

# FORMATION AND ELECTROCHEMICAL BEHAVIOUR OF POLYION COMPLEXES FOR ELECTROCHROMIC DISPLAY MATERIAL\*

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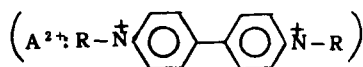
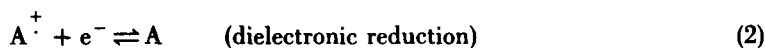
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## ABSTRACT

Formation of intermacromolecular complexes containing viologen and electron-transfer reaction occurred on the electrode modified by the complex films were studied. Compositions and morphology of the complexes depend on the properties of polyanion and chemical environment of complexation. The analytical results of cyclic voltammetry (CV) and rotating disk voltammetry(RDV) indicated: (1) active sites of viologen in network of complexes transferred single electron reversibly; (2) the redox peak currents showed excellent symmetry and stability; (3) redox potentials were related to properties of polyanions, varying from  $-0.4$  to  $-0.6\text{V}$  (vs. SCE). Electrochromic materials with different displaying colors could be obtained by changing the structure of polyviologen.

## INTRODUCTION

Electrochromic(EC) phenomenon has been found in various inorganic and organic substances, of which the research of the inorganic type EC materials, such as  $\alpha\text{-WO}_3$ , seems to have reached a certain level<sup>[1,2]</sup> but their monocolour characteristic and the difficulty in controlling the amount of coloration are still not fully studied. Among the several organic type EC materials, viologen derivatives are still attractive because of their multicolority. However, there exists a rather complicated problem in this type of materials. It is known, when N,N'-substituted 4,4'-bipyridine is reduced in aqueous solution, an electron-transfer reaction will occur:



and the reduced viologen will show a very strong absorption in the range of visible light and turn colored. It is the reduced viologen that may dimerize and then deposit on the surface of electrode, resulting in irreversible electron-transfer and erasing failure, which is called "aging" effect<sup>[3]</sup>. Itaya and Masumi et al.<sup>[4,5,6]</sup> reported that an intermacromolecular complex containing viologen group possessed excellent stability and the peak current declined only 5% after 100 cycles in CV measurement. Currently, Yasuda et al.<sup>[7]</sup> reported that aqueous solution of an inclusion complex

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based on small molecular viologen and  $\beta$ -cyclodextrin is capable of inhibiting the dimerization of viologen derivatives. It has been supposed from the reports mentioned above that the key point to avoid "aging" phenomenon is to weaken the intermolecular interaction between viologen groups. For this purpose, authors have studied the formation of polyion complexes containing viologen and the electrochemical behaviours of electrode modified by the complex films.

## EXPERIMENTAL

### 1. Preparation of polymers

Polyviologens were synthesized by quaternization(eq.3) of equimolar 4,4'-bipyridine and dihalogen alkanes in refined DMF. After reacted at 50°C for 72 hrs under  $N_2$ , the polymer precipitate was filtered, and the filtered solution was precipitated with acetic ether. Combining the precipitates, the product was washed with acetone and dried in vacuum. The results are shown in Table 1. The monomer residue contained in polymer was detected by TLC and was found to be less than 0.5%.

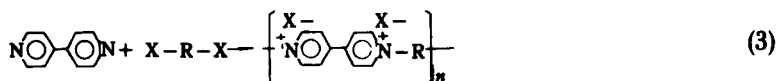


Table 1 Syntheses of polyviologens

| Polymer** | R Group                                          | Conversion (%) | $[\eta]^*$ (dl/g) |
|-----------|--------------------------------------------------|----------------|-------------------|
| PXV       | $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$ | 71.0           | 0.03              |
| PTV       | $-(\text{CH}_2)_3-$                              | 76.5           | 0.03              |
| PPV       | $-(\text{CH}_2)_5-$                              | 87.2           | 0.05              |
| PDV       | $-(\text{CH}_2)_{10}-$                           | 65.8           | 0.06              |

\* According to Factor<sup>[8]</sup>, light-scattering method was used, the inherent viscosity of PXV  $[\eta] = 0.06\text{dl/g}$  corresponds to molecular weight of 1000(g/mol).

