times, then dried under reduced pressure.

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* To whom correspondence should be addressed

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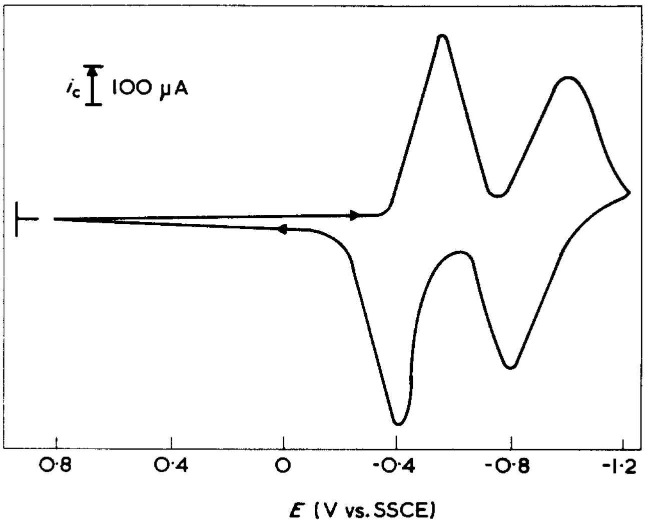


Figure 1 Cyclic voltammogram for the electrode coated with poly(xylylviologen) in 0.20 M $NaClO_4$ aqueous solution at 25.0°C: PXV, 1.4×10^{-7} unit mol cm^{-2}; scan rate, 190 mV.s^{-1}

Finely cut chips of the membrane were soaked in dimethyl sulphoxide (DMSO) and the resulting solution was boiled again for 3 h and then filtered through a glass filter. The filtrate was used as the stock solution of 'Nafion', after adding ethanol (EtOH) to the filtrate until the concentration of Nafion reached 5.6 mg ml^{-1}. An aqueous solution containing 1.2 mM viologen unit as PXV was prepared as the PXV stock solution. An aqueous solution containing 2.4 mM of styrene sulphonate unit as PSS was also used as the PSS stock solution.

Reagent-grade $K_4Fe(CN)_6$ was used after recrystallization from water and complete drying. $K_4Mo(CN)_8$ was synthesized and purified by a conventional method[4].

Electrode coating

Pyrolytic graphite electrodes were prepared by binding and sealing a disc of basal plane pyrolytic graphite (BPG) (Union Carbide Co.) on the edge of a stainless cylinder with heat-shrinkable olefin tube. All electrodes employed in this study had geometric areas of 0.17 cm^2. Fresh electrode surfaces were produced by cleaving the disc of BPG with a scalpel. The polymer-coated electrodes were prepared by the same method as described before[1].

PXV coating. 2.0 μl of PXV stock solution was pipetted onto the freshly cleaved surface of BPG and then air-dried to remove water.

PXV–PSS complex coating. 2.0 μl of PXV stock solution and 2.0 μl of PSS stock solution were pipetted and mixed directly on the surface of BPG to form PXV–PSS complex instantaneously. This electrode was used after air-drying.

PXV–Nafion complex coating. 2.0 μl of PXV stock solution and 2.0 μl of Nafion stock solution were pipetted out onto the surface of BPG. The following procedure was the same as that of PXV–PSS complex coating.

Electrochemical experiment

The potentiostat, frequency generator and other apparatus employed were purchased from Nikko-Keisoku Co., and cyclic voltammograms were recorded continuously with an *X–Y* recorder (Watanabe Sokki Co.). The quantities of coated viologen were calculated by integrating the measured current of the cyclic voltammogram which was observed at a slow scan rate (2.0 mV s^{-1}). Solutions were bubbled with argon to expel oxygen. The supporting electrolytes used were NaCl (0.20 M), CF_3COONa (0.20 M) or sea water. All the experiments were conducted at 25.0°C. Potentials were corrected with respect to a sodium-chloride-saturated calomel reference electrode (SSCE).

