

Influence of Doping Anions on the Ion Exchange Behavior of Polypyrrole

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ABSTRACT: The ion exchange behavior of polypyrrole (PPy) doped with a variety of dopants (A), namely chloride, nitrate, para-toluene sulfonate (pTS⁻), and dodecyl sulfonate (DS⁻), was investigated by means of cyclic voltammetry (CV) in NaCl, NapTS, and AlCl₃ aqueous solutions. The results show that PPy/pTS and PPy/DS films had the best anion and cation exchange ability, respectively. However, the ion exchange ability evaluated by CV charge cannot describe the exact amount of exchanged ions. For that reason, a new ion exchange experiment was designed to evaluate the amount of ions removed from NaCl aqueous

solution to AlCl₃ or NapTS aqueous solution. In addition, the ion exchange ratio is defined as the ratio of the charge associated with ion ejection to the synthesis charge, and can be conveniently converted to operating exchange capability (OEC). The ion exchange ratio and OEC can be used to characterize and evaluate the ion exchange ability of PPy/A films in different conditions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2307–2314, 2009

Key words: polypyrrole; anion doping; electrochemistry; ion exchangers; purification

INTRODUCTION

The redox behavior of conducting polymers, e.g., polypyrrole (PPy), has been widely studied in recent years. It has been found that the ion exchange ability of PPy depends on the polymerization conditions,^{1–4} the solvent and solution,^{3–5} the type and size of dopant counterions,^{4,6–8} the valence and size of the ions present in the electrolyte solution,^{8–10} the temperature,¹¹ and the film thickness.^{12,13}

PPy with small incorporated counterions, e.g., chloride (Cl⁻), nitrate (NO₃⁻), perchlorate (ClO₄⁻), and sulfate (SO₄²⁻), mainly exhibits anion exchange behavior due to the high mobility of these ions in the polymer matrix.^{2,4,6,8,10} However, under certain conditions, cation exchange also occurs in some systems.¹² Cation exchange is found to take place primarily on PPy modified with large and bulky shaped anions, e.g., dodecyl sulfonate (DS⁻), dodecyl benzene sulfonate (DBS⁻), polyvinylsulfonate (PVS_n⁻), and polystyrene sulfonate (PSS_n⁻), due to the immobility of these ions in the PPy chain.^{8,11,14–16} When the counterions are medium sized anions, e.g., bezenesulfonate (BS⁻) and para-toluene sulfonate (pTS⁻), PPy exhibits both anion and cation exchange behavior, and the exchange processes are controlled by the different polarization potentials.^{1,13,17–19} As

noted above, there have been many reports on the ion exchange behavior of PPy films under different conditions. On the basis of the ion exchange behavior, many articles have focused on the application of PPy as ion exchanger,^{7,10,13,16,17} ion transport membrane,^{15,18–22} and for water purification.^{14,23}

Electrochemically-controlled ion exchange of PPy can be employed for solution purification, using the ion exchange behavior of PPy for removing the object ions from solution. There are two steps in this process. First, at a certain polarization potential, the object ions get inserted in the PPy film, thus removing the ions from solution. In the second step, the ions incorporated in the PPy film are ejected to regenerate the PPy ion exchanger.^{14,23} It is very important that these two ion exchange processes do not result in significant alteration of the basic structure of PPy/A.²⁴ It seems that the ability of PPy films to purify the solutions is related to their ion exchange ability in the different solutions of two steps. In this case, evaluation of the ion exchange ability of PPy films will be a problem.

In this article, ion exchange behavior of PPy/A (A: Cl⁻, NO₃⁻, pTS⁻, and DS⁻) films, and the influence of dopant anions on ion exchange were investigated by means of cyclic voltammetry (CV) in aqueous solutions. The aim of this work was to choose appropriate dopant anions for the study of anion and cation exchange behavior of PPy films, and to find a suitable and simple method to evaluate the ion exchange ability of the films.

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TABLE I
Detailed Electropolymerization Conditions

Electrolyte aqueous solution			Electrosynthesis condition					Synthesis charge
Counterions	Pyrrole	Adjust acid (pH = 3)	Current density, time, and potential region (V)					
			P01	P02	P03	P04		
			0.8 mA cm ⁻² 8 minutes	1.6 mA cm ⁻² 4 minutes	3.2 mA cm ⁻² 2 minutes	6.4 mA cm ⁻² 1 minutes		
0.10 mol L ⁻¹ NaCl	0.10 mol L ⁻¹	HCl	0.62–0.68	0.66–0.71	0.71–0.75	0.76–0.79	384 mC cm ⁻²	
0.10 mol L ⁻¹ NaNO ₃		HNO ₃	0.62–0.65	0.64–0.67	0.69–0.71	0.73–0.76		
0.10 mol L ⁻¹ NapTS		HpTS	0.62–0.64	0.66–0.67	0.72–0.74	0.75–0.77		
0.01 mol L ⁻¹ NaDS		HCl	0.62–0.66	0.73–0.77	0.97–1.1	1.25–1.55		

EXPERIMENTAL

Pyrrole (obtained from Chinese National Reagents Group in Shanghai, China) was distilled before use. Other reagents and chemicals were all of analytical grade, and used as received. All solutions were prepared with deionized water.

