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Electrochemical behaviour of polypyrrole films modified with poly-$Cu(v\text{-}bpy)_2^{2+}$

SEONG K. CHA*
Department of Chemistry, Kyungnam University, Masan, 630-701, Korea
JONG-JAE CHUNG, EUI-HWAN PARK, CHI K. CHA
Department of Chemistry, Kyungpuk National University, Taegu, 702-701, Korea
H. D. ABRUÑA
Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, USA

Poly-$Cu(v\text{-}bpy)_2(ClO_4)_2$ was electrochemically implanted into a polypyrrole-polymer matrix at levels of 10 to 12% in order to improve the electrical properties of the electrode. To increase the porosity and orientation of the pyrrole polymer, the electrode was pretreated with nitrile butadiene rubber (NBR) and PF_6^- was the dopant anion. The presence of poly-$Cu(v\text{-}bpy)_2^{2+}$ enhanced the doping level to 65.6%, the conductivity by a factor of two, and the carrier concentration by a factor of ten. However, the cyclability was reduced by half, relative to polypyrrole alone, and the doping/undoping efficiency was diminished slightly from 0.94 (for polypyrrole alone) to 0.90.

1. Introduction

Polypyrrole, first reported by Diaz and Kanazawa [1], is one of the most thoroughly studied electronically conducting polymers. Its applications have varied widely to include use as an organic electrode, for information storage, and as an excellent cathode in secondary batteries. Structural studies by Yang *et al.* [2] showed that this polymer contains two types of ordered helical structures, simple and superhelix, but that they gradually transform to an amorphous phase at the air–polymer interface.

Using surfaces precoated with nitrile butadiene rubber (NBR), Naoi and Osaka [3] were able to prepare ordered films of polypyrrole which exhibited highly enhanced anion doping/undoping processes compared to untreated surfaces. They also reported that electrodes made with such oriented films had excellent cyclability (1800) but that the doping level (25–33%) was much lower than that of polyaniline (50–60%). Genies and Syed [4] measured a conductivity of about $1 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ for a poly-n-methylpyrrole–BF_4 polymer which was much lower than that of a simple polypyrrole. According to Street *et al.* [5] grafting other polymers to polypyrrole or electrochemical deposition of polypyrrole in the matrix of other polymers that can swell, such as polystyrene, can significantly modify the mechanical properties. Applying these concepts to a polypyrrole-polymer electrode, it is anticipated that the electrochemical properties may be effectively improved by implanting other polymeric materials into it so as to enhance the doping level, carrier concentration, conductivity and doping/undoping efficiency.

This paper describes the effect of doping oriented (with NBR) films of polypyrrole with poly-$Cu(v\text{-}bpy)_2$ (where v-bpy = 4-vinyl, 4′-methyl 2,2′-bipyridine). This material was chosen because of its potential for improving the electrochemical properties of polypyrrole. This is due to the fact that the complex is square planar with one vinyl group on each of the bipyridine ligands allowing for the growth of linear polymer chains. In addition, each monomer unit can carry two dopant anions so that doping levels can be greatly enhanced even with modest amounts of the incorporated complex. In addition, it can extend the Coulomb efficiency of the doping/undoping process.

2. Experimental procedure

Pyrrole (Merck) was dried with sodium hydroxide, and fractionally distilled under reduced pressure from sodium; it was then stored under nitrogen [6]. Acetonitrile (Merck) was dried over 0.3 nm molecular sieves and was used without further purification. The supporting electrolyte, tetra-n-butyl ammonium perchlorate (TBAP, Fluka), was recrystallized three times from ethyl acetate, dried *in vacuo* at 90 °C for 72 h, and stored in a desiccator. NBR (Aldrich) with 30–32% of acrilonitrile content was chosen since it had been previously shown to be most effective in orienting polypyrrole films. The v-bpy was prepared as previously described [7]. $Cu(v\text{-}bpy)_2(ClO_4)_2$ and $Cu(v\text{-}bpy)_2(PF_6)_2$ were prepared by reacting $Cu(ClO_4)_2$ and v-bpy in 1:1 ethanol/water under reflux for 3 h while under a nitrogen atmosphere. After the reaction had cooled, the solution volume was divided in half. From

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* Author to whom all correspondence should be addressed.

