Effective Adsorption–Desorption of Cations on a Polypyrrole–Polymer Anion Composite Electrode

Takeo Shimidzu,* Akira Ohtani, Tomokazu Iyoda, and Kenichi Honda

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

A polypyrrole–polymer anion composite electrode which efficiently absorbs and desorbs has been developed and applied to an electrochemical deionization system.

We report here a new application for a conducting polymer utilizing the cation-exchange ability of a polypyrrole–polymer anion (polyanion) (PPy/PA) composite electrode. Conducting polymers have applications in electronic devices, polymer modified electrodes, and functional membranes. In these applications, the doping–undoping ability on electrochemical oxidation and reduction is an important feature of the conducting polymer. The size of a dopant anion influences the doping–undoping ability of PPy.[1] When an anionic polymer is used as dopant it is not released from the PPy matrix, owing to its large size, *i.e.* undoping does not occur. Therefore the electrochemically reduced PPy/PA composite membrane acts as a cation-exchange membrane.[2] This cation-exchange ability of PPy/PA is in contrast to the anion-exchange property of the PPy doped with a small anion.[3]

We attempted to hybridize PPy with a positively-charged functional molecule using the cation-exchangeable PPy/PA composite electrode. Figure 1 shows visible absorption spectra of electrochemically reduced PPy/poly(vinyl sulphate), (PVS$^-$ molecular weight 1.8×10^5) on an indium tin oxide (ITO) electrode, which supports the PPy/PVS$^-$ composite membrane. The PPy/PVS$^-$ film was prepared by electrochemical polymerization [+1.0 V *vs.* standard calomel electrode (s.c.e.), 10—50 mC cm^{-2}] of 0.1 M pyrrole in H_2O containing 0.01 M PVSK (potassium salt of PVS$^-$). Electrochemical reduction of the PPy/PVS$^-$ was by potentiostatic electrolysis (−550 mV) in dimethylformamide (DMF) containing 1×10^{-3} M cationic dye [Pd-tetrakis(4-*N*-methylpyridyl)porphyrin complex, PdTMPyP]. The characteristic absorption bands of PdTMPyP (435, 540 nm) appeared with the original absorption spectrum of PPy. The surface concentration of PdTMPyP

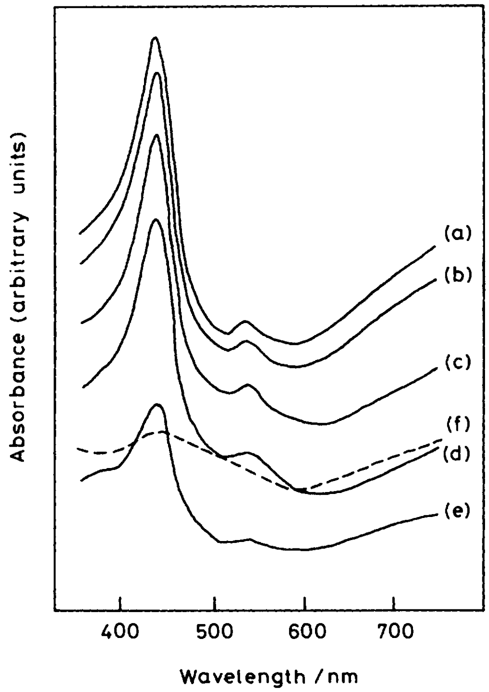
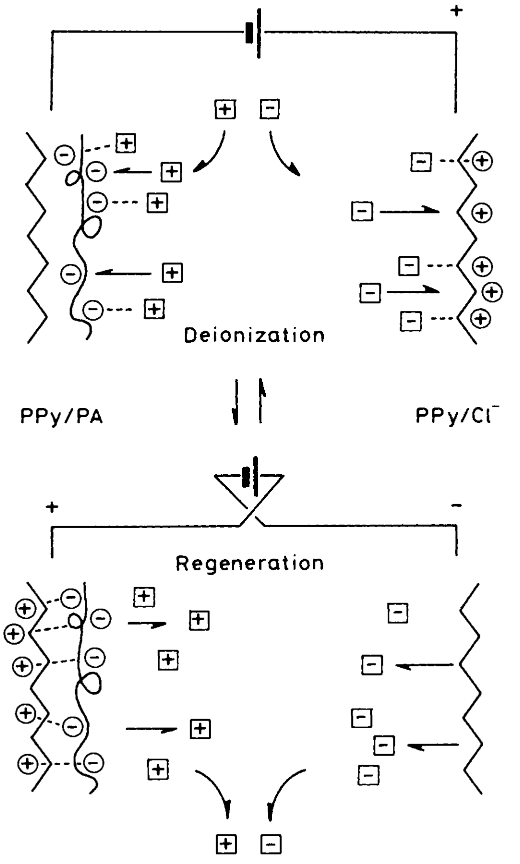


