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Electrochemical behavior of a composite of polyimide and polypyrrole

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Conducting composites composed of polypyrrole (PPy) and polyimide (PI) have been successfully synthesized by electrochemical oxidative polymerization of pyrrole in a PI matrix. The PPy–PI composite has higher permeability to ions than a PPy–poly(amic acid) composite. The charge storage ability of the PPy–PI composite was found to be higher than those for PPy film and for a PPy–poly(amic acid) composite containing the same amount of PPy. This behavior may be due to the intrinsic electroactivity of the PI matrix and the high permeability of PI to ions during the electrochemical process. This makes composites containing conducting polymer as a filler and PI as a matrix to be a promising candidate for charge storage devices application.

Introduction

Intrinsically conducting polymers (ICP's) have attracted a lot of attention during the last decades because of their unique electronic structure—conjugated double bonds in their backbone. Polypyrrole [Fig. 1, (a)], polythiophene [Fig. 1, (b)], polyaniline [Fig. 1, (c)] and their derivatives are the most studied conducting polymers. They possess high electrical conductivity, excellent electroactivity and relatively high environmental stability. Since their discovery ICP's have been investigated for application in different electronic devices: rechargeable batteries,[1,2] and capacitors,[3] pH sensors and electrochromic devices,[4] selective membranes,[5] optoelectronic devices,[6] electromagnetic screens,[7] corrosion protection,[8] wetting agents for improving compatibility in composites with carbon fibers.[9,10]

Preparation of composites with a chemically inert and mechanically stable matrix is the most effective way to improve the mechanical properties and environmental stability of ICP's.

Conducting polymer–polyimide composites have attracted much attention because of their high temperature stability, good mechanical properties, and high chemical stability. Polyaniline–polyimide blends have been used in gas separation.[11–13] For the same purpose Langmuir–Blodgett films containing conducting polymers have been reported.[14]

Composites comprising ICPs and thermostable matrixes with high mechanical characteristics significantly expand the area of ICPs applications. PI is a promising candidate for composites with ICP fillers for applications, especially as electromagnetic screens and antistatic coatings,[15–17] active elements in rechargeable batteries[18] and gas separation membranes.[14]

In 1983 electrochemical activity of polyimides was reported by Haushalter and Krause.[19] Cathodic reduction in PIs followed by formation of anions and dianions (shown in Fig. 2) has been described. In this paper we compare the electrochemical behavior of PPy and PPy–PI composites. Stainless steel (SS) was chosen as the working electrode as a low cost material with high inertness to cathodic processes.

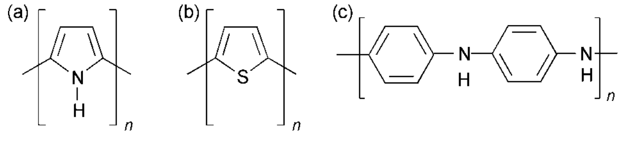

Fig. 1 Schematic representation of polypyrrole, polythiophene and polyaniline.

Experimental

Polyimide (PI) is a product obtained from its precursor poly(amic acid) (PAAc) by a catalytic cyclization reaction that is shown in Fig. 3.

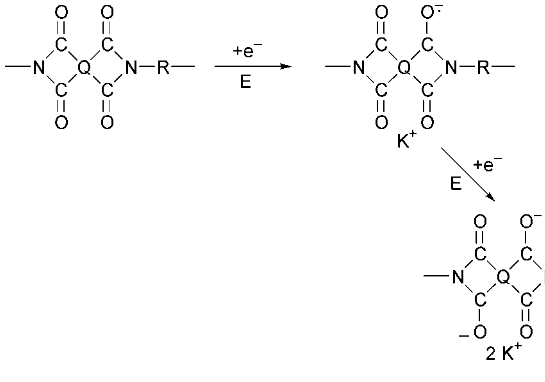

Fig. 2 Schematic representation of cathodic electrochemical reduction of aromatic polyimides followed by formation of anion radicals and dianions. K$^+$ denotes a counter-ion, Q and R denote aromatic radicals.