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the first half, $Cu(v\text{-}bpy)_2(ClO_4)_2$ was isolated, whereas from the other half, $Cu(v\text{-}bpy)_2(PF_6)_2$ was obtained by precipitation with KPF_6. These products were purified by chromatography on alumina with acetone as eluent. They were further recrystallized from acetone/ethanol. All other chemicals were used as-received.

NBR was deposited on the tip of the electrode from a 5 wt % NBR solution in butanone to give a film 2–4 μm thick. The butanone was completely evaporated at 40 °C in a vacuum oven. A PAR model 273 Potentiostat was employed. The potentials are reported versus the saturated calomel electrode (SCE). Polypyrrole (with and without a film of NBR) was prepared by electrolysis at + 0.80 V. For polymer films prepared in the presence of NBR, the NBR must be completely removed by stirring in butanone for 5 h. The electrochemical cell was Pt(graphite)/NBR(no NBR) prepolymer/CH_3CN, TBAP(KPF_6), pyrrole/Pt.

After the NBR is washed out, the pyrrole polymer is highly porous and oriented [3] (as shown in Fig. 1a). This porous structure allows for the incorporation of poly-$Cu(v\text{-}bpy)_2(ClO_4)_2$, by scanning the potential from 0 to − 1.50 V (Fig. 3a) in an acetonitrile solution of the monomer. The amount of the deposited polymer can be coulombically controlled with a coulometer. It should be mentioned that when using KPF_6 as a supporting electrolyte, the cell material must be a non-corroding material, such as Teflon.

In order to study the surface morphology and thickness of the polymers by scanning electron microscopy (SEM, model ISI-SX-40) and to carry out Hall-effect measurements (CENCO magnet, apparatus), platinum sheet and graphite rods were chosen as the electrode materials. When the Hall effect was measured, vacuum evaporation was used to make a connection with a gold wire onto the polymer electrode. From these measurements the values of the conductivity and carrier concentration of the electrodes were determined. The doping levels of the electrodes were determined from the ratio of doped sites to total hole sites. Carrier concentrations were determined by integration of the reduction wave of a cyclic voltammogram.

The values of doping/undoping efficiency were coulometrically determined from the cathodic- and anodic-wave areas of each cyclic voltammogram.

3. Results and discussion

Figs 1 and 2 are SEM micrographs of polypyrrole films prepared under a variety of conditions. Fig. 1a and b are for polymers prepared in the presence of NBR with PF_6^- and ClO_4^- as anions, respectively Fig. 1c and d are for the analogous films prepared in the absence of NBR with PF_6^- and ClO_4^- as the doping anions, respectively. These results clearly show a difference in granular size and porosity arising from the different polymerization conditions.

Fig. 2 is a SEM micrograph of a polymer film deposited in the presence of NBR with ClO_4^- as the doping anions; this film was further treated by electropolymerization of $Cu(v\text{-}bpy)_2(PF_6)_2$. The image is in-