Synthesis was carried out with a conventional three electrode system in a single compartment electrochemical cell. The counter electrode and the reference electrode were platinum foil (1 cm²) and saturated calomel electrode (SCE), respectively. The working electrode was a platinum plate (0.25 cm²), which was sealed with epoxy resin. Electropolymerization was carried out galvanostatically at room temperature (~ 25°C), and with the same electropolymerization charge (approximately 384 mC cm⁻²). The detailed polymerization conditions are given in Table I. Under these conditions, black, smooth, and uniform PPy/A (A: Cl⁻, NO₃⁻, pTS⁻, and DS⁻) films with metallic luster were obtained on the Pt plate. The PPy/A films obtained were kept in distilled water before use.

CV measurements were performed at room temperature (~ 25°C) with the three electrode system with an SCE reference electrode and a platinum counter electrode (1 cm²). NaCl (0.100 mol L⁻¹), NapTS (0.100 mol L⁻¹), and AlCl₃ (0.033 mol L⁻¹) were used as test solutions. In a full CV measurement (3–5 cycles), the potential was scanned from -1.0 to 0.6 V¹⁰ and then the reverse, at 20 mV s⁻¹ scan rate.

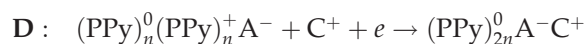
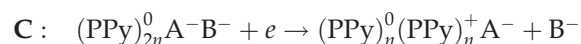
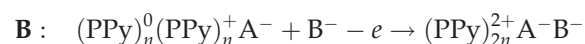
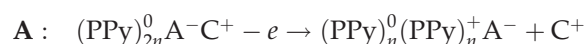
Simulation of removal of anion and cation by PPy/A films was carried out using (CV). A new cation exchange experiment with PPy/A (A: Cl⁻, NO₃⁻, pTS⁻, and DS⁻) was conducted with the following steps. (1) Polarizing PPy/A at -1.0 V in 0.100 mol L⁻¹ NaCl for 3 min; (2) rinsing the PPy film with distilled water; (3) performing CV immediately in 0.033 mol L⁻¹ AlCl₃ from -1.0 to 0.6 V. In similar way, the anion exchange behavior of PPy/A was conducted by (1) polarizing the PPy/A at 0.6 V

in 0.100 mol L⁻¹ NaCl for 3 min; (2) rinsing the PPy film with distilled water; (3) performing CV immediately in 0.100 mol L⁻¹ NapTS from 0.6 to -1.0 V.

RESULTS AND DISCUSSION

The ion exchange behavior of PPy/A films

The CVs of different PPy/A films in 0.100 mol L⁻¹ NaCl are presented in Figure 1. Generally, the CVs in Figure 1 display four ion exchange processes which can be represented by the following equations, where AD are cation ejection, anion insertion, anion ejection, and cation insertion, respectively.^{5,8,10,11,17,19,21} These ion exchange processes are associated with anodic current peaks (A and B) and cathodic current peaks (C and D) in the CVs so that they can be clearly distinguished.



CV charge can be calculated from CV measurement results, which is important for evaluating the ion exchange ability of PPy/A films, even though the CV charge is not wholly from the ion exchange process. When an electrochemical quartz crystal microbalance (EQCM) in association with the CV measurement was used for studying the ion exchange behavior of PPy, it was confirmed that the exchange charge of PPy film was suitable for characterizing the amount of exchanged ions.^{5,8,16} As the molar quantity of pyrrole monomer in the PPy/A film is constant and the test condition is the same, the larger the CV charge the better the ion exchange ability of the PPy/A film.