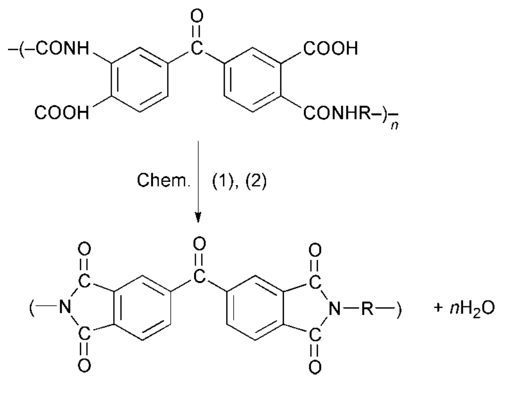

Fig. 3 Schematic representation of poly(amic acid)–polyimide conversion, R = 1,3-phenylene for Pyralin. *Reagents and conditions*: (1) reaction medium containing pyridine and acetic anhydride, (2) 20 °C.

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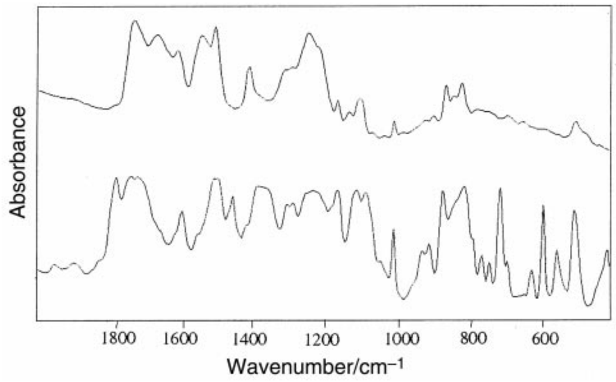

Fig. 4 IR spectra for PAAc (top), and chemically imidized PI (bottom).

A 28% solution of Pyralin [the poly(amic acid) poly(1,3-phenylene-3,3′,4,4′-benzophenonedicarboxylic diamide)] in *N*-methylpyrrolidone was used for casting of films onto the surface of the working electrode (WE) which was previously polished and cleaned ultrasonically in an acetone–methanol mixture. The poly(amic acid) (PAAc) coated electrode was dried at 60 °C under reduced pressure (550 mmHg) for 4 hours. All films were processed immediately after the completion of drying.

For the preparation of PI coated electrodes, samples obtained by the above method were further subjected to catalytic cyclization as described elsewhere.[20] IR spectra of PI and PAAc (Fig. 4) show that extensive imidization has occurred, as shown by changes in the characteristic PAAc IR peaks at: 1410 $\mathrm{cm^{-1}}$, 1513 $\mathrm{cm^{-1}}$ (1560 $\mathrm{cm^{-1}}$), 1660 $\mathrm{cm^{-1}}$ (1680 $\mathrm{cm^{-1}}$) and corresponding increase in the imide peaks at: 1780 $\mathrm{cm^{-1}}$, 1380 $\mathrm{cm^{-1}}$ and 725 $\mathrm{cm^{-1}}$, respectively.

Electrodeposition of PPy was carried out in a one-compartment electrochemical cell that is schematically shown in Fig. 5 at a current density of 0.5 mA $\mathrm{cm^{-2}}$ in a solution containing 0.01 M pyrrole† and 0.1 M $\mathrm{KPF_6}$ in acetonitrile (AN) until 1 C $\mathrm{cm^{-2}}$ was passed. A galvanostatic regime was chosen in order to polymerize the same amount of a conducting polymer in both cases when PAAc and PI were used as matrix and to control this amount precisely.

Potentiostat–galvanostat Model 273A (Princeton Research Company) was used to maintain regimes of the experiment. *I–t*, and cyclic voltammetry curves were recorded using 4.0 Research electrochemistry software.

