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Enhanced Charge Transfer Through Polypyrrole Electropolymerized on Poly(acrylonitrile-co-butadiene)/Pt Electrodes

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Abstract : The charge transfer rate in polypyrrole(PPy) electropolymerized within poly(acrylonitrile-co-butadiene)(PAB) was compared with that in PPy deposited Pt electrodes by using cyclic voltammetry, chronoamperometry, and chronopotentiometry in acetonitrile. For both electrodes anodic and cathodic peak currents were proportional to scan rates below 100 mV/sec, but to square root of scan rates beyond 200 mV/sec. The apparent diffusion coefficient of ClO_4^- in the PPy/PAB composite is estimated to be 1.6 times larger than that in PPy. The PPy films composited within PAB layer showed higher anodic and cathodic currents and possessed faster charging-discharging process and larger capacity.

Keyword : poly(acrylonitrile-co-butadiene), polypyrrole, charging-discharging

1. Introduction

Conductive polypyrrole can be reversibly switched between electronically insulating and conducting states[1-4]. The transition involves a charge transport process by the movements of charges in oxidized pyrrole units and of compensating counter anions through the PPy film. The rate of charge transfer process is mainly studied by scan rate dependence on anodic or cathodic peak currents of PPy. When the relationship between

peak current(i_p) and scan rate(υ) becomes linear, the charge transport is governed by a heterogeneous electrode reaction. However, the linear relationship between i_p *vs.* $\upsilon^{1/2}$ suggests that ionic diffusion controls the charge transport process[5, 6].

The currently available data are not unequivocal about the mechanism of the rate of charge transport, although majority of the data agree with that the rate of this charge transport process is controlled by ionic diffusion in the polymer phase[4]. Depending on the difference in even counter anions employed during the electropolymerization of pyrrole, the peak currents show linear dependence either on scan rate or on the square root of scan rate[5]. The scan rates employed in the previous studies were limited to the low region of less than about 100 mV/sec. In this report, we attempt to increase the scan rate up to 1800 mV/sec and to find whether the mechanism of charge transport rate within a given PPy film is influenced by the scan rate.

The rate of charge transport can become faster when the PPy morphology is varied. For example, Naoi and Osaka found that a PPy film grown Pt substrate, which had been precoated with poly(acrylonitrile-co-butadiene)(PAB) film as an insulating material, showed enhanced anion doping-dedoping process because of its oriented grown structure[7]. The charge transport becomes faster also when PPy films were formed to have a porous and rough structure since counter anions incorporated in the PPy films were found to accompany a smooth doping-dedoping reaction.

In this report, we also attempt to investigate the effect of PAB on the rate of charge transport through PPy film. To achieve this aim, comparisons were made between a PPy coated Pt electrode and a PPy and PAB coated Pt electrode by using cyclic voltammetry, chronoamperometry, and chronopotentiometry in acetonitrile.

2. Experimental

Pyrrole purchased from Janssen(98 %) was purified by fractional distillation before use. Acetonitrile (J.T.Baker, HPLC reagent) was used as solvent without further purification. Lithium perchlorate(Janssen) was used as supporting electrolyte. All solutions were purged with Ar gas for 15 min before electrochemical measurements.

An EG & G Princeton Applied Research Co.(PARC) M362 potentiostat/galvanostat was used for the polymerization of pyrrole and for the measurement of cyclic voltammetry. Current- and potential-transients were performed using a PARC M273. A cell was suited for a solution volume of about 20 mL, and allowed for the introduction of three electrodes and a deaeration tube. A Pt(Aldrich, 99.99 %) plate and a Pt wire served as a working electrode for the substrate of polymerization and a counter electrode, respectively. A reference electrode, Ag/Ag^+(0.10 M $AgNO_3$ /acetonitrile), was encased in a bridge tube connected to the test solution by a Vycor-tip. All potentials were cited against the Ag/Ag^+ reference electrode.