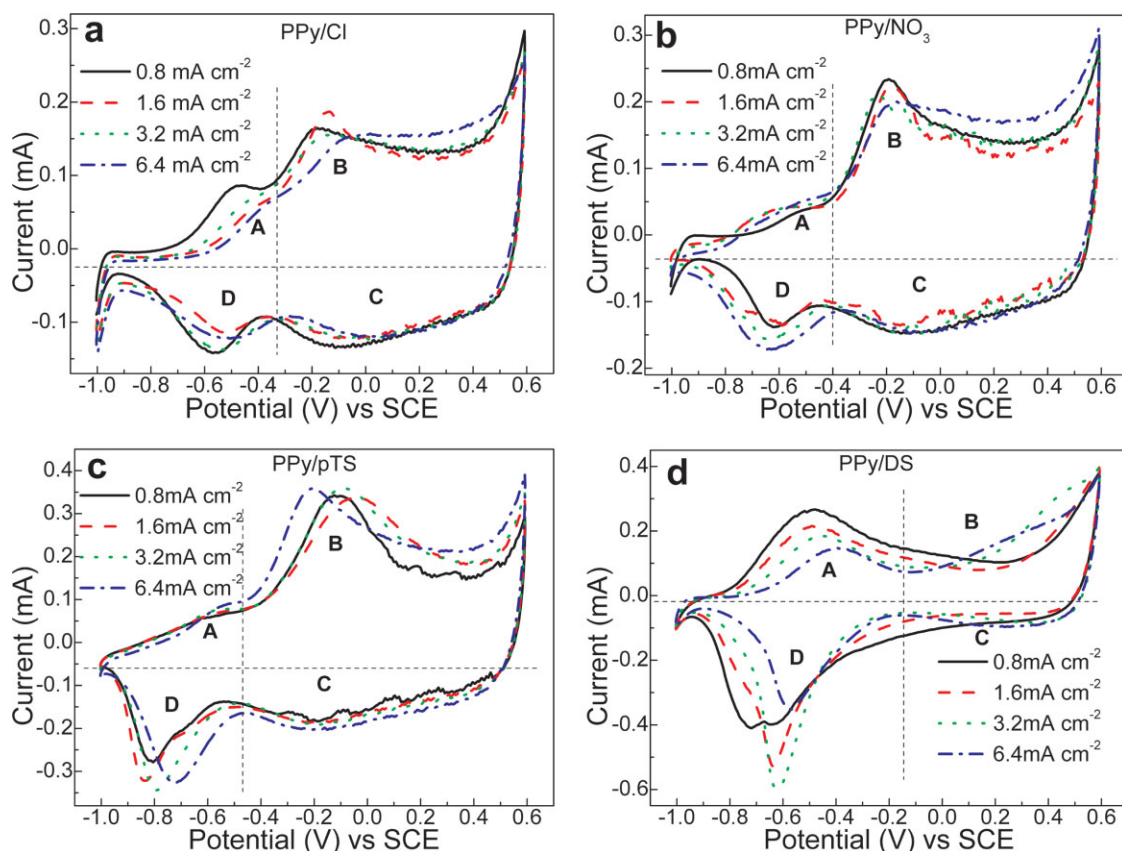


Figure 1 CVs in $0.100 \text{ mol L}^{-1} \text{ NaCl}$ of different PPy/A films. (a) PPy/Cl, (b) PPy/ NO_3 , (c) PPy/pTS, (d) PPy/DS, synthesized at different current densities. Scanning from -1.0 to 0.6 V and the reverse; scan rate 20 mV s^{-1} ; the third cycle of five cycles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

From Figure 1, it can be seen that PPy/A (A: Cl^- , NO_3^- , and pTS^-) films polymerized with different current densities display similar voltammograms [shown in Fig. 1(a–c)], which indicates that the ion exchange behavior of these films is only slightly affected by the synthesis current density. However, the PPy/DS film is different, as shown in Figure 1(d). As the current density applied during membrane growth increases, the voltammetric peak current for process A decreases remarkably, which might result from over oxidation under high potentials at large current density (as shown in Table I), so lower current density or potential is proposed for synthesis of PPy/DS film. In subsequent experiments, a current density of 1.6 mA cm^{-2} was chosen for synthesizing PPy films.

The effects of counterions on the anion/cation exchange behavior of PPy/A films

Figure 2(a) shows typical CVs of the PPy/A films in $0.033 \text{ mol L}^{-1} \text{ AlCl}_3$. Al^{3+} cannot be exchanged because it is a trivalent ion, so the CVs exhibit only Cl^- exchange behavior. Figure 2(b) shows typical CVs of PPy/A films in $0.100 \text{ mol L}^{-1} \text{ NapTS}$, in which PPy/A shows only Na^+ exchange behavior,

because pTS^- cannot be exchanged due to its large size. The continuous and dashed lines of the CVs correspond to insertion and ejection of Cl^- and Na^+ respectively, so the charges during these processes were the ion exchange charges of different processes. Specifically, the charges of the continuous lines in Figure 2(a,b) were the insertion charges of Cl^- and Na^+ respectively, and the dashed lines correspond to ejection of those ions. The CV charges (the absolute value of the integrated current over the scanning region) of the PPy/A films for the processes of Na^+ and Cl^- insertion and ejection were calculated, and the results are shown in Figure 3.