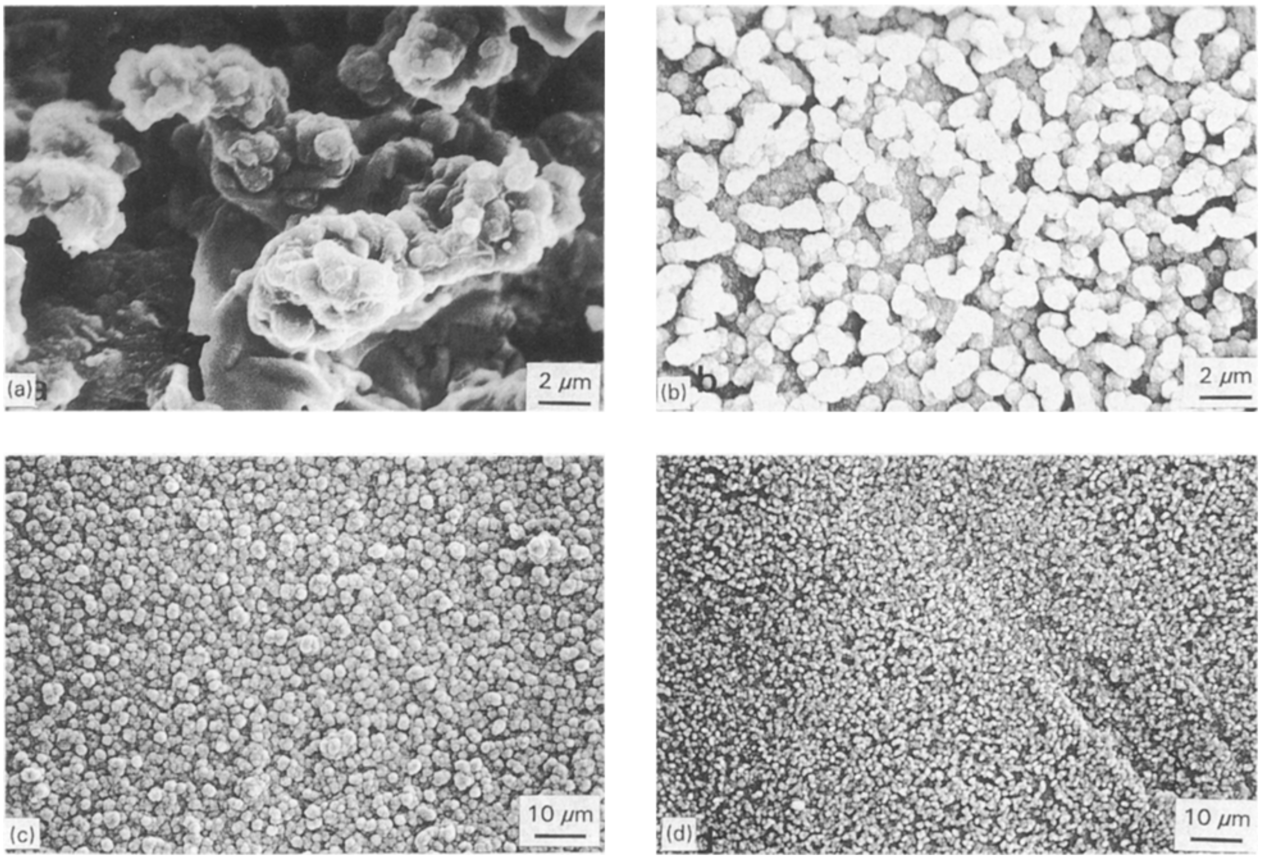

Figure 1 SEM micrographs of: (a) a polypyrrole electrode doped with PF_6^- anions, (b) ClO_4^- anion, where the electrode was modified with a film of NBR; and for electrodes without NBR modification where (c) PF_6^- and (d) ClO_4^- were the doping anions. (All at 10 kV.)

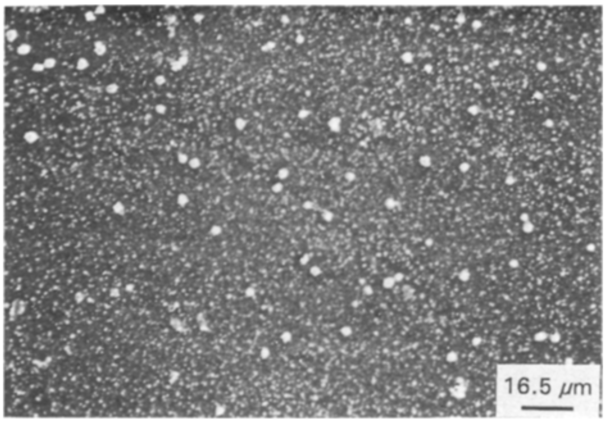

Figure 2 SEM micrograph of poly-Cu(v-bpy)$_2$(PF$_6$)$_2$ implanted into a polypyrrole polymer doped with ClO$_4^-$ ions; the large and small dots represent the polymer and the ions, respectively. (At 10 kV.)