Figure 1. Visible absorption spectra of PPy/PVS$^-$ on ITO electrodes, after electrochemical reduction (——) and soaking (– – –) of the PPy/PVS$^-$ in DMF containing PdTMPyP. Treatment time was 10 min. Polymerization conditions were (a) 50, (b) 40, (c) 30, (d), (f), 20, and (e) 10 mC cm^{-2}.



Scheme 1. Electrochemical deionization system utilizing a cation-exchangeable PPy/PVS$^-$ electrode and an anion-exchangeable PPy/Cl$^-$ electrode.

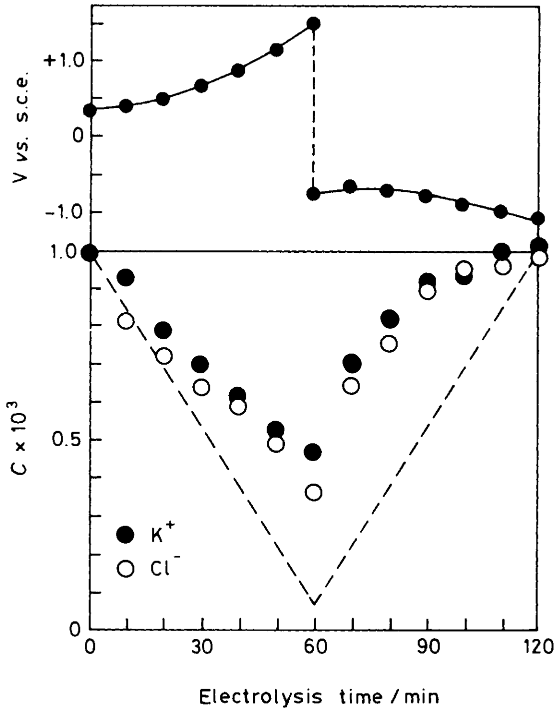


Figure 2. Electrolysis potential of a working electrode and ion concentration (*C*) of the electrolytic solution under electrochemical deionization and regeneration using a working PPy/Cl$^-$ electrode, a counter PPy/PVS$^-$ electrode, and a reference s.c.e. electrode cell system. The dashed line indicates the concentration of KCl estimated by the consumed electricity with 100% efficiency assumed.

in the PPy/PVS$^-$ (20 mC cm^{-2} of polymerization) was estimated to be 2.3 × 10^{-9} mol cm^{-2} using the molar extinction coefficient of PdTMPyP in solution. This suggests that PdTMPyP was incorporated in the PPy/PVS$^-$ matrix as a counter cation of the doped PVS$^-$. The hybridization of PPy with a negatively-charged functional molecule by an anodic doping process in electrochemical polymerization of pyrrole has been reported.[4] The hybridization of PPy by a positively-charged functional molecule has been accomplished by using the cation-exchange property of the PPy/PA electrode.