RESULTS AND DISCUSSION

The cyclic voltammogram of *m*-PXV is shown in *Figure 1*. The redox potentials of *o*, *m*- and *p*-PXV are listed in *Table 1*. These values were compared with those of benzyl viologen (the first reduction, $E_{1/2} = -0.60$ V; the second reduction, $E_{1/2} = -0.78$ V vs. SSCE, pH 9.0). The half-wave potential ($E_{1/2}$) of the first reduction wave was shifted to the anodic side by about 200 mV, and that of the second reduction wave was shifted to the cathodic side by 30–100 mV. Such potential shifts seemed to be based on the effect of the intramolecular interaction between redox-active sites of the polymer. The stability of the coated film depended greatly on the given potential range. The stability of PXV on BPG could be detected as the changes of peak areas as shown in *Figure 2*. *Figure 2a* shows the voltammogram of PXV when the potential was given from +0.80 V to −0.80 V vs. SSCE (the valency of viologen unit changed from di-cation to cation radical state). The peak current i_p was nearly constant even after 2 h scanning. In this condition, PXV was fixed stably on the electrode. However, with potential scanning from +0.80 V to −1.20 V vs. SSCE (the valency of viologen unit changed from di-cation to non-ion state) (*Figure 2b*), i_p decreased gradually and it did not become constant even after 2 h. The PXV film seemed to be unstable when it was reduced to a non-ion state.

Ferrocyanide $Fe(CN)_6^{4-}$ and octacyanomolybdate $Mo(CN)_8^{4-}$ were chosen as the applied anions. CF_3COONa (0.20 M), NaCl (0.20 M), $NaClO_4$ (0.20 M) and sea water were employed to clarify the effect of supporting electrolyte for the adsorption behaviour of $Fe(CN)_6^{4-}$ on PXV film-coated electrodes. The adsorption quantity of $Fe(CN)_6^{4-}$ reached a maximum when CF_3COONa was employed as the supporting electrolyte. But the coated film itself was not stable in CF_3COONa solution. As there are several divalent cations in sea water, they interfered with the adsorption of complex anions on the polymer matrix. Thus, NaCl seemed to be best (see *Table 2*) as a supporting electrolyte and it was used in the following experiments.

Figure 3 shows the cyclic voltammorgrams for a PXV-coated electrode soaked in a 0.2 mM solution of $Fe(CN)_6^{4-}$. The peak current i_p corresponding to the redox

Table 1 Redox potentials of applied PXV

	Redox potential (V vs. SSCE)	
PXV	First wave	Second wave
o-PXV	−0.41	−0.81
m-PXV	−0.44	−0.89
p-PXV	−0.39	−0.89
Benzyl viologen	−0.60	−0.78

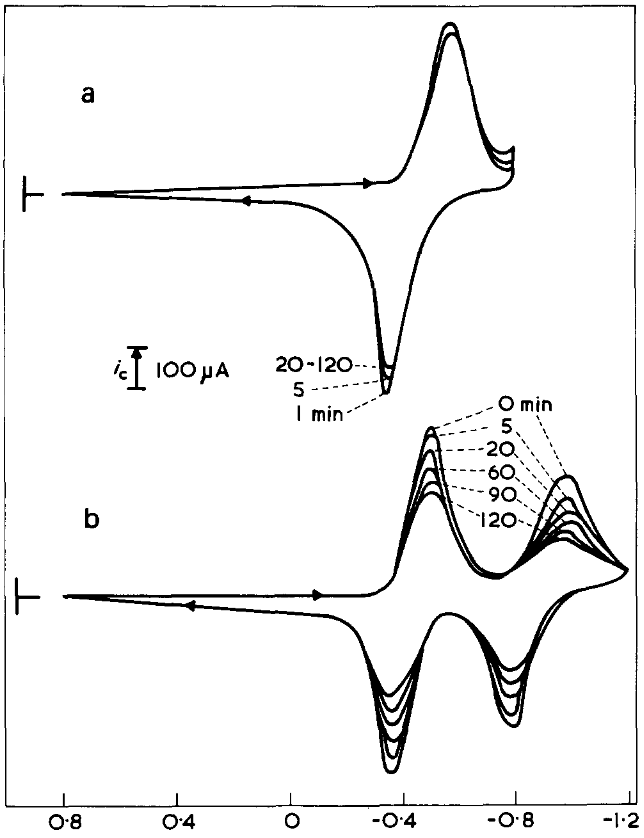


Figure 2 Changes of cyclic voltammograms for the electrode coated with PXV: (a) potemtial cycling from +0.80 V to −0.80 V; (b) potential cycling from +0.80 V to −1.20 V. Conditions were the same as in *Figure 1*