From Figures 2 and 3, the Cl^- exchange CV charges of PPy/A films have the relative order

$$\text{PPy/pTS} > \text{PPy/Cl}, \quad \text{PPy/NO}_3 > \text{PPy/DS}$$

and the Na^+ exchange CV charges of PPy/A films have the relative order

$$\text{PPy/DS} > \text{PPy/pTS} > \text{PPy/Cl}, \quad \text{PPy/NO}_3.$$

Normally, PPy doped with a small sized counterion shows good anion exchange behavior. However, as shown in Figure 2(a), the PPy/pTS film exhibits

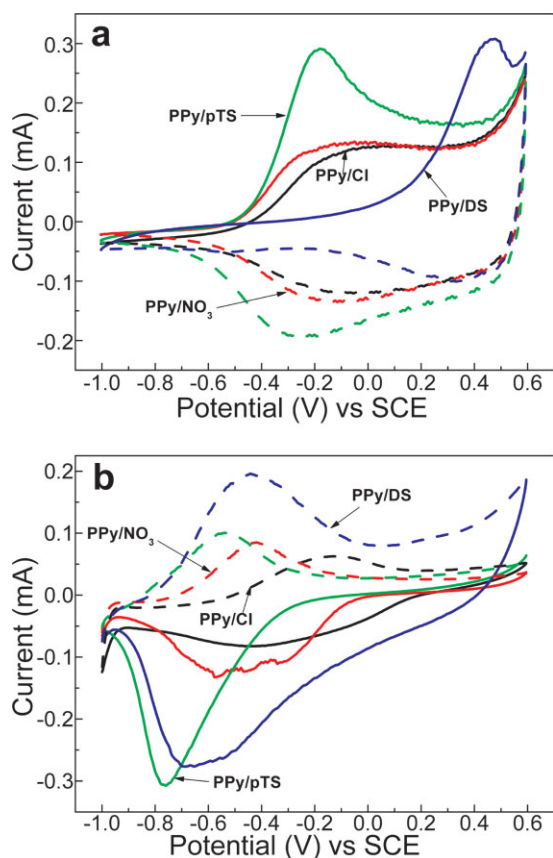


Figure 2 CVs of different PPy/A (A: Cl^- , NO_3^- , pTS^- , and DS^-) films in (a) $0.033 \text{ mol L}^{-1} \text{ AlCl}_3$ and (b) $0.100 \text{ mol L}^{-1} \text{ NapTS}$. Scanning from -1.0 to 0.6 V and the reverse; scan rate 20 mV s^{-1} ; the second of three cycles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

much better Cl^- exchange behavior than PPy/Cl and PPy/ NO_3^- , though pTS^- is larger than Cl^- and NO_3^- . Thus, when the counterions are small and medium sized, the anion exchange behavior of PPy/A is not directly related to the size of the anion dopant, and may be determined mainly by the PPy chain structure which would be affected by the dopant. PPy/DS (doped with the large DS^-) still shows the worst Cl^- exchange ability, and its CVs exhibit a more positive peak potential and smaller CV charge than other films. Thus, when PPy/A is doped with bulky anions, the anion size still has a dominant influence on the Cl^- exchange ability.

The PPy/A films with larger sized dopant anions should exhibit better cation exchange ability. The above results agree with this general rule and some published works.^{8,13,16} Consequently, it can be concluded that under the conditions of the experiments, the cation exchange ability of PPy/A is determined primarily by the size of the dopant anions.

From Figure 3, it is apparent that there was a difference between the ion insertion and ejection charges. In particular, the insertion charge of Na^+

was much larger than its ejection charge. In addition, part of the CV charge arises from other process such as the charge and discharge of electrochemical double layer. Hence, the CV charges do not come wholly from the ion insertion and ejection processes in the CV measurement, and the charges obtained from CV measurements are influenced by a number of other factors. The CV charges can be used to evaluate the relative ion exchange ability of PPy/A films under the same controlled conditions, but cannot give the ion exchange charges quantitatively. Consequently, the CV charges are not appropriate for the estimation of the ion exchange behavior of PPy films. For those reasons, the following experiment was designed.

Removal of anion and cation from NaCl aqueous solution

Simulation experiments

To determine how many object ions can be removed from a test solution, a new ion exchange experiment was designed comprising the following two steps. The object ions were first inserted into PPy/A film by polarizing it at certain potential in cell 1, then CV measurements of the PPy/A film, beginning from the polarization potential in the cell 1, were performed in cell 2 to cause the inserted ions to be ejected. The ions removed are counted using a brief simple method.