From a combination of the cation-exchangeable PPy/PA electrode and the anion-exchangeable PPy/SA [PPy doped with a small anion (SA)] electrode we have constructed an electrochemical deionization system. The electrochemically reduced PPy/PA incorporates an electrolyte cation and the electrochemically oxidized PPy/PA releases the incorporated cation. On the other hand, electrochemically oxidized PPy/SA incorporates an electrolyte anion, and electrochemically reduced PPy/SA releases the doped anion.[5] Therefore, the combination of these two PPy electrodes provides a novel electrochemical deionization procedure[6] using a conducting polymer (Scheme 1). The electrochemical deionization system consisted of a PPy/PVS$^-$ electrode and a partially undoped PPy/Cl$^-$ electrode. The PPy/PVS$^-$ and the PPy/Cl$^-$ were prepared by electrochemical polymerization of 0.1 M pyrrole in H_2O containing 0.01 M PVSK and KCl, respectively. The Pt plate was adopted only as a support for the membrane. The partially undoped PPy/Cl$^-$ was prepared by potentiostatic electrolysis (−1.0 V) of the polymerized PPy/Cl$^-$ in H_2O containing 0.1 M KCl. Under electrolysis of these two electrodes, the PPy/PVS$^-$ and the partially undoped PPy/Cl$^-$, an electrolyte cation is incorporated in the PPy/PVS$^-$ cathode and an electrolyte anion in the PPy/Cl$^-$ anode. Moreover, these electrodes are regenerated by the reverse electrochemical reaction, *i.e.*, the incorporated electrolytes are released from the electrodes. Figure 2 shows electrochemical deionization data with 10^{-3} M KCl aqueous solution for this system. Galvanostatic conditions (0.05 mA cm^{-2}) were used for the electrolysis. The PPy/Cl$^-$, the PPy/PVS$^-$, and an s.c.e. were used as a working electrode, a counter electrode, and a reference electrode, respectively. When the PPy/Cl$^-$ electrode was the anode, the concentration of both K^+ and Cl^- in the electrolytic solution decreased. When PPy/Cl$^-$ was the cathode, the concentration of K^+ and Cl^- increased to the original concentration. The efficiency of electrochemical reaction in this system was *ca.* 60% after 60 min electrolysis. Therefore electrochemical deionization and electrochemical regeneration of the electrodes was achieved using the combination of the cation-exchangeable PPy/PA electrode and the anion-exchangeable PPy/SA electrode.

This study provides two novel applications, (i) a hybridization procedure for PPy using a positively-charged functional molecule and (ii) an electrochemical deionization system, utilizing the cation-exchange property of the PPy/PA composite electrode.

We acknowledge a Grant-in-Aid from the Ministry of Education of Japan for partial support of this work.

Received, 12th May 1986; Com. 635

References

1 T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Electroanal. Chem.*, submitted for publication.

2 T. Iyoda, A. Ohtani, T. Shimidzu, and K. Honda, *Chem. Lett.*, 1986, 687.

3 P. Burgmayer and R. W. Murray, *J. Am. Chem. Soc.*, 1982, **104**, 6139; *J. Phys. Chem.*, 1984, **88**, 2515.

4 R. Noufi, D. Tench, and L. F. Warren, *J. Electrochem. Soc.*, 1981, **128**, 2596; K. Okabayashi, O. Ikeda, and H. Tamura, *J. Chem. Soc., Chem. Commun.*, 1983, 684; R. A. Bull, F.-R. Fan, and A. J. Bard, *J. Electrochem. Soc.*, 1984, **131**, 687; G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, 1984, **161**, 407; T. Shimidzu, T. Iyoda, and K. Fukui, *Annu. Rep. Jpn. Fiber Res.*, 1985, **42**, 79; K. Murao and K. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1984, 238; M. V. Rosenthal. T. Skotheim, and J. Warren, *ibid.*, 1985, 342; N. Bates, M. Cross, R. Lines, and D. Walton, *ibid.*, 1985, 871; F.-R. Fan and A. J. Bard, *J. Electrochem. Soc.*, 1986, **133**, 301.

5 A. F. Diaz, J. Castillo, J. A. Logan, and W.-Y. Lee, *J. Electroanal. Chem.*, 1981, **129**, 115.

6 A. Factor and T. O. Rose, *J. Electrochem. Soc.*, 1980, **127**, 1313.