Table 2 Influence of supporting electrolytes on the concentration of Fe(CN)$_6^{4-}$ in the PXV film

Supporting electrolyte	Fe(CN)$_6^{4-}$ (μC cm^{-2})	
	Anodic wave	Cathodic wave
0.20 M CF$_3$COOH	118	138
0.20 M NaCl	119	123
Sea water	32	38

of Fe(CN)$_6^{4-}$ ($E_{1/2}$ = +0.18 V vs. SSCE) increased gradually, and saturated after 8 min. The i_p of the PXV-coated electrode was higher than that of the bare BPG electrode. Fe(CN)$_6^{4-}$ seemed to be accumulated and fixed selectively through an electrostatic force in spite of the presence of a large excess of chloride ions (1000 times equivalent). Such behaviour of ion accumulation has already been reported by Oyama and Anson[1]. This can be explained by an increase of the equilibrium constant of the multivalent anions compared with that of monovalent anions with polycation matrix. The dotted line in *Figure 3* shows the voltammogram of redox curve for PXV. Quantities of adsorbed Fe(CN)$_6^{4-}$ in the PXV film were measured by integrating the current of the peak (see *Table 3*). A similar experiment was carried out for Mo(CN)$_8^{4-}$ ($E_{1/2}$ = +0.50 V vs. SSCE) as shown in *Figure 4*. About 30% of the cationic sites in the PXV matrix were occupied by Mo(CN)$_8^{4-}$. This fixation efficiency (see *Table 4*) was higher than that of the Fe(CN)$_6^{4-}$ system (cf. *Table 3*).

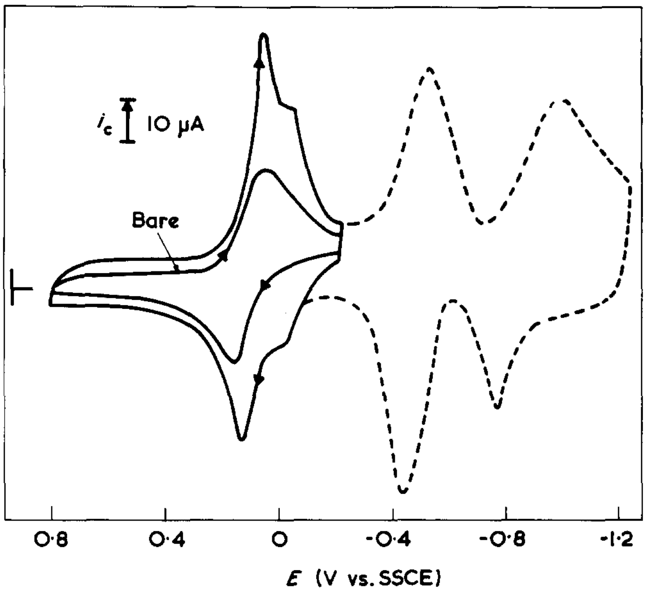


Figure 3 Cyclic voltammograms for Fe(Cn)$_6^{4-}$ fixed on bare or PXV-coated electrodes after 10 min cycling at 25.0°C: PXV, 1.4 x 10^{-7} unit mol cm^{-2}; [Fe(CN)$_6^{4-}$], 0.20 mM in 0.20 M NaCl aqueous solution; scan rate, 190 mV s^{-1}

Table 3 Adsorption of Fe(CN)$_6^{4-}$ on the electrode coated with PXV

Anodic wave	Coverage, Q (μC cm^{-2})
Fe(CN)$_6^{4-}$	
bare electrode	120
PXV-coated electrode	282
adsorption amounts in PXV matrix	162
PXV	
first wave	318
second wave	250