\*\* PXV: poly (xylyl viologen dibromide); PTV: poly (trimethylene viologen dibromide); PPV: poly (pentamethylene viologen dibromide); PDV: poly (decamethylene viologen dibromide)

Polyanions used were polymethacrylic acid (PMAA) of molecular weight  $3 \times 10^4$ , poly (sodium styrenesulfonate) (PSSNa) of molecular weight  $2 \times 10^5$ , polyglutamic acid (PGA) of molecular weight  $2 \times 10^4$ , and Nafion 501. The PMAA and PSSNa were synthesized in this laboratory and the PGA and Nafion 501 were purchased.

Equimolecular aqueous solutions of polyviologen and polyanion were mixed together, yielding solid polyion complexes.

### 2. Measurements

The inherent viscosity of polyviologens were determined at 30°C in 0.2M KCL electrolyte solution. Compositions of complexes were calculated from the ratio of C/N or S/N in elemental analyses.

Cyclic voltammogram (CV) and rotating disk voltammogram (RDV) were drawn with FA-1 type cyclic voltammetry. A three-electrode electrolytic cell was used, which consisted of a working

electrode (a pyrolytic graphite electrode), a counter electrode (a platinum rail), and a reference electrode (a KCL saturated calomel electrode, SCE).

## RESULTS AND DISCUSSION

### 1. Formation of polyion complexes

Polyion complexes can be obtained through electrostatic interaction by mixing aqueous solutions of polyviologen and polyanion. The following scheme shows a complex structure composed of PMAA and PXV with repeating unit of molar ratio  $[PMAA]/[PXV] = 2/1$ .

The formation of polyion is governed by the characteristics of the individual polyelectrolyte components (e.g. properties of ionic sites—strong or weak electrolyte, position of ionic sites, charge density, rigidity of macromolecular chains, etc.) and the chemical environment (e.g. pH value, ionic strength, concentration and solvent, etc.).<sup>[9,10]</sup> The formation and compositions of complexes depend greatly on pH value and concentration of polymer solution since PMAA, a weak acid, can only partially dissolve. Figure 1 illustrates the phase diagram of the complexes obtained by mixing PXV with PMAA under different conditions.

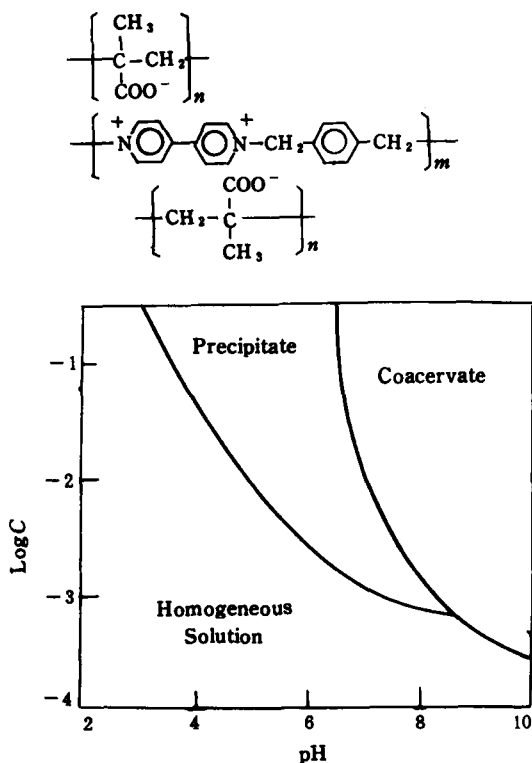


Fig. 1 Conditions of the formation of PXV-PMAA complexes

There is no phase separation when  $\text{pH} < 3$  or concentration of polyion solution less than  $5 \times 10^{-3} M$ , and the mixture of the solutions exists in a homogeneous state. It may be caused in two cases. If pH is low enough, PMAA in undissociated state can not form the complex directly with polycation. So individual components exist freely in solution. On the other hand, if the concentration of polyion solution is low enough, the complex may have a ladder structure and