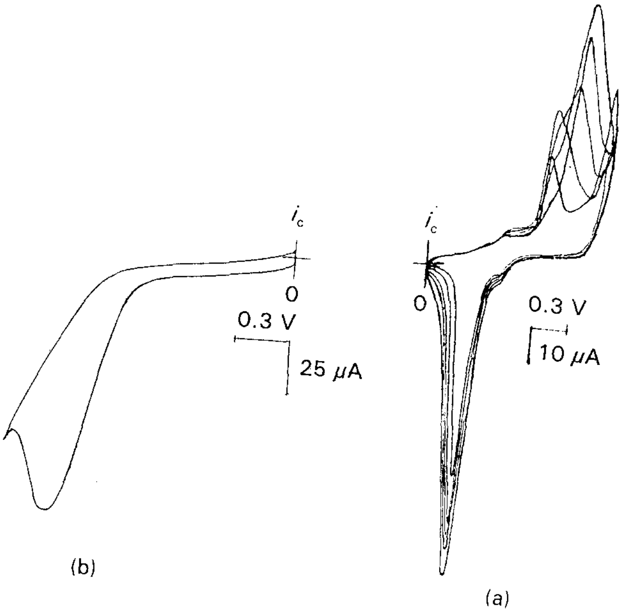

Figure 3 Cyclic voltammogram of: (a) electropolymerization of poly-Cu(v-bpy)$_2^{2+}$ on a Pt electrode, at a sweep range of 0 to − 1.5 V, with respect to a SCE, at a sweep rate of 100 mV s^{-1}; and (b) cyclic voltammetry of a modified electrode over the range 0 to + 1.5 V at a sweep rate of 100 mV s^{-1}.

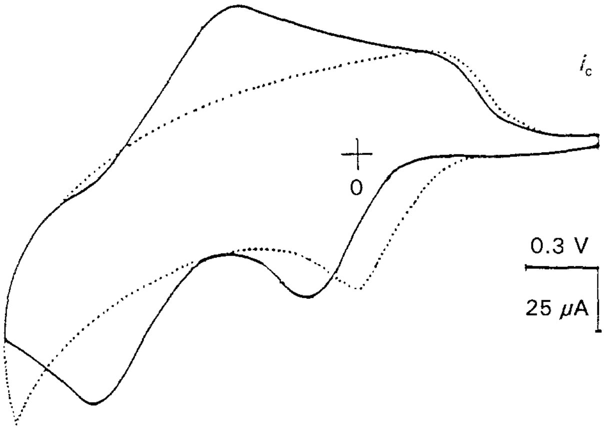

Figure 4 Cyclic voltammograms of (---) polypyrrole, and (——) polypyrrole with implanted poly-Cu(v-bpy)$_2^{2+}$: at a sweep range of 0 to + 1.5 and a sweep rate of 100 mV s^{-1}.

tended to allow distinction of the latter which forms the larger granules that are clearly distinguishable in the micrograph. The quantities of the host (polypyrrole) and guest (poly-Cu(v-bpy)$_2^{2+}$) polymer deposited were 0.65 and 0.39 C cm^{-2}, and this ratio, which is too high for other purposes, was only used to make identification of each site easier.

In practical electrodes the host polypyrrole polymer is doped with PF$_6^-$ anions in order to enhance porosity while the guest (poly-Cu(v-bpy)$_2^{2+}$) had ClO$_4^-$ as counter-ions.

Fig. 3a shows a cyclic voltammogram for the electropolymerization of Cu(v-bpy)$_2$(ClO$_4$)$_2$ at a platinum electrode in an acetonitrile solution containing 0.1 M TBAP. There is a single irreversible redox process whose current grows as the number of scans increases, indicating electropolymerization. Whereas the peak potential of the cathodic wave shifts to more negative potentials with increasing polymer thickness, the potential of the anodic counterpart remains relatively constant at about − 0.36 V. Fig. 3b shows the voltammetric response of a platinum electrode modified with a polymer film of Cu(v-bpy)$_2^{2+}$. A single irreversible oxidation at + 1.24 V is observed.

Fig. 4 presents cyclic voltammograms for polypyrrole doped with PF$_6^-$ (dashed line) and for the same polymer doped with poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$ (solid line). As can be seen, the peak potentials for polypyrrole alone are + 0.05 and − 0.35 V. For the polypyrrole implanted with poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$, the values for the polypyrrole host are + 0.205 and − 0.325 V, and for the guest poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$ they are + 1.10 and + 0.56 V. These last two values correspond to oxidation and reduction processes, respectively. It is clear from these voltammetric responses that when the guest polymer is implanted, the redox profile of the electrode is greatly improved so that the capacity of charge storage can be greatly increased.

In order to determine the optimal quantity of electropolymerized polypyrrole, the values of the conductivity were investigated over a broad range of film thicknesses. The results are presented in Table I. As can be seen, there is an abrupt increase in the conductivity at 0.5 C cm^{-2} with a maximum in the range 0.64 to 0.72 C cm^{-2}. Thus, in all subsequent experiments this amount of polypyrrole was deposited.