A thin film of PAB(Aldrich, 30~32 wt. % acrylonitrile) was coated, prior to the polymerization of pyrrole, by dropping 50 μL of 1 %(w/w) PAB in $CHCl_3$ on a 1 cm^2 Pt plate. The PAB precoated Pt electrode was then immersed in 0.10 M $LiClO_4$ acetonitrile containing 0.10 M pyrrole and PPy was grown electrochemically by scanning over the voltage range between -1.4 V and+0.7 V. Thickness of the PPy film was estimated by

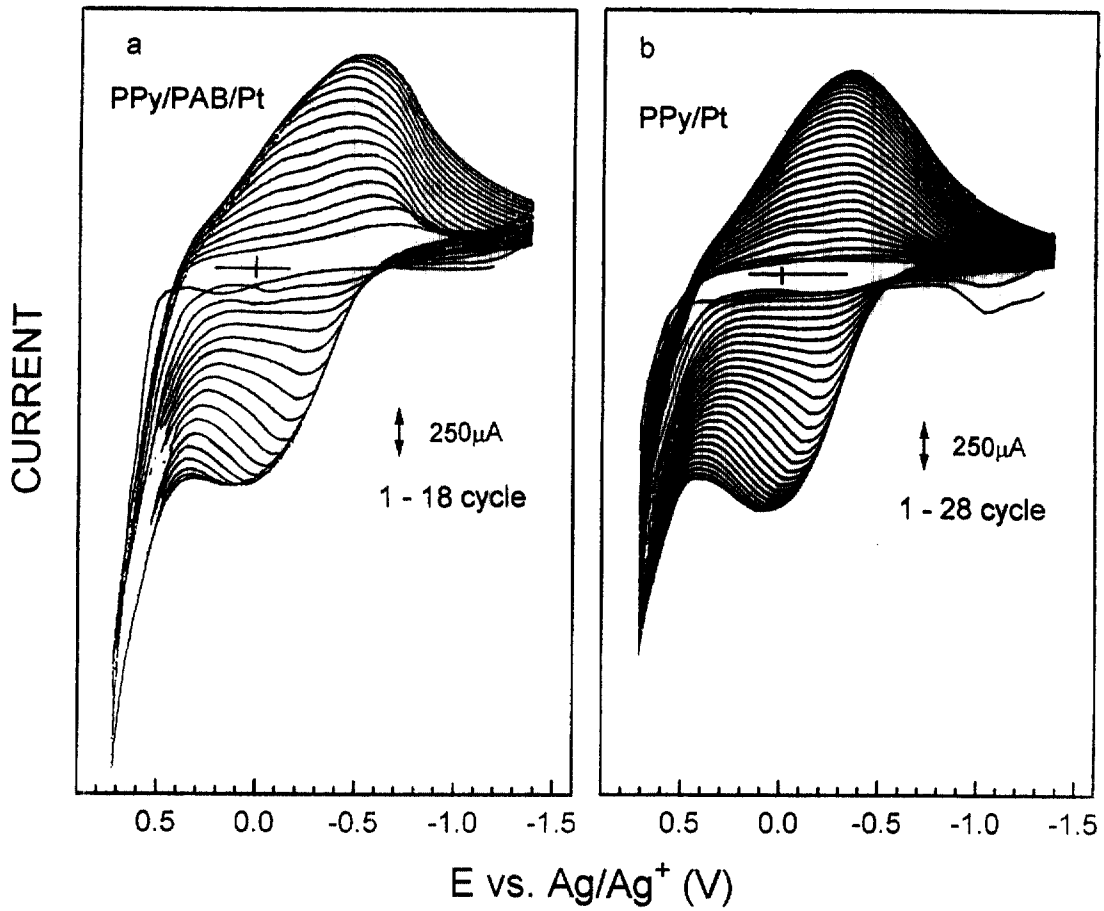

Fig 1 Typical cyclic voltammograms for the polymerization of PPy on PAB/Pt(a) and Pt(b) electrodes from 0.1 M pyrrole in 0.1 M $LiClO_4$/acetonitrile. Scan rate ; 50 mV/sec.

using the relationship that 8 mC/cm^2 of charge provides 20 nm of PPy film, as proposed by Diaz et al.[8]. Typical thickness of the PPy film was 0.25 μm. After polymerization, since it was found to be nontrivial to wash away the host PAB polymer with methylethylketone employed by Naoi et al.[7], PAB film was retained in the subsequent measurements. Thin films of PPy were inspected with a Hitachi S-4200 scanning electron microscope. Contrary to PPy film of a PPy/Pt electrode, the micrograph a PPy/PAB/Pt electrode showed a smooth surface of PAB itself. This indicates that PPy was grown within PAB film and was not protruded the surface of PAB.