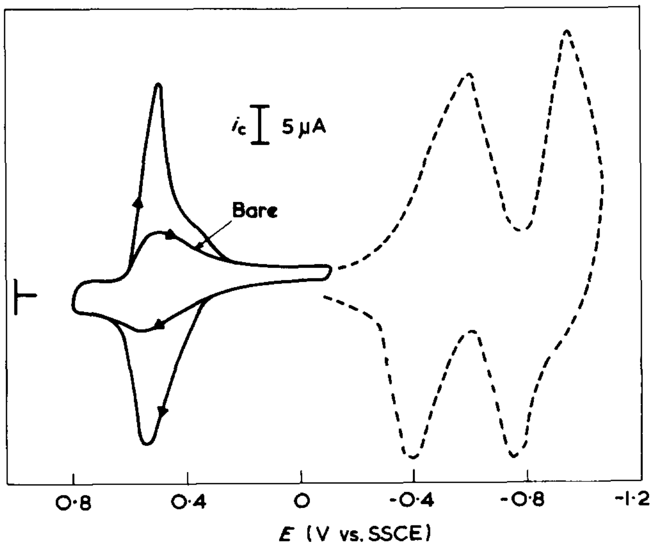


Figure 4 Cyclic voltammograms for Mo(CN)$_8^{4-}$ fixed on bare or PXV-coated electrodes after 10 min cycling at 25.0°C: PXV, 1.4 x 10^{-7} unit mol cm^{-2}; [Mo(CN)$_8^{4-}$], 0.20 mM in 0.20 M NaCl aqueous solution; scan rate, 190 mV^{-1}

Table 4 Adsorption of $Mo(CN)_8^{4-}$ on the electrode coated with PXV

Anodic wave	Coverage, Q ($\mu C\ cm^{-2}$)
$Mo(CN)_8^{4-}$	
bare electrode	29
PXV-coated electrode	184
adsorption amounts in PXV matrix	155
PXV	
first wave	259
second wave	202

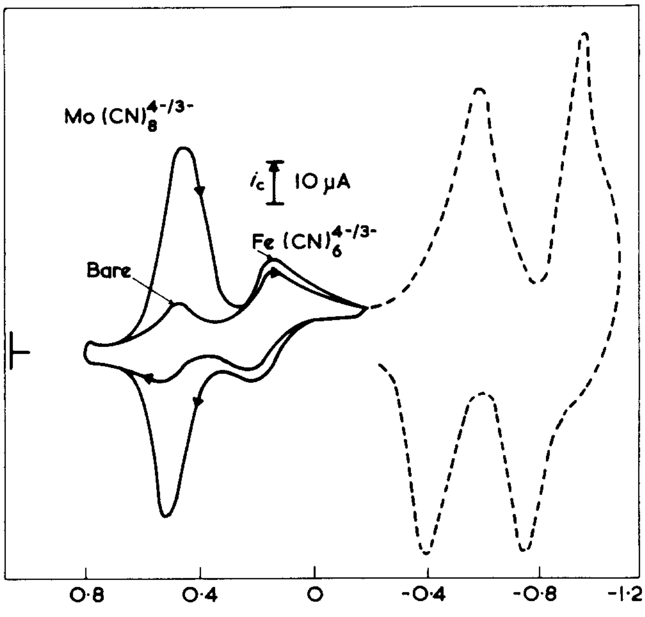
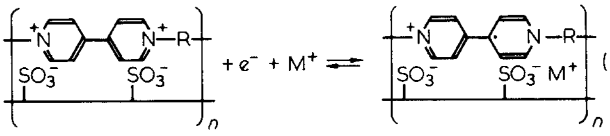


Figure 5 Cyclic voltammogram for the electrode coated with PXV soaked in the mixed solution of $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ at 25°C: PXV, 1.4×10^{-7} unit mol cm^{-2}; [$Fe(CN)_6^{4-}$], 0.20 mM; [$Mo(CN)_8^{4-}$], 0.20 mM after 10 min cycling; scan rate, 190 mV s^{-1}

Selective adsorption was observed in the mixed solution of $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$. *Figure 5* shows the voltammogram for the PXV-coated electrode soaked in a mixed solution of 0.20 mM $Fe(CN)_6^{4-}$ and 0.20 mM $Mo(CN)_8^{4-}$. $Mo(CN)_8^{4-}$ was predominantly adsorbed in the PXV matrix, and the adsorbed amount of $Fe(CN)_6^{4-}$ was small and was almost the same as that for the bare electrode. The quantity of adsorbed $Mo(CN)_8^{4-}$ was the same as that obtained for the PXV-coated electrode system soaked in only $Mo(CN)_8^{4-}$ solution. Thus, PXV shows apparent selectivity to the concentration of complex anion. This selectivity was considered to be based on the difference of anion radius or hydrophobicity of these complex anions.