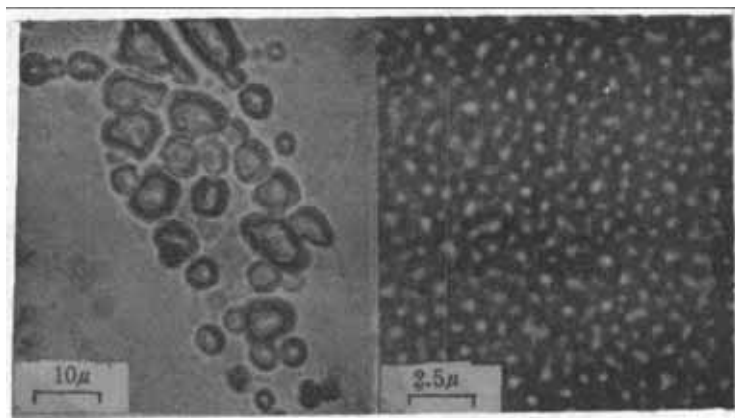


Fig. 2 Complex morphology formed under different conditions

become soluble. When  $\text{pH} > 3$  and the concentration higher than  $5 \times 10^{-3}\text{M}$ , phase-separation occurs. When  $\text{pH} < 7$ , precipitate is formed; when  $\text{pH} > 7$ , coacervate complex with high hydration is yielded (see Fig.2). By centrifugal separation and drying in vacuum, the complex appears to be a deep blue solid.

A relationship between composition of complexes and pH is demonstrated in Table 2. Content of nitrogen in PXV-PMAA complexes increases with the increase of pH. The composition expressed as repeating unit of molar ratio  $[\text{PMAA}]/[\text{PXV}]$  will be from 10/1 to 2/1, calculated from the ratio of C% over N% (C/N), in the range of  $\text{pH} = 5 \sim 9$ . When  $\text{pH} > 3.5$ , the ratio will be 2/1, which indicates that all carboxyl groups on PMAA chain have reacted with polycation  $\text{PXV}^{2+}$ . When  $\text{pH} < 8.5$ , only partial carboxyl groups have reacted with  $\text{PXV}^{2+}$  and there exist different numbers, depending on pH, of free carboxyl groups. There are, for instance, 80% of free  $-\text{COOH}$  groups in the  $[\text{PMAA}]/[\text{PXV}] = 10/1$  complex.

Table 2 Dependence of complex composition on pH

| No. | pH   | Elemental anal. C/N |        | Composition<br>[PMAA]/[PXV] |
|-----|------|---------------------|--------|-----------------------------|
|     |      | found               | calcd. |                             |
| 1   | 4.99 | 25.36               | 25.20  | 10.2/1                      |
| 2   | 5.50 | 23.40               | 23.48  | 9.2/1                       |
| 3   | 6.00 | 17.12               | 16.97  | 5.4/1                       |
| 4   | 6.50 | 14.59               | 14.57  | 4.0/1                       |
| 5   | 7.00 | 13.03               | 13.19  | 3.2/1                       |
| 6   | 8.23 | 11.36               | 11.49  | 2.2/1                       |
| 7   | 9.22 | 11.09               | 11.14  | 2.0/1                       |

Feed ratio:  $[\text{PMAA}]/[\text{PXV}] = 2/1$

A complex with uniform composition can be obtained when poly (sodium styrenesulfonate) (PSSNa) reacts with polyviologen. The ratio S/N = 2.36, calculated from the results of elemental

analysis, corresponds to the complex composition of  $[\text{PSSNa}]/[\text{PXV}] = 2/1$  ( $S/N = 2.30$ , theoretically). It means that all sulfonic acid ions have reacted entirely with complementary ions, yielding a complex with composition 2/1.

## 2. Electron-transfer reaction in the film of complexes

Polyion complexes formed from polyviologen and polyanion possess a highly crosslinked network structure, so they can not be dissolved in water and in common organic solvents at all<sup>(9)</sup>. When a film of a complex is coated on an electrode, a reversible electron-transfer reaction will take place according to eq.1 and eq.2 in the electroactive viologen sites within the film. The bipyridines as chromic groups are fixed in the network of complex tightly, therefore, the tendency of dimerization caused by cation radical is inhibited. On the other hand, it become important if electrons can be transported to the part far away from the electrode by the active sites in the stable structure and if the distribution of the active sites are uniform. For this purpose, the following analyses on electrochemical behaviours of modified electrode of complex film were made.

Graphite electrode coated with polysulfonic acid (Nafion 501), forming a film of  $1.3 \times 10^{-7}$  mol/cm<sup>2</sup>, was immersed in 0.1 mM PXV solution.  $\text{PXV}^{2+}$  enter the film through tunnels in the film, and combine with pendent sulfonic acid anion electrostatically, forming a complex. Amount of charge ( $Q$ ) on the surface of electrode with different soaked time was determined by CV method and corresponding electroactive site concentration  $\Gamma_{\text{PXV}^{2+}}$  was calculated in accordance with  $Q$ . The results are shown in Table 3. The  $\Gamma_{\text{PXV}^{2+}}$  increased with the increase of soaked time and reached an equilibrium after 30 minutes.