3. Results and Discussion

Fig. 1 shows cyclic voltammograms for the growth of PPy film on PAB/Pt(*Fig. 1*a) and on Pt(*Fig. 1*b). As is evident from the figures, the growth rate of PPy on a PAB/Pt electrode was faster than that on a Pt electrode under identical conditions. This result is most likely

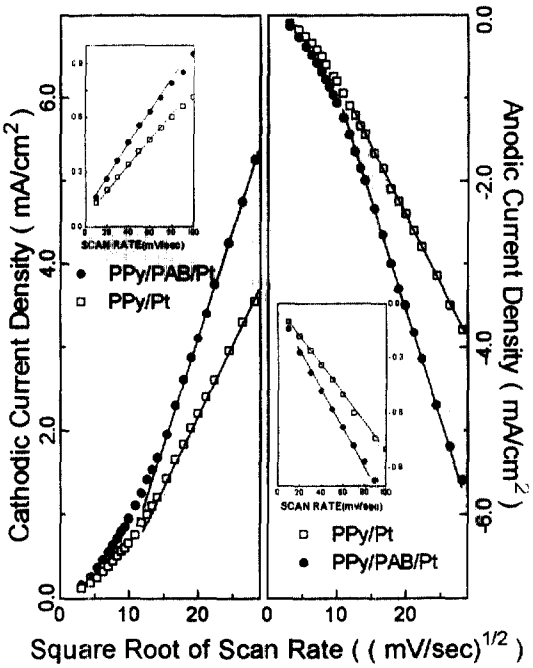

Fig. 2 Plots of cathodic and anodic peak current *vs.* scan rate.

attributable to the increased effective surface area of an electrode when PAB is coated prior to PPy polymerization. The result is consistent with the literature by Naoi et al.[7], where PPy film was found to grow toward the direction of solution side in the presence of PAB film and thus had more porous morphology. On Pt surface, however, PPy was grown largely to the direction of electrode surface and to have relatively compact morphology.

To compare redox characteristics of the PPy/PAB/Pt and PPy/Pt electrodes, cyclic voltammograms were recorded in pyrrole free acetonitrile solution containing 0.10 M $LiClO_4$. For both of the electrodes, the differences between the anodic and cathodic peak potentials were increased with the increase in scan rate, implying that the electrochemical process responsible for the currents is irreversible[6,9]. The relationship between the peak currents and scan rates(υ) are compared quantitatively in *Fig. 2*. At the scan rates of lower than about 100 mV/sec, both of the anodic and cathodic peak currents are proportional to scan rate, however, at υ > 200 mV/sec the peak currents are proportional to the square root of scan rate.

Published results seem to support the linear dependence of peak currents on scan rate of below 100 mV/sec[8]. Osaka et al.[10] reported a similar result showing that as the PPy film thickness became thinner the peak current approached to a linear dependence on scan rate. The PPy film thickness of 0.25 μm employed here belongs to their linear dependence regime. The linear dependence may be quite analogous to the current-voltage curves for the case when electroactive species are adsorbed[11]. Thus at lower scan rate than 100 mV/sec irrespective of the presence of PAB film, the currents are mainly controlled by the heterogeneous electrode reaction which can be expressed as

$$\text{-Py-} \longrightarrow \text{-Py}^{+}\text{-} + e^{-} \qquad (1)$$

where -Py- and -Py$^+$- symbolize reduced and oxidized monomer units, respectively. Since ClO_4^- concentration[12] inside PPy film can be higher than 3 mol/L depending on rinsing method after PPy polymerization and since small current density of less than about 1 mA/cm^2 was involved at lower scan rates(*Fig. 2*), charge compensation was apparently achieved faster by the movement of counter anions between the two phase of solvent swollen polymer and solvent filled pores inside PPy film than the charge transfer process through the polymer film(Eq. 1). This means that even when PPy is in the reduced state

substantial amount of ClO_4^- stays in the solvent filled pore phase inside PPy film and that the movement of ClO_4^- across the boundary of the two phases inside PPy film does not require much activation energy.