Figure 4 shows a schematic of Na^+ and Cl^- exchange experiments with PPy/A films. In the first step, PPy/pTS and PPy/DS films were polarized at 0.6 and -1.0 V for insertion of Cl^- and Na^+ in $0.100 \text{ mol L}^{-1} \text{ NaCl}$, respectively. Figure 5 shows the change of polarization currents with time in this step, which indicates that stable and saturated insertion should be achieved. Then the ejection processes

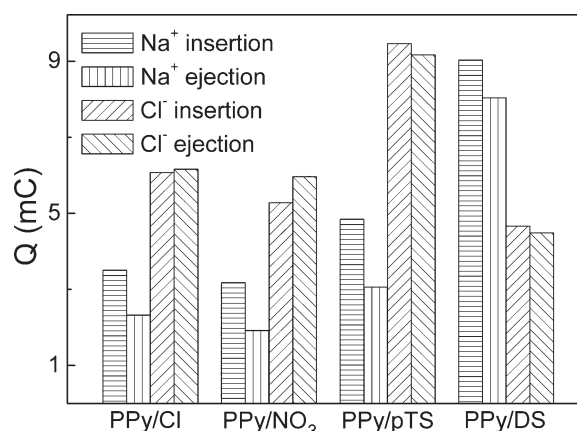


Figure 3 CV charges of PPy/A films in the processes of Na^+ insertion and ejection in $0.100 \text{ mol L}^{-1} \text{ NapTS}$, and Cl^- insertion and ejection in $0.033 \text{ mol L}^{-1} \text{ AlCl}_3$.

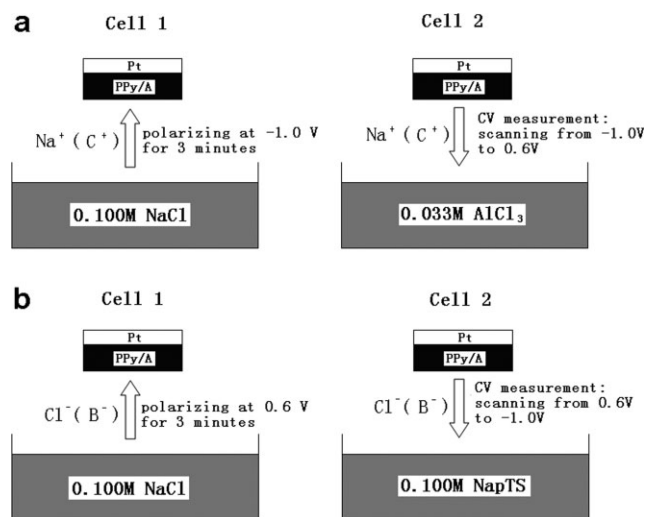


Figure 4 Schematic of (a) Na^+ and (b) Cl^- exchange simulation experiment.

were carried out by CV tests in cell 2 containing $0.033 \text{ mol L}^{-1} \text{ AlCl}_3$ or $0.100 \text{ mol L}^{-1} \text{ NapTS}$: typical results are shown in Figure 6.

As shown in Figure 6, there was a significant difference between the parts of the first and the second cycles shown by the dashed lines, whereas the second and the third cycles were almost superimposed. It should be noted that the significant difference in the two cycles was unlike the large overpotential phenomenon in the first reduction during the CV test, which resulted from change of the PPy film structure.^{25,26}

From the CVs in Figure 6(a), it can be concluded that during scanning from 0.6 to -1.0 V , the exchange processes in the first cycle should be both Cl^- ejection and Na^+ insertion. During the reverse scan from -1.0 to 0.6 V , however, only Na^+ ejection would occur because pTS^- cannot be exchanged due

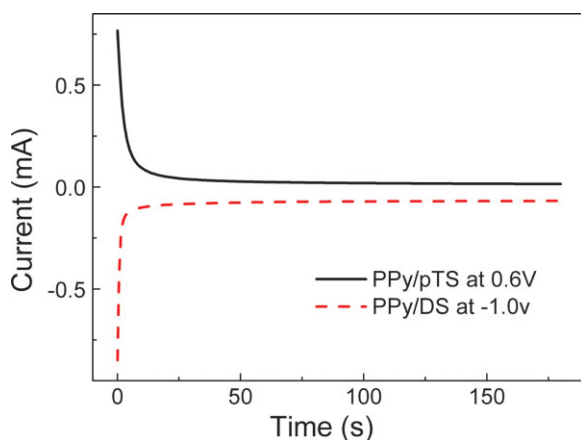


Figure 5 I - t curves of the insertion processes for Cl^- and Na^+ in PPy/pTS and PPy/DS films, respectively, in $0.100 \text{ mol L}^{-1} \text{ NaCl}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

