CONDUCTING POLYMERS AND DOPING-DEDOPING BEHAVIOUR

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Abstract Conducting polymer, as polypyrrole (PPy), has been prepared electrochemically in aqueous solution containing $\text{Fe}(\text{CN})_6^{3-/4-}$ as supporting electrolyte. The redox couple $\text{Fe}(\text{CN})_6^{3-/4-}$ in the PPy film acts like a probe to monitor the doping-dedoping behaviour of anions and cations from/to the electrolyte solution. A novel method for measuring the ion exchange selectivity coefficient of a conducting polymer film by cyclic voltammetry is proposed.

Key words conducting polymer, polypyrrole, ion exchange, potassium ferrocyanide

Conducting polymers, such as polypyrrole (PPy), polythiophene (PTh), and polyaniline (PAn), behaving like a metal, semiconductor or even superconductor, have become attractive new materials and various conducting polymers have been synthesized by chemical and electrochemical methods [1-3]. To get a conducting polymer thin film, our laboratory pays much attention to the electropolymerization in aqueous solution. A new kind of chemical sensors based on a conducting polymer film has been firstly proposed [4-7], which exhibits a stable potential response for the doping ion in solution. It is very interesting to examine further the electrochemical behaviour of the doped conducting polymer film. Taking PPy as an example, during electrolysis anions of supporting electrolyte dope into the PPy film formed on electrode in order to neutralize the positive charge on the chain of PPy, which shows obvious influence on electrochemical behaviour of the PPy film [8]. When PPy film is reduced, the small doping anions will dedope from the film. In contrast, the polyelectrolyte anions with large size can not leave the film very rapidly, whereas the cations of the supporting electrolyte will dope into the film to neutralize the negative charge of the polyelectrolyte anions.

We have

here ME^- and PE^- represent small and large anions. PPy° and PPy^+ are the oxidized and reduced form of the PPy respectively.

We try to electropolymerize Py in aqueous solution at glassy carbon electrode by using potassium ferrocyanide as supporting electrolyte. The electroactive redox couple $\text{Fe}(\text{CN})_6^{3-/4-}$ doped in the PPy film can act as a probe for monitoring the electro-

chemical behaviour of PPy.

1. Ion gate effect

Fig.1 shows the cyclic voltammograms of the $\text{Fe}(\text{CN})_6^{3-/4-}$ doped in PPy film in electrolyte solution containing NO_3^- . Two pairs of redox couple appear (curve 1), one corresponds to $\text{Fe}(\text{CN})_6^{3-/4-}$ in the film (E_{pc} : 0.03V and E_{pa} : 0.23V), another corresponds to redox reaction of PPy itself (E_{pc} : -0.57V and E_{pa} : -0.24V). When potential scans from 0.5 to -0.8V, the doped $\text{Fe}(\text{CN})_6^{3-/4-}$ will dedope out to keep the neutrality of the reduced form of PPy. If the later is reoxidized, the NO_3^- anions will dope in the film from solution. Through several cycles, the $\text{Fe}(\text{CN})_6^{3-/4-}$ anions in PPy film are replaced gradually by NO_3^- (curve 2-10). On the other hand, if the potential scans from 0.5 to -0.2V, the

Fig.1 CV curves of PPy contained $\text{Fe}(\text{CN})_6^{3-/4-}$ film (1.6 μm) electrode. 0.2M KNO_3 , +0.5 - -0.8V(vs.SCE), 50mV/s.

anions in PPy film would be reduced, while that of PPy^+ keeps its oxidized form still resulting in cations dope in the PPy film from solution. The cyclic voltammograms of the PPy film show stable responses of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox behaviour see Fig.2 which can be used as a probe.

Fig.2 CV curves of PPy contained $\text{Fe}(\text{CN})_6^{3-/4-}$ film (1.6 μm) electrode. 0.2M KNO_3 , +0.5 - -0.2V(vs.SCE), 50mV/s.