However, at 200 mV/sec ≤ υ ≤ 1800 mV/sec the peak currents were found to be proportional to the square root of scan rate(*Fig. 2*) for both electrodes, implying that the current generation process is controlled by the diffusion of electrolyte,

$$ClO_4^-{}_{bulk} \rightleftharpoons ClO_4^-{}_{PPy} \qquad (2)$$

where $ClO_4^-{}_{bulk}$ and $ClO_4^-{}_{PPy}$ stand for ClO_4^- in bulk solution outside PPy film and in the polymer phase inside PPy film, respectively. At high scan rates under which high current is involved, counter anion movement should be high, too. In such a case, counter anions inside PPy film are not sufficient enough to compensate all the oxidized PPy. Majority of counter anions should then be supplied from the bulk solution outside PPy film, and therefore the rate of diffusion process(Eq. 2), which is slower than the charge transfer process(Eq. 1), controls the overall current. Thus, the mechanism of the charge transfer process is mainly determined by the amount of charge compensating.

Although both electrodes exhibit the same characteristics of current density *vs.* scan rate, their slopes are quite different(*Fig. 2*). Specifically, at a given scan rate of υ ≤ 100 mV/sec, where the ClO_4^- diffusion is not important, the ratio of peak current of the PPy/PAB/Pt to that of PPy/Pt can be assumed, using the peak current-scan rate relationship for adsorbed electroactive species[6, 9, 11], as

$$(i_{PAB} / i)^l = (AC_0^*)_{PAB} / (AC_0^*) \qquad (3)$$

where A and C_0^* are the area of the electrode and the concentration of anion near the electrode surface, both of which in the PPy/PAB/Pt electrode are generally not equal to those in the PPy/Pt electrode. The subscript PAB signifies the PPy/PAB/Pt electrode. The superscript *l* stands for the current ratio at lower scan rates. From *Fig. 2*, we obtain $(i_{PAB}/i)^l$ = 1.2 for both anodic and cathodic currents. At υ > 200 mV/sec, where anion diffusion controls the currents, the ratio of peak currents of PPy/PAB/Pt and to that of PPy/Pt at higher scan rates can be simplified as[6,9]

$$(i_{PAB} / i)^h = (AC_0^* D^{1/2})_{PAB} / (AC_0^* D^{1/2}) \qquad (4)$$

where D is the diffusion coefficient of ClO_4^-. From *Fig. 2*, we obtained $(i_{PAB}/i)^h$ = 1.5 for both anodic and cathodic currents. Taking the ratio of Eq. (4) to Eq. (3) we get

$$(D_{PAB} / D)^{1/2} = (i_{PAB} / i)^h / (i_{PAB} / i)^l \qquad (5)$$

Using the values obtained from Eq.(3) and Eq.(4) we obtain that $D_{PAB}/D \cong 1.6$, that is, the apparent diffusion coefficient of ClO_4^- into and out from the PPy film of PPy/PAB/Pt electrode is approximately 60 % larger than that of the PPy/Pt electrode. This result confirms that the PPy/PAB/Pt electrode is composed of a rougher and more porous PPy film and consequently has a high degree of efficiency in anion releasing than the PPy/Pt electrode. This ratio, however, is about 20 % less than that obtained by Osaka et al., in a slightly different way of analysis[10]. Assuming that the presence of PAB film would not change greatly the value of C_0^*, the discrepancy of the ratio of the apparent diffusion coefficients can be firstly attributed to the differences in