Table II presents the various electrical properties of polypyrrole films doped with poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$. The first column refers to electrodes that were not treated with NBR, whereas all other entries are for pretreated electrodes. As can be seen from the first row, the amount of polypyrrole deposited coincides with the maximum conductivity, as determined above.

Fig. 5 is a plot of the percentage of poly-Cu(v-bpy)$_2^{2+}$ against the conductivity of the electrodes; there is a significant enhancement in the range 12–16%.

Fig. 6 is a plot of the carrier concentration against the percentage of implanted poly-Cu(v-bpy)$_2^{2+}$. A maximum value of 4.11×10^{20} cm^{-3} is obtained at

TABLE I The effects of thickness on the conductivity of polypyrrole

Deposited quantity of p-py($C\,cm^{-2}$)	0.127	0.242	0.462	0.506	0.642	0.862
Conductivity ($\Omega^{-1}\,cm^{-1}$)	36	37	39	43	67	47

TABLE II The electrochemical properties of poly-Cu(v-bpy)$_2^{2+}$ implanted in polypyrrole electrode

P-py($C\,cm^{-2}$)	0.64	0.64	0.65	0.64	0.66	0.64	0.66
P-Cu(v-bpy)$_2^{2+}$ ($C\,cm^{-2}$)	0	0	0.042	0.087	0.082	0.102	0.125
Cu(v-bpy)$_2^{2+}$ (%)	0	0	6.5	10.7	12.4	16.2	18.9
Conductivity ($\Omega^{-1}\,cm^{-1}$)	62	67	75	121	162	190	217
Carrier conc. ($\times 10^{19}\,cm^{-3}$)	0.62	0.84	2.5	5.6	13.0	41.1	11.0
Doping level (%)	29.0	35.5	36.2	65.6	55.6	26.8	25.0
Doping/undoping efficiency	0.94	0.95	0.94	0.93	0.91	0.90	0.82

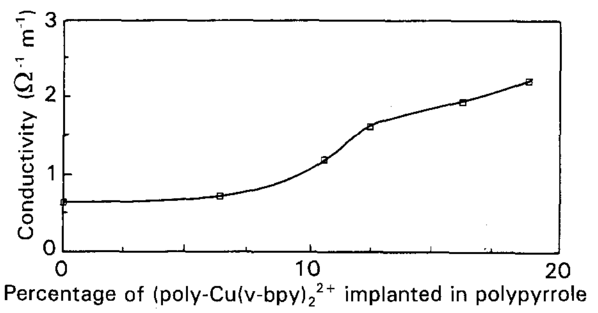

Figure 5 Plot of the conductivity of electrodes as a function of the amount of poly-Cu(v-bpy)$_2^{2+}$ implanted in polypyrrole.

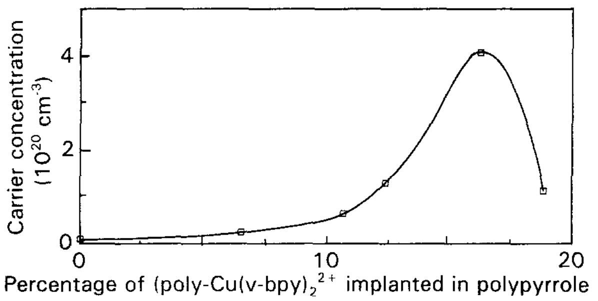

Figure 6 Plot of carrier concentration against the quantity of poly-Cu(v-bpy)$_2^{2+}$ implanted in polypyrrole.

16% implantation; however, further increases result in a significant diminution in the carrier concentration. Finally, the maximum in the doping level, as a function of the percentage of poly-Cu(v-bpy)$_2^{2+}$ implanted, of 65.6% is reached for 10% implantation.

4. Conclusion

It is clear that over the range 10–12% the incorporation of poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$ into polypyrrole films significantly enhances the electrochemical properties of the resulting material. It is, however, not clear whether the poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$ is grafted on the polymer or the plating at the bottom of the substrate. However, Fig. 2 would suggest that it is distributed throughout the material.

The only deleterious effect of incorporating poly-Cu(v-bpy)$_2$(ClO$_4$)$_2$ is in the cyclability of the electrodes. The cyclability decreases to about half of that of polypyrrole alone. However, it is clear that a significant enhancement in all other properties was achieved.

The authors are currently exploring the use of other materials for a similar application and where, at the same time, cyclability will not be affected.

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