**Table 3** Dependence of electroactive site concentration in coated film on soaked time

| Soaked time<br>(minute)                                      | 1    | 2    | 5    | 10    | 30    | 60    |
|--------------------------------------------------------------|------|------|------|-------|-------|-------|
| Amount of charge $Q$<br>( $10^{-3}$ mC)                      | 35.0 | 56.3 | 84.4 | 105.0 | 117.5 | 117.6 |
| $\Gamma_{\text{PXV}^{2+}}$ ( $10^{-9}$ mol/cm <sup>2</sup> ) | 2.13 | 3.43 | 5.14 | 6.40  | 7.16  | 7.16  |

The above modified electrode was immersed in a 1mM electrolyte solution of  $\text{K}_3\text{Fe}(\text{CN})_6$  and both cyclic voltammogram and rotating disk voltammogram show two distinguished waves (see Fig.3). The half wave potential of the first wave is + 0.2 V(vs. SCE), it coincides with the redox potential of uncoated graphite electrode in the  $\text{K}_3\text{Fe}(\text{CN})_6$  solution. Therefore, a response current  $i_1$  related to more negative potential than  $E_1$  (+ 0.2V) is resulted from the facts that the  $\text{Fe}(\text{CN})_6^{3-}$  ions obtain electrons directly from the surface of graphite electrode by penetrating through complex film and are reduced into  $\text{Fe}(\text{CN})_6^{4-}$  (see Fig.3 and Fig.4A). The second wave at - 0.56 V(vs. SCE) is nearly equal to the single electronic reduction potential of polyviologen. Thus, when the potential  $E_2$  is more negative than - 0.56 V, the response current  $i_2$  is resulted from the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  which gain electrons from electroactive sites within the film (see Fig.3 and Fig.4B). This suggestion can be verified according to the relations of  $i_1$  and  $i_2$  with concentration of the active sites. Fig. 5 shows the dependence of response current on rotating speed of electrode ( $\omega$ ). Both  $i_1$  and  $i_2$  increase with the increase of  $\omega$ . A linear curve can be drawn by plotting  $i^{-1}$  vs.  $\omega^{-1}$  (Koutecky-Levich method). A response current  $i_\infty$  can be obtained by extrapolation of  $\omega$  to  $\omega = \infty$ . Figure 6 shows a relationship between  $(i_1)_\infty$ ,  $(i_2)_\infty$  and  $\Gamma_{\text{PXV}^{2+}}$ . It can be seen that  $(i_1)_\infty$  is almost independent of

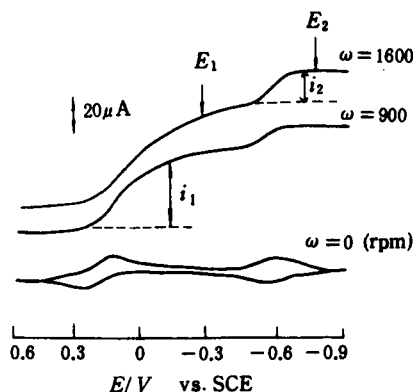


Fig. 3 Rotating disk voltammogram and cyclic voltammogram of Nafion-PXV complex film coated on graphite electrode in 1 mM  $K_3Fe(CN)_6$  solution,  $\Gamma_{SO_3^-} = 1.3 \cdot 10^{-8}$  mol/cm<sup>2</sup>,  $\Gamma_{PXV^{2+}} = 5.7 \cdot 10^{-9}$  mol/cm<sup>2</sup>

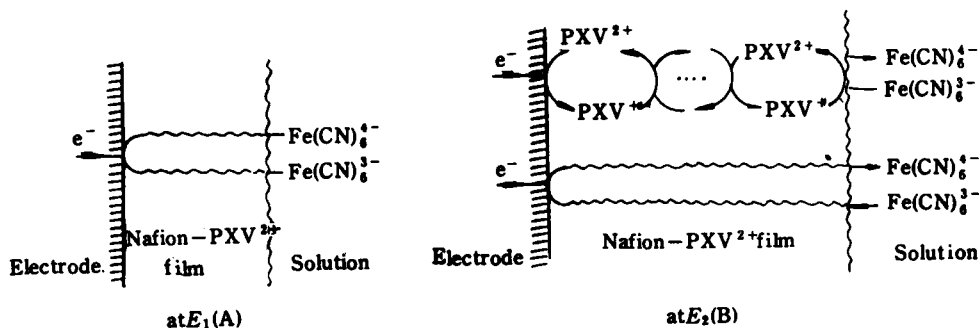


Fig. 4 Schematic depictions of electron-transfer processes on complex film coated electrode