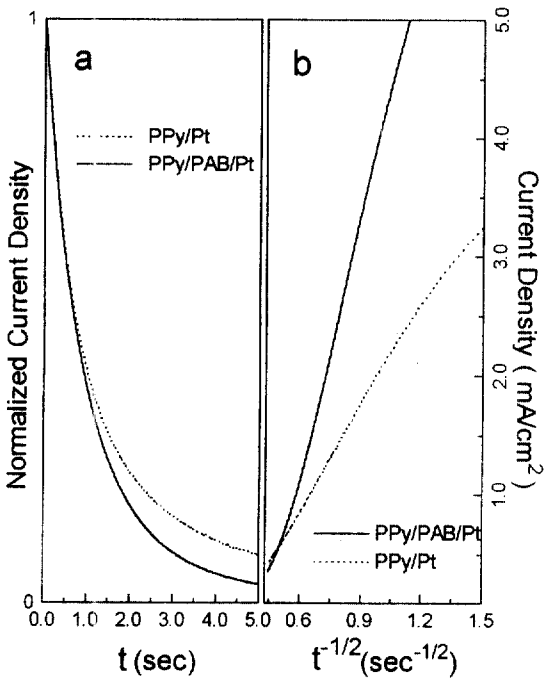

Fig. 3 Chronoamperometry response at PPy/PAB/Pt(solid lines) and PPy/Pt(dotted lines) electrodes in 0.1 M $LiClO_4$/acetonitrile, $E_{app.}$ = -0.3 V(dedoping process) after charging at +0.5 V for 3 min.

the their values of effective surface area between the PPy/PAB/Pt and PPy/Pt electrodes. Secondly, since the PAB film was retained, contrary to their electrodes, the anion diffusion from or into the PPy film of the PPy/PAB/Pt electrode is somewhat retarded.

These results suggest that the PPy/PAB/Pt and PPy/Pt electrodes possess the same charge-transport process, but their electrochemical kinetics are different. The latter property was further tested by chronoamperometry. *Fig. 3* presents a set of chronoamperometric responses obtained with PPy/PAB/Pt and PPy/Pt electrodes. The potential of the electrode was initially kept at +0.5 V for 3 min in order to ensure that the PPy film was in equilibrium with its cations, after which a negative potential, $E_{app.}$ = -0.3 V, was abruptly applied and the cathodic current of the electrode was measured as a function of time. The results show that the current of the PPy/PAB/Pt electrode was about 2.5 times larger than that of the PPy/Pt electrode at all times(*Fig. 3*b), and that in the normalized chronoamperometric responses(*Fig. 3*a) the current decay of the PPy/PAB/Pt electrode is faster than that of the PPy/Pt electrode. These chronoamperometric data have been utilized to calculate the apparent diffusion coefficients of anions for the dedoping from PPy to bulk electrolytes after converting to Cottrell plots[13](*Fig. 3*b). The ratio of slopes of Cottrell plots for a PPy/PAB/Pt electrode to that of a PPy/Pt electrode formally has the same expression as given by Eq. (4). However, we noted that a significant difference existed between the two electrodes that we were comparing. That is, the electrodes were influenced differently by the applied potential of -0.3 V in terms of dedoping of ClO_4^-. As can be seen in *Fig. 1*, cathodic peak potentials shift toward more negative values for the PPy/PAB/Pt electrode in comparison with those for the PPy/Pt electrode at all scan rates, which implies that at -0.3 V the concentrations of ClO_4^- in PPy of the two electrodes can be significantly different. Therefore it appears difficult to obtain the ratio of the apparent diffusion coefficients from Cottrell plots in the present experiment. If the applied potential were changed to a somewhat more negative value, the difference in the anion concentration would become smaller. Even in this case it is not justified to utilize the data of *Fig. 2* to obtain the ratio of the apparent diffusion coefficients on the same ground as above. The slope ratio of 2.5 obtained from *Fig. 3* can be best explained by that the ratio of the apparent diffusion coefficients(Eq. (5)) is