To prepare freestanding PPy films electrodeposition was carried out on bare SS electrodes. To prepare PPy–PAAc and PPy–PI composites, electrodeposition was carried out on the working electrode preliminarily coated with PAAc and PI respectively.

Results and discussion

Fig. 6 shows the variation of electrode potential with time for electrodeposition of PPy on bare substrate and PI and PAAc coated SS.

The *E–t* curve for the electrodeposition of PPy on PI coated SS is very similar to that for deposition of PPy on bare SS. However, the *E–t* curve for deposition of PPy on a PAAc coated electrode shows a higher steady state potential of ~2.8 V *vs.* SCE‡ that is due to the high resistance of the film to ion flux in diffusion limited process.

Cyclic voltammetry (CV) of different types of films was taken under anodic potentials. CV graphs corresponding to the second and third circles are shown in Fig. 7. CV graphs for various films at applied conditions (scan rate 20 mV $\mathrm{s^{-1}}$, scan range −0.2–1.2 V, $[\mathrm{KPF_6}] = 0.1$ M, $S_{\mathrm{el}} = 10\ \mathrm{cm^2}$) resemble elongated loops. Maximum values of current when potential changes within the range $|E| \leqslant 1.3$ V are compared in Table 1. This potential range was chosen because it includes the window of electrochemical activity of PIs (0.7–1.3 V).[19] We did not observe any signs of PIs or PPy or solution decomposition by IR analysis at these potentials. The anodic peak at 0.6 V for PAAc is due to the electrochemical oxidation of PAAc. Table 1 and Fig. 7 (a) and (b) show that the electrochemical activity of PAAc is much weaker than that of PI. For PAAc this behavior can be explained by the low permeability of films to ions. This is confirmed by the integration of areas under the CV curves which was done in order to determine the amount of charge consumed during the electrochemical oxidation–reduction process and to determine the properties of the film.

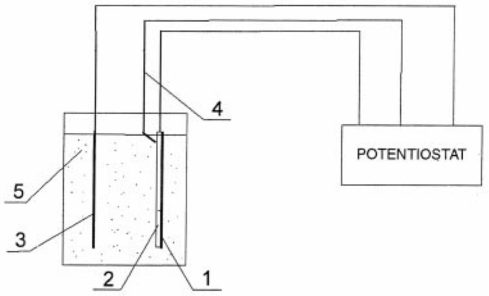

Fig. 5 Schematic representation of the electrochemical cell used for experiments, (1 – working SS electrode, 2 – polyimide coating, 3 – counter electrode, 4 – reference electrode, 5 – solution).

The high permeability of PI film to ions in electrochemical processes may originate in the porous structure of the PI matrix or the ion exchanging properties of functional groups belonging to the imide radicals. The interactions between matrix and filler in a composite needs further research, which we plan to do in the future.

The PPy–PAAc system showed significantly higher stored charge of about 35 mC, Fig. 7 (c) and Fig. 9, which is higher than that for pure PAAc, 1 mC. The charge stored by pure PI film is 50 mC, which is possibly due to the electrochemical activity of the PI matrix which is therefore related to anodic oxidation (Fig. 8). The PPy–PI film showed the highest charge storage ability (162 mC) which is larger than that obtained for PPy film (110 mC) and is equal to the sum of the matrix and filler electroactivities.

To evaluate the permeation of the matrix to ion flux quantitatively, the slope of the *I–t* curves at the initial stage of

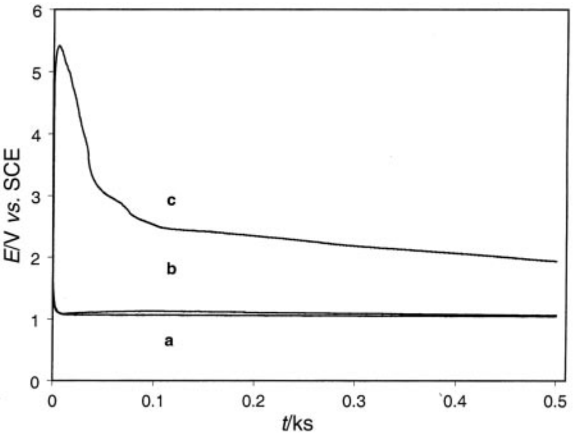

Fig. 6 Potential–time curves for the deposition of PPy on (a) PI coated SS, (b) uncoated SS, (c) PAAc coated SS, ($[\mathrm{Py}] = 0.01$ M, $[\mathrm{KPF_6}] = 0.1$ M, $I = 0.5\ \mathrm{mA\ cm^{-2}}$).