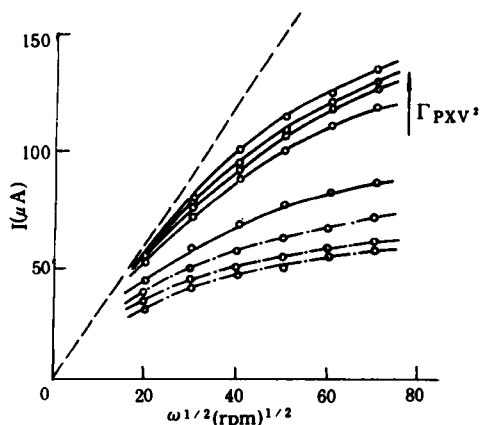


Fig. 5 Dependence of response current on rotating speed of electrode.

---: uncoated electrode; —:  $i_1$ ; ---:  $i_2$

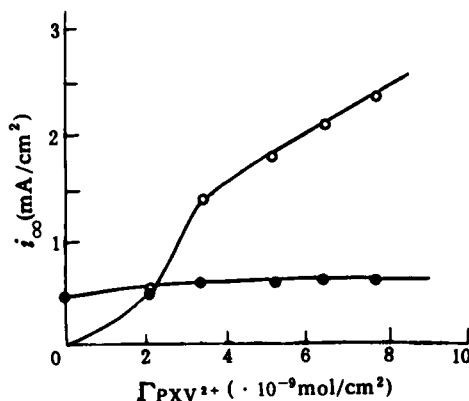


Fig. 6 Relation of response current with concentration of electroactive sites when  $\omega = \infty$

—●—  $i_1$ ; —○—  $i_2$

$\Gamma_{PXV^{2+}}$  but  $(i_2)_\infty$  increases with the increase of  $\Gamma_{PXV^{2+}}$ . It is verified further that  $Fe(CN)_6^{3-}$  does gain electrons from electroactive sites within complex film and is then reduced into  $Fe(CN)_6^{4-}$  at  $E_2$ . It also means that the electroactive groups in the film are able to transfer electrons to any position far

away from the surface of the electrode. The mechanism is shown in Figure 4B.

Figure 6 also reveals when  $\Gamma_{\text{PXV}^{2+}} \geq 3.4 \times 10^{-6} \text{ mol/cm}^2$ ,  $(i_2)_\infty$  is directly proportional to  $\Gamma_{\text{PXV}^{2+}}$ , which implies that there is an uniform distribution of electroactive sites in the film within certain thickness. It shows a promising possibility that the network complex film as a kind of display material is capable of possessing high chromic concentration and uniform tone.

### 3. Electrochromic behaviours of the complex film modified electrode

Practical display devices require reflecting contrast coefficient more than  $5/1^{[11]}$ . The coefficient is dependent on the thickness of display material which should be generally over thousands Å. Fig.7 shows a cyclic voltammogram of modified electrode coated with  $1 \mu\text{m}$  thick PXV-PMAA complex film. When potential scans repeatedly in the range of 0 to  $-0.8 \text{ V (vs. SCE)}$ , single electron redox reaction of viologen group will occur as shown in eq.4. When potential is zero, polyviologen exists in double cation state ( $\text{PXV}^{2+}$ ), and the film is colorless and transparent. When potential scans toward negative direction, single electron reduction will occur at  $-0.54 \text{ V}$ , and  $\text{PXV}^{2+}$  will be changed into cation radical  $\text{PXV}^{+\cdot}$ , the film displays deep blue color. When

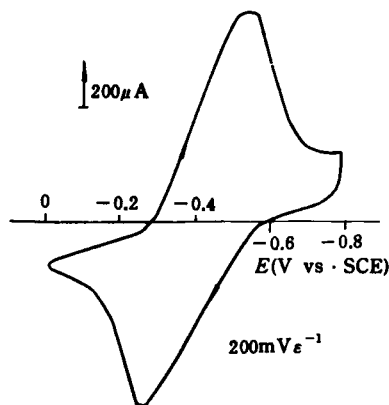
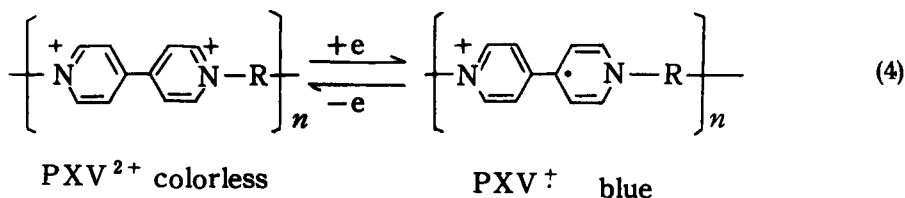