Incorporated multivalent complex anions in PXV matrix were desorbed by a decrease of cationic charge density of PXV. About half and all of the cationic charges of PXV were reduced when the potential was given to −0.70 V and −1.20 V, respectively. The potential was fixed at −0.70 or −1.20 V (vs. SSCE) for 5 min and then the first scanning curve was recorded. The desorption efficiency (%) is summarized in *Table 5*. Though $Fe(CN)_6^{4-}$ was desorbed theoretically (about 50%), the desorption efficiency of $Mo(CN)_8^{4-}$ at −0.70 V was half that of $Fe(CN)_6^{4-}$. This might correspond to the strength of the interaction between PXV matrix and complex anion, or to the hydrophobicity of $Mo(CN)_8^{4-}$.

The overall charge density of the PXV-poly(sulphonic acid) complex can be varied dynamically only by regulating the given potential. Equation (1) shows a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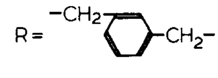

schematic adsorption behaviour of cations on PXV-poly(sulphonic acid) complex-coated electrode. As the charge density of the complex domain could be controlled by the potential, repetition of adsorption and desorption of cation was performed quite easily. The authors have already studied the formation process and the basic characteristics of polyion complexes[3,5–7]. Our summarized results gave important suggestions for the concentration of multivalent small ions, namely, once formed, a polyion complex is insoluble in water and almost all organic solvents, but it has a well solvated domain. The equilibrium constant of complexation between oppositely charged polyelectrolytes was much larger than that between polyelectrolyte and small ions. These facts provided us with a demonstration of a rapid adsorption–desorption system for several ions.

The half-wave redox potentials of PXV–poly(styrene-sulphonic acid) complex were −0.50 V vs. SSCE (the first wave), and −0.91 V (the second wave), and those of PXV–Nafion complex were −0.53 V, and −0.93 V vs. SSCE, respectively. Compared with $E_{1/2}$ of PXV, that of the first wave was shifted 60–90 mV, and that of the second wave 20–40 mV to the cathodic side. The potential shift seemed to be based on the difference of chemical environment of PXV. Namely, the redox behaviour was depressed a little by shrinkage of the domain which was induced by complexation. Shrinkage of the domain corresponded to depression of the motion of micro-ions. The redox reaction of polymers requires the migration of micro-ions. Though PXV–PSS complex film and PXV–Nafion complex film were more stable than PXV film, they were not so stable when PXV was reduced to the non-ionic state, because PXV could not form a complex with PSS or Nafion any more when PXV was reduced to the non-ionic state. Every component polymer was dissolved in the bulk solution. *Figure 6* shows voltammograms for PXV–PSS

Table 5 Desorption of complex anions from PXV domain by changing the applied potential

	Desorption (%)	
Anion species	at −0.7 V	at −1.2 V
0.2 mM $Fe(CN)_6^{4-}$	50	48
0.2 mM $Mo(CN)_8^{4-}$	25	46
0,2 mM $Fe(CN)_6^{4-}$	0	0
+		
0.2 mM $Mo(CN)_8^{4-}$	36	45

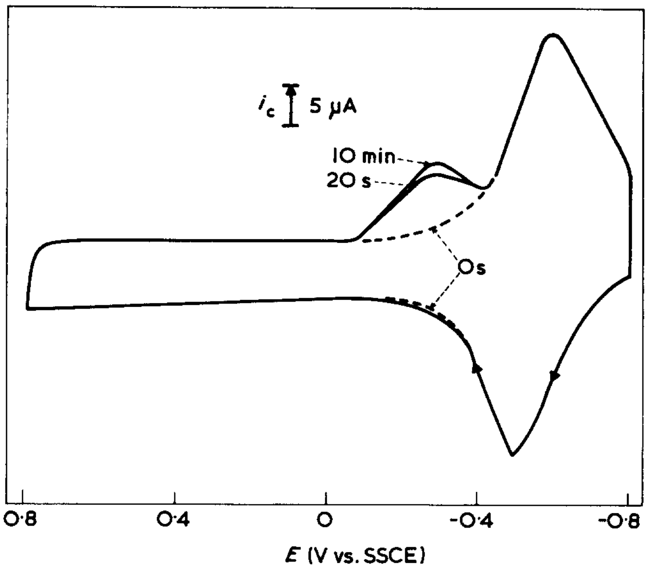

Figure 6 Cyclic voltammograms for $Ru(NH_3)_6^{3+}$ fixed on bare or PXV–PSS complex-coated electrodes: PXV, 6.0 x 10^{-9} unit mol cm^{-2}; polyion complex was formed with equimolar mixing of PSS; $[Ru(NH_3)_6^{3+}]$, 50.0 μM; scan rate, 190 mV.s^{-1}