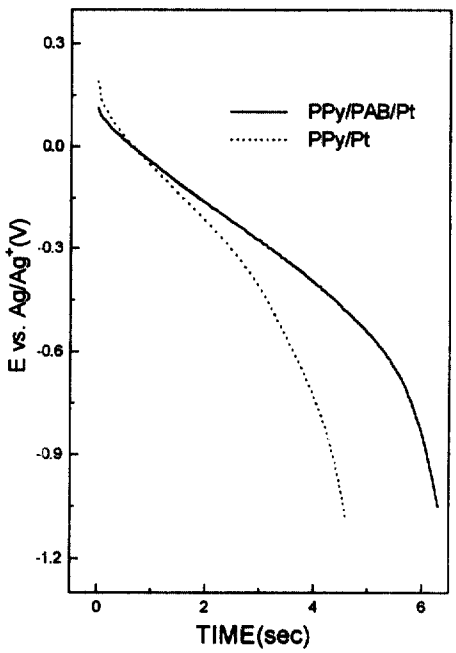

Fig. 4 Chronopotentiograms at PPy/PAB/Pt(solid line) and PPy/Pt(dotted line) electrodes in 0.1 M $LiClO_4$/acetonitrile, $J_{app.}$ = +1.0 mA/cm^2(dedoping process) after oxidation at +0.5 V for 3 min.

greatly increased in comparison with that obtained from the cyclic voltammograms obtained under high scan rates. It is noteworthy to observe that the PPy/PAB/Pt and PPy/Pt electrodes exhibit almost the same anodic peak potentials and the similar anodic waves, whereas their corresponding cathodic characteristics are quite different(*Fig. 1*). That is, the cathodic peak for the reduction of oxidized PPy occur at more negative potentials in the case of the PPy/PAB/Pt electrode than those of the PPy/Pt electrode. This can be explained by assuming that positive sites of PPy in oxidized form of the PPy/PAB/Pt electrode are somewhat stabilized with the nitrile groups of PAB polymer. This type of ion-dipole interaction largely disappears in the reduced, neutral PPy.

Chronopotentiometry was utilized so as to compare the capacity of the electrode, another criterion of a battery, in 0.10 M $LiClO_4$ acetonitrile. The experiment was performed by holding an initial potential of +0.5 V for 3 min in order to establish a charging state before injection of cathodic current density of $J_{app.}$ = 1.0 mA/cm^2. *Fig. 4* shows that discharging transient time[14], of the PPy/PAB/Pt electrode is longer than that of the PPy/Pt electrode. Higher overpotential should be applied on the PPy/PAB/Pt electrode to obtain the same amount of current density at a given time from PPy film of a more compact structure in the case of PPy/Pt was more easily imposed on overpotential because of the difficulty of anion releasing[7,15]. The result is consistent with a smaller apparent diffusion coefficient in the PPy/Pt electrode. The difference in the area under the potential-time transient curve reflects the difference in the amount of anions discharged during the dedoping process at a constant current density. The amount of anion discharged should be proportional to the AC_0^*d, where d is the thickness of PPy film. Since the PPy/PAB/Pt electrode has larger AC_0^* as obtained above and thicker film than the PPy/Pt electrode, we obtain $(AC_0^*d)_{PAB} > (AC_0^*d)$, which is what we can extract from *Fig. 4*. It is concluded that for a same amount of PPy deposited a PPy/PAB/Pt electrode has a larger capacity than a PPy/Pt electrode.

Conclusions

The presence of PAB made electropolymerized PPy to be more porous and rougher. At lower scan rates the currents are controlled by a heterogeneous electrode

reaction whereas they are controlled by diffusion of counter anions at higher scan rates, irrespective of the presence of PAB layer. The apparent diffusion coefficient of ClO_4^- in PPy/PAB composite is 1.6 times larger than in PPy. As a consequence, PPy/PAB/Pt electrodes showed faster charging-discharging process compared with PPy/Pt electrodes. Cathodic peak potentials of PPy/PAB/Pt electrode were shifted toward more negative values with respect to those of PPy/Pt. This is attributed to the existence of ion-dipole interaction between oxidized PPy and PAB. Larger capacity and faster charging-discharging behavior of PPy/PAB composites can be useful as active materials in battery applications.

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