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†All chemicals were obtained from Aldrich Chemical Company and were used without further purification.

‡All the potentials below are given *vs.* Standard Calomel Electrode (SCE).

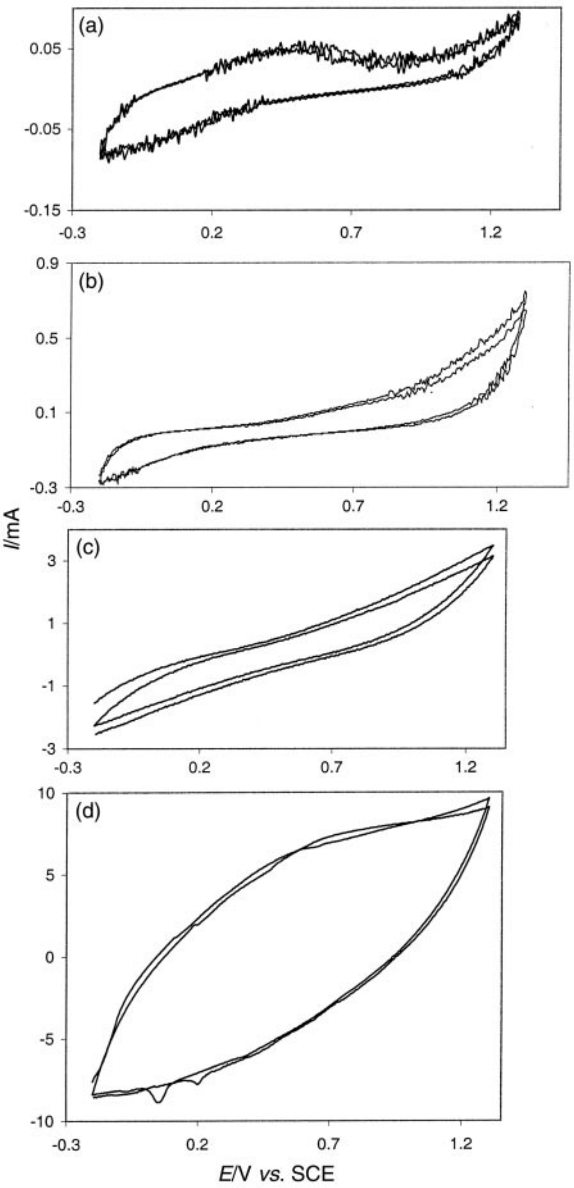

Fig. 7 Cyclic voltammograms of (a) PAAc, (b) PI, (c) PPy–PAAc composite, (d) PPy–PI composite (scan rate 20 mV s^{-1}. [KPF_6] = 0.1 M in AN, S_{el} = 10 cm^2).

the deposition process was plotted *vs.* the current density. A higher dependence was established for PPy–PAAc composite than that for PPy–PI (Fig. 10). This is in correlation with the higher resistance of PAAc to the diffusion of the monomer and electrolyte through the film. Two regions with different slopes were observed on both curves (Fig. 10). They possibly originate from regimes of nucleation (A1, B1) and growth (A2, B2) of PPy particles.