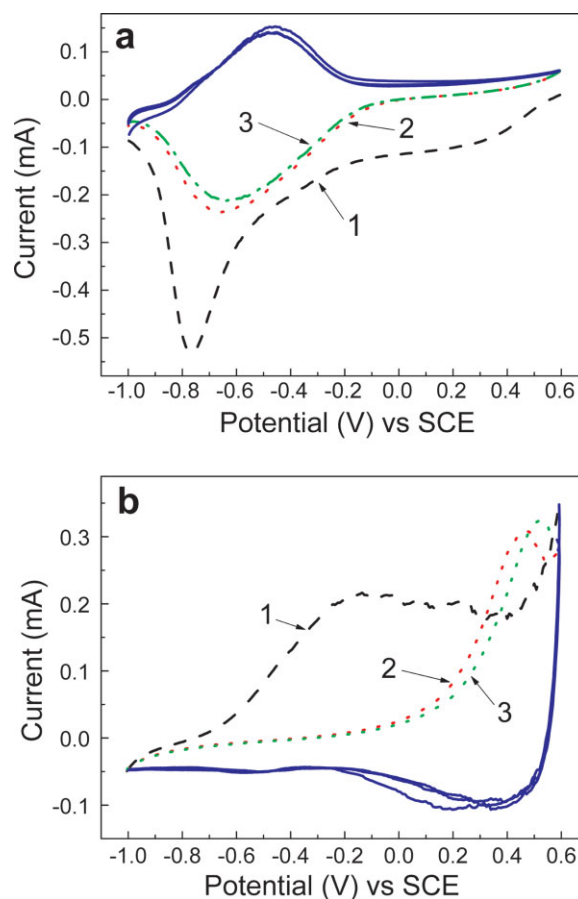


Figure 6 Typical CVs of (a) Cl^- exchange experiment (PPy/pTS film synthesized at 1.6 mA cm^{-2} , polarized at 0.6 V in $0.100 \text{ mol L}^{-1} \text{ NaCl}$ for 3 min, scanned from 0.6 to -1.0 V , and reversed in $0.100 \text{ mol L}^{-1} \text{ NapTS}$, scan rate 20 mV s^{-1} , 3 cycles) and (b) Na^+ exchange experiment (PPy/DS film synthesized at 1.6 mA cm^{-2} , polarized at -1.0 V in $0.100 \text{ mol L}^{-1} \text{ NaCl}$ for 3 min, scanned from -1.0 to 0.6 V and the reverse in $0.033 \text{ mol L}^{-1} \text{ AlCl}_3$, scan rate 20 mV s^{-1} , 3 cycles). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to its large size, and there is virtually no insertion of Cl^- . The superimposability of the second and the third cycles indicates that only Na^+ ejection and insertion processes still occur. The ejection of inserted Cl^- should occur only in the first cycle. Similarly, in Figure 6(b) the ejection of inserted Na^+ should occur only in the first cycle. Only Cl^- ejection and insertion processes still occur in the second and third cycles, because Al^{3+} cannot be exchanged, and there is virtually no insertion of Na^+ .

According to the above analysis, the difference between the first and second CV cycle should mainly come from ejection of the ions inserted in the first cycle. Thus, after subtracting the same electrochemical processes, the charge (Q_E) produced by ejection of the inserted ions can be evaluated from the difference ($|Q_{CV1} - Q_{CV2}|$) of two cycles (Q_{CV1} , Q_{CV2}) in the potential range of ejection of the