The cations with different sizes dope into the PPy film show apart abilities as Fig.3. If the cations in solution were small (as K^+ and NH_4^+), a well-defined redox wave appears, but it becomes unsymmetrical and small when the cations with larger sizes (as NMe_4^+). Only cathodic wave can be seen if the cations become more large. Under the potential scans from 0.5 to -0.2V, the cathodic waves shift to more positive and the currents decrease pronously.

II. Ion exchange behaviour

The anions $\text{Fe}(\text{CN})_6^{3-/4-}$ doped in PPy film can be exchanged by other anions in solution, acting as an anion exchange resin. Based on this fact, a novel method for measuring the ion exchange selectivity coefficient of $\text{Fe}(\text{CN})_6^{3-/4-}$ in PPy film with other anions in solution by cyclic voltammetry has been proposed.

Fig.3 CV Curves of PPy contained $\text{Fe}(\text{CN})_6^{3-/4-}$ film (1.6 μm) electrode.

+0.5 ~ -0.2V (vs. SCE), 50mV/s.

a. 0.2M NH_4Br

c. 0.2M Et_4NBr

b. 0.2M Me_4NBr

d. 0.2M Bu_4NBr

The ion exchange equilibrium of an anion exchange resin can be expressed as

Where P^+ is the anion exchange resin, A^{m-} and B^{n-} represent anions in solution (L). P^+A^{m-} and P^+B^{n-} represent anions in the ion exchange resin (S). According to its electrochemical potential of ions in different phases are equal to each other at ion exchange equilibrium, an equation expressing ion exchange selectivity coefficient K is derived.

$$K = \frac{[\gamma_{B^{n-}}^{(S)}]^{m-} [\gamma_{A^{m-}}^{(L)}]^{n-}}{[\gamma_{B^{n-}}^{(L)}]^{m-} [\gamma_{A^{m-}}^{(S)}]^{n-}} \times \frac{[C_{B^{n-}}^{(S)}]^{m-} [C_{A^{m-}}^{(L)}]^{n-}}{[C_{B^{n-}}^{(L)}]^{m-} [C_{A^{m-}}^{(S)}]^{n-}} \quad (4)$$

Suppose A^{m-} is an electroactive anion, but B^{n-} is an electroinactive one, by using coulometric measurement the amount of A^{m-} in the anion exchange resin can be measured without the influence of other A^{m-} ions in solution. Therefore

$$K = \gamma_{B^{n-}}^{(L)} (V_L/V_S)^{m-} (Q_{A^{m-}}^{(S)}/Q_{A^{m-}}^{(L)} - 1)^{n-} \times \{C_{B^{n-}}^{(L)}/V_L F k n / [(Q_{A^{m-}}^{(S)}/Q_{A^{m-}}^{(L)} - 1)^{m-}]\}^{m-} \quad (5)$$

if $\text{Fe}(\text{CN})_6^{4-}$ doped only in the PPy film which is exchanged with Cl^- ions in a solution containing KCl, at open circuit we have

the initial amount of $\text{Fe}(\text{CN})_6^{4-}$ in PPy film and the rest amount after ion exchange in solution are measured coulometrically at potential scanning between 0.5 to -0.2V.

Examples from the results of $\text{Fe}(\text{CN})_6^{3-/4-}$ doped PPy film being exchanged with Cl^- , NO_3^- and F^- separately (assuming $\gamma = 1$), then the values of K

$$K_{\text{Fe}(\text{CN})_6^{4-}}^{\text{Cl}^-} = 4.0 \times 10^{-3} \quad (7)$$

$$K_{\text{Fe}(\text{CN})_6^{4-}}^{\text{NO}_3^-} = 4.1 \times 10^{-3} \quad (8)$$

$$K_{\text{Fe}(\text{CN})_6^{4-}}^{\text{F}^-} = 1.7 \times 10^{-3} \quad (9)$$

are obtained.

The method proposed is also suitable for measurement of K to cation exchange resin. Study on other factors, such as the holes in the prepared PPy film, the applied potential and etc., which show influence on the ion exchange reaction is now undergoing.

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