complex coated electrode soaked in a 50 μM solution of $Ru(NH_3)_6^{3+}$. By the repetition of potential cycling from +0.80 V to −0.80 V, the peak current i_p, corresponding to reduction of $Ru(NH_3)_6^{3+}$ ($E_p^c = -0.28$ V vs. SSCE), increased. $Ru(NH_3)_6^{3+}$ was incorporated in the complex domain only after 20 s. The PXV–PSS complex electrode was completely saturated with $Ru(NH_3)_6^{3+}$ when the potential was fixed at −0.80 V for 10 min. The peak current was constant after 1 h, so that no desorption was observed. It was recognized that $Ru(NH_3)_6^{3+}$ was fixed in the PXV–PSS complex domain stably and theoretically.

Desorption of a multivalent complex cation was also tried by regulating the overall charge density in the domain. The fixation of PXV in Nafion film was performed by the formation of a polyion complex. The concentration change of $Ru(NH_3)_6^{3+}$ is shown in *Figure 7*. As mentioned above, the domain of PXV–Nafion complex seemed to be loosely shrunk by comparison with that of PXV–PSS complex. The peak current i_p, corresponding to the oxidation of the fixed $Ru(NH_3)_6^{3+}$ ($E_p^a = -0.30$ V), increased when the potential was fixed for a certain period of time at −0.80 V (○) or −1.2 V (●), respectively. Especially, when viologen sites were reduced to the non-ion state, the quantity of free sulphonic group doubled, and adsorption quantity and efficiency increased (see *Figure 7*, closed circles). After adsorption, the potential was reduced to 0.0 V and all of the adsorbed $Ru(NH_3)_6^{3+}$ was desorbed within a few seconds. Such a rapid desorption seemed to be based on the strong interaction force between Nafion and PXV. So the fixed $Ru(NH_3)_6^{3+}$ was put out immediately. From the result described above, it was seen that a PXV–Nafion complex-coated electrode could adsorb and desorb $Ru(NH_3)_6^{3+}$ reversibly by changing the given potential only. This knowledge may enable one to concentrate almost all other multivalent ions from very dilute solution.

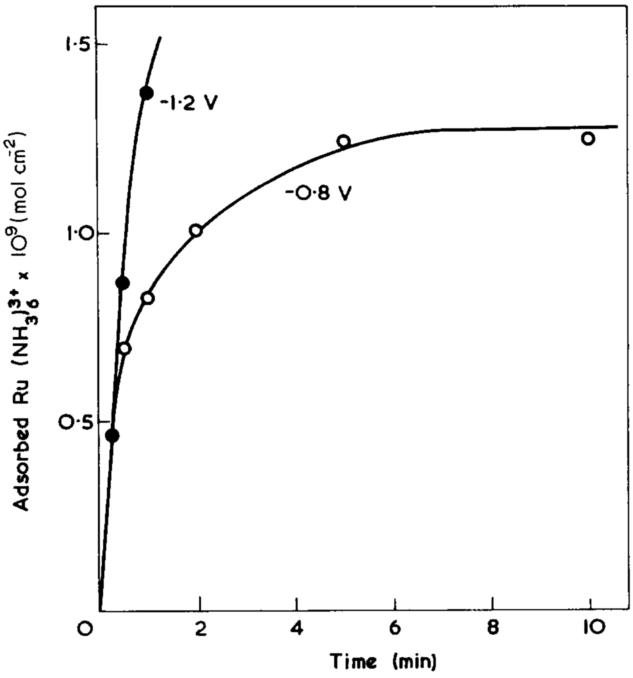

Figure 7 Adsorption of $Ru(NH_3)_6^{3+}$ in the domain of PXV–Nafion complex at 25.0°C: PXV, 1.5 x 10^{-9} unit mol cm^{-2}; $[Ru(NH_3)_6^{3+}$ 50.0 μM; polyion complex was formed with equimolar mixing of sulphonate groups of Nafion

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