Scanning electron microscopy

The SEM pictures of the films are shown in Fig. 11. The upper surfaces of the PPy–PI and PPy–PAAc composites (in contact with solution) have a globular structure [Fig. 11 (a) and (b)]. The same structure has been reported for PPy films grown by electrochemical methods.[21] The lower surfaces of the PPy film (in contact with the electrode) have a porous structure [Fig. 11 (c)]. PPy–PI and PPy–PAAc composites have a dense morphology. A network consisting of PPy filaments impregnated in the smooth lower surface of a PI matrix covers the lower surface of the PPy–PI composite [Fig. 11 (d)]. This

Table 1 Maximum and minimum values of current during CV

Type of film	I_{min}/mA at −1.3 V	I_{max}/mA at 1.3 V
Uncoated electrode	−0.05	+0.05
PAAc	−0.1	0.08
PI	−0.3	0.75
PPy–PAAc	−2.5	3.5
PPy–PI	−7	9.5

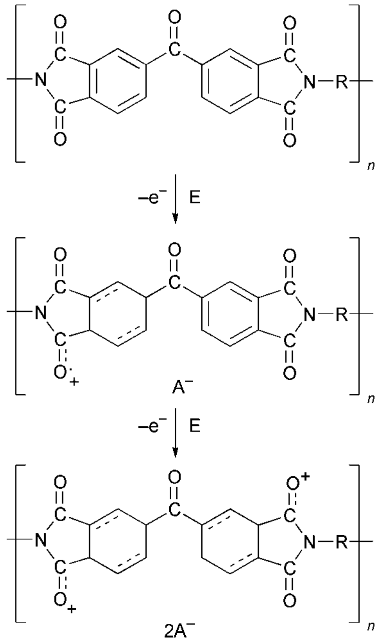

Fig. 8 Schematic representation of anodic electrochemical oxidation in aromatic polyimide followed by formation of a cation radical or dication; A^- denotes the counter-ion.

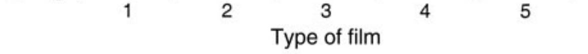

Fig. 9 Diagram showing the dependence of charge storage ability of composite films on their composition, 1: PAAc, 2: PPy–PAAc, 3: PI, 4: PPy, 5: PPy–PI.

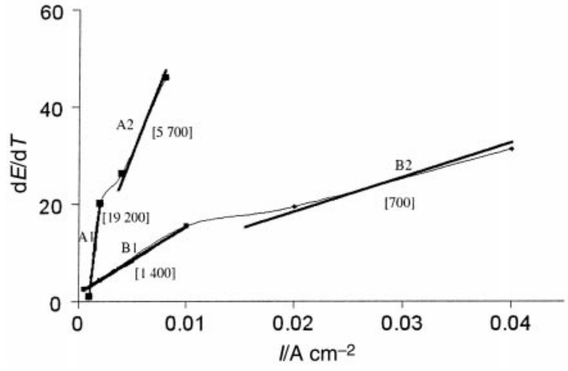

Fig. 10 d*E*/d*t* *vs.* *I* for the initial stage of deposition of PPy in PAAc (A) and of PPy in PI (B) matrixes, on stainless steel in a galvanostatic regime. In brackets slopes of the curves (*V*/*C*) are shown ([Py] = 0.01 M, [KPF_6] = 0.1 M in AN, E_{el} = 10 cm^2).