Fig. 7 Cyclic voltammogram of modified electrode coated with PXV-PMAA, thickness  $1 \mu\text{m}$ , in  $0.2 \text{ M NaClO}_4$  aqueous solution



potential scans from  $-0.8 \text{ V}$  toward positive direction,  $\text{PXV}^{+\cdot}$  will be oxidized into  $\text{PXV}^{2+}$  by losing an electron, the film becomes colorless and transparent again. The oxidation peak potential  $E_{\text{pa}}$  is  $-0.27 \text{ V}$ . Figure 7 also indicates that reduction peak current  $i_{\text{pa}} = 1.36 \text{ mA}$ , and oxidation peak current,  $i_{\text{pa}} = 1.38 \text{ mA}$ , are in very good symmetry, which means the redoxation is highly reversible. Furthermore, on repeated scanning within  $0 \sim -0.8 \text{ V}$ , on decrease of redox peak current was observed after 500 cycles, on the contrary, the peak current of individual PXV decreased by 30% (see Figure 8). Therefore, it indicated that dimerization of the cation radicals in complex network will no longer occur.

The influence of polymer structure on redox potential and displaying color is shown in Table 4. The strength of polyacids does not affect displaying color but it does affect redox potential.

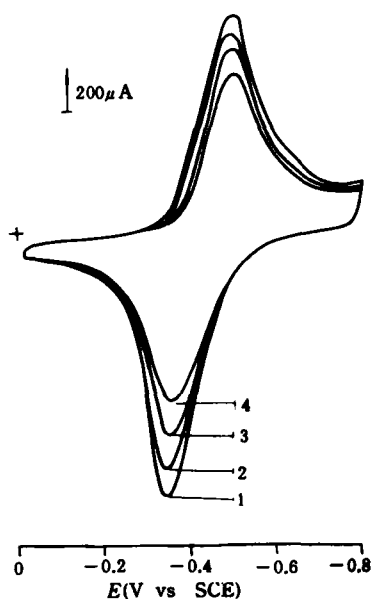


Fig. 8 Cyclic voltammogram of modified electrode coated with PXV in 0.2M NaClO<sub>4</sub> aqueous solution,  
1) 10; 2) 100; 3) 200; 4) 500 cycles

Although the redox potential of a strong acid, sulfonic acid, is 0.1V higher than that of a weak acid, carboxylic acid, it still belongs to low potentials ( $-0.4 \sim -0.6V$ ), with which the displaying devices can be driven directly by integrated circuit.

**Table 4** Redox potential and color of polyion complexes

| Anion            | R group<br>of cation                             | Polyion<br>complex | Redox<br>potential(V) | Displaying<br>color |
|------------------|--------------------------------------------------|--------------------|-----------------------|---------------------|
| $-\text{COO}^-$  | $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$ | PMAA-PXV           | $-0.44$               | blue                |
|                  |                                                  | PGA-PXV            | $-0.45$               | blue                |
| $-\text{SO}_3^-$ |                                                  | PSSNa-PXV          | $-0.54$               | blue                |
|                  |                                                  | Nafion-PXV         | $-0.56$               | blue                |
| $-\text{SO}_3^-$ | $-(\text{CH}_2)_3-$                              | PSSNa-PTV          | $-0.51$               | red                 |
|                  | $-(\text{CH}_2)_5-$                              | PSSNa-PPV          | $-0.52$               | violet              |
|                  | $-(\text{CH}_2)_{10}-$                           | PSSNa-PDV          | $-0.55$               | blue                |

In contrast, the structure of the neighbouring group R of bipyridine does not obviously affect redox potential but displaying color. When R is xylylene, the material displays blue color; when R is a methylene chain, the displaying color varies with the length of the chain. So display materials with different color may be obtained by changing the structure of R group, which provides a promising approach for multiple coloration of EC materials.

**Keywords:**

Polyion Complexes; Polyviologen; Electrochromic Display Material

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