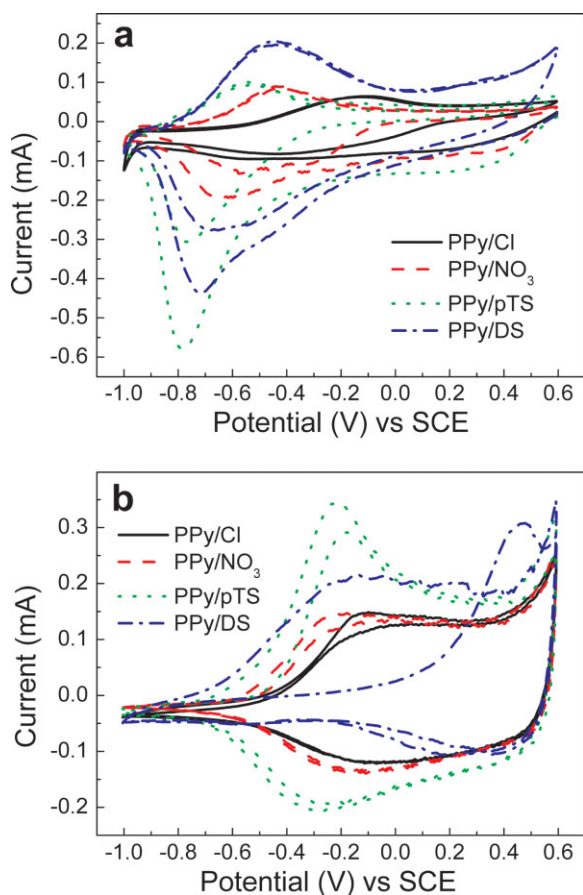


Figure 7 Typical CVs of (a) anion exchange experiments (PPy/A films synthesized at 1.6 mA cm^{-2} , polarized at 0.6 V in 0.100 mol L^{-1} NaCl for 3 min, scanned from 0.6 to -1.0 V and the reverse in 0.100 mol L^{-1} NaPTs, scan rate 20 mV s^{-1} , 2 cycles) and (b) cation exchange experiments (PPy/A films synthesized at 1.6 mA cm^{-2} , polarized at -1.0 V in 0.100 mol L^{-1} NaCl for 3 min, scanned from -1.0 to 0.6 V and the reverse in 0.033 mol L^{-1} AlCl₃, scan rate 20 mV s^{-1} , 2 cycles). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

inserted ions. That quantity is a measure of the amount of ions removed by PPy films from the object solution to the regenerating system. It appears that the ion exchange ability of PPy films can be estimated by this method more directly and exactly than by the previous method.

Q_{CV1}, Q_{CV2} for Cl⁻ exchange experiments is the integrated current corresponding to the dashed lines of the first and second CV cycles of cathodic scanning from 0.6 to -1.0 V. These corresponding quantities for Na⁺ exchange were obtained from the dashed lines of the first and second CV cycles of anodic scanning from -1.0 to 0.6 V. Then the ion exchange ability of PPy/A films for Cl⁻ and Na⁺ could be determined by Q_E .

According to the above designed conditions, similar ion exchange experiments were carried out for other PPy/A films, and the CVs are displayed in

Figure 7, where Figure 7(a,b) shows CVs of ejection of Cl⁻ and Na⁺, respectively. Figure 7 shows that the potential range of ejection of inserted ions, the current in the first CV cycle is always larger than in the second cycle. The difference between the first and second CV cycle in Figure 7(a) is distinct, however, it is not obvious in Figure 7(b) except for the PPy/DS film.

According to the results in Figure 7, Q_E values of PPy/A films for Cl⁻ and Na⁺ were calculated by the method described above: the results are shown in Figure 8. All of the PPy/A films were synthesized with the same charge, so the ion exchange ability of PPy/A films can be directly evaluated by Q_E , i.e., the larger is Q_E , the better the ion exchange ability of the PPy/A film.

The results in Figure 8 show clearly that the relative order of Cl⁻ exchange ability of PPy/A films is

$$\text{PPy/pTS} > \text{PPy/NO}_3 > \text{PPy/DS} > \text{PPy/Cl},$$

whereas the relative order of Na⁺ exchange ability of the films is

$$\text{PPy/DS} > \text{PPy/pTS} > \text{PPy/NO}_3, \text{ PPy/Cl}.$$

The above results are similar to the previous results (section under Results and discussion). However, comparison of the CV charges in Figure 3 and the ion exchange charges in Figure 8 show that for all PPy/A films studied, the Na⁺ exchange charges are always smaller than the Na⁺ CV charges, though the charges for Cl⁻ exchange show an ambiguous relationship. The CV charges include all the electrochemical processes including charge and discharge of the electrical double layer, electrolysis of water, etc during CV measurement, whereas the ion exchange charges are only from removal of the ions by PPy/A films to the regenerating solution.

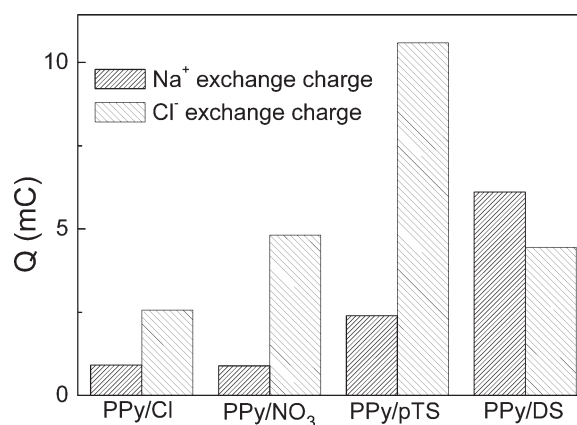


Figure 8 Exchange charges for removal of Na⁺ and Cl⁻ by PPy/A films, which were synthesized for 4 min at 1.6 mA cm^{-2} .