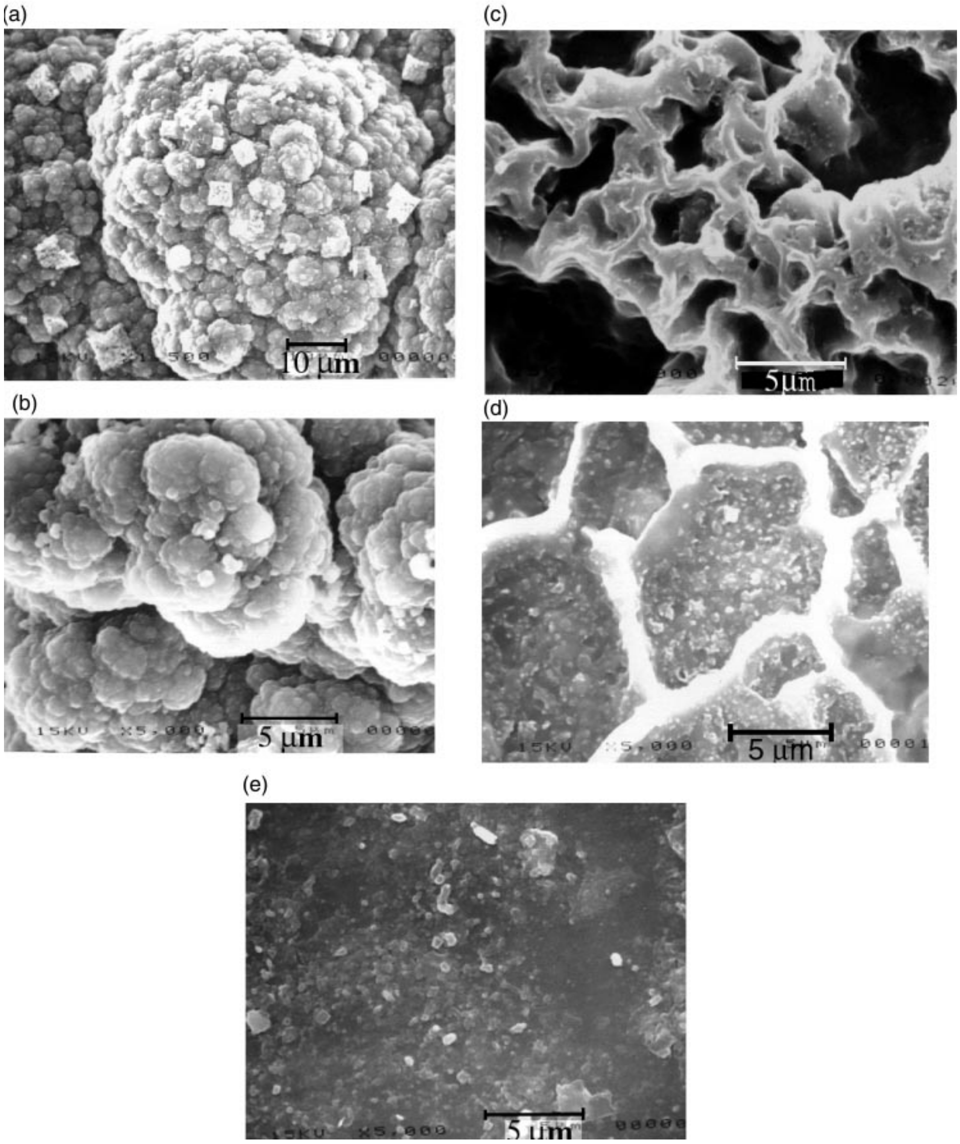

Fig. 11 SEM microphotographs of the composites (a) PPy–PI composite, upper side, (b) PPy–PAAc composite, upper side, (c) PPy, lower side, (d) PPy–PI composite, lower side, (e) PPy–PAAc composite, lower side.

picture is very similar to the surface of SS that is covered by a channel network. Formation of PPy in these channels prior to growth within the PI matrix is probably responsible for the morphology of the lower side of the PPy–PI composite. On the contrary, the lower surface of the PPy–PAAc composite looks more uniform and this may be caused by better adhesion between the PAAc and SS during the process of electrolysis. The lower surface of the PPy–PAAc composite consists of PPy globules impregnated in PAAc matrix, [Fig. 11 (e)].

Conclusion

Evaluation of the charge storage abilities of PPy and composites comprising PPy filler and polyimide matrixes have shown the highest value for the PPy–PI composite. The charge storage ability of PPy–PI films was as high as that for PPy coated on SS. This behavior can be explained by the addition of the intrinsic electroactivities of the PI matrixes and PPy filler and by the high permeability of PI to ions which was found to be higher than that for the PAAc film. High PI permeability to ions during the electrochemical process may be caused by high porosity of PI film.

High charge storage properties observed in PPy–PI composite make PI a promising candidate as a matrix for conducting polymer filled composites, especially in charge storage devices.

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