Although the new experiment might have many defects and would be affected by scanning potential, sweep rate, concentration of the test solution, temperature, and so on, it is nonetheless a brief and simple method to more exactly describe the ion exchange processes.

Ion exchange ratio

According to the above analysis, the ion exchange ability of PPy/A films can be evaluated from ion exchange charge under the precondition that the PPy/A films must be synthesized at the same charge. To conveniently compare the ion exchange ability of PPy/A synthesized under different conditions, the ion exchange ratio is proposed as the average quantity of ion removed by a specified number of Py units in PPy films.

The ion exchange charges can be used to describe the amount of exchanged ions,^{5,8,16} and the synthesis charge Q_{Poly} can be used to characterize the amount of pyrrole monomer in the PPy chain. In this work, all of the ions exchanged with PPy/A films were univalent ions. Consequently, the ion exchange ratio (R_E), defined as the amount of ion exchanged by 100 pyrrole units of PPy chain, can be calculated by the following formulae.

$$R_E = |Q_{\text{CV1}} - Q_{\text{CV2}}| / ZQ_{\text{poly}} \times 100\% \quad (1)$$

$$= Q_E / ZQ_{\text{poly}} \times 100\% \quad (2)$$

$$= n_E / n_{\text{py}} \times 100\% \quad (3)$$

where, Z = valence of the ion (unity, in this study), n_E = molar quantity of object ion carried by PPy film, n_{py} = molar quantity of pyrrole monomer oxidized during electropolymerization or the molar amount of pyrrole unit in the PPy film.

The operating exchange capability (OEC) (q), which is important for evaluating the exchange ability of ion exchange resins, is the ratio moles of ions exchanged/resin mass. The relationship of operating exchange capability and ion exchange ratio can be described by the following formulae.

$$q = \frac{n_E}{m_{\text{exchanger}}} = \frac{n_E}{n_{\text{py}} \times M_{\text{PPy}}} = \frac{R_E}{M_{\text{PPy}}} \quad (4)$$

$$= \frac{R_E}{M_{\text{Py}} - 2 + M_{\text{DA}} \times d} \quad (4)$$

$$= \frac{R_E}{d \times M_{\text{DA}} + 65.09} \quad (5)$$

where $m_{\text{exchanger}}$ = mass of PPy film, M_{PPy} = average molecular weight per molar pyrrole unit in PPy film, M_{Py} = molecular weight of pyrrole (67.09 g

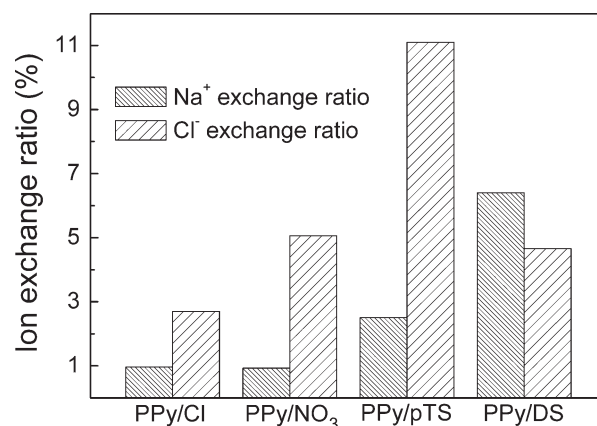


Figure 9 Ion exchange ratio of PPy/A (A: Cl⁻, NO₃⁻, pTS⁻ and DS⁻) films synthesized at different current densities.

mol⁻¹), M_{DA} = molecular weight of dopant anion, d = degree of doping of counterions in PPy chain.

The ion exchange ratio of PPy/A films calculated by eq. (1) are presented in Figure 9, which shows that the ion exchange abilities of the PPy/A films are consistent with those obtained from Figure 8, because the synthesis charge was 95.2 mC for all PPy/A films in this work.

CONCLUSIONS

1. Among the studied PPy/A (A: Cl⁻, NO₃⁻, pTS⁻, and DS⁻) films, PPy/pTS (doped with the medium sized counterion pTS⁻) shows the best anion exchange ability, whereas PPy/DS (doped with the large counterion DS⁻) exhibits the best cation exchange ability.
2. Ion exchange simulation experiments were designed to evaluate the actual quantity of ions that can be removed by PPy/A films. The ion exchange charges and ion exchange ratio are proposed for characterizing ion exchange behavior. Moreover, the ion exchange ratio can be conveniently converted to the operating exchange capability. This method confirms that PPy/pTS and PPy/DS films show the best anion and cation exchange ability, respectively.

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