

A Novel Type of Polymer Battery using a Polypyrrole–Polyanion Composite Anode

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Polypyrrole incorporating an anionic polymer dopant was used as the anode of a polymer battery utilizing its pseudo-cathodic doping process.

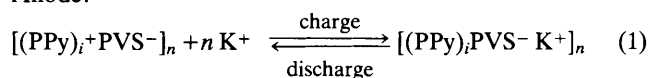
We report here that a polypyrrole–polyanion (PPy–PA) composite electrode can be used as the anode of a polymer battery. Recently, conducting polymers have been used in the construction of polymer batteries in view of the advantages their use conveys, for example, high energy density, high power density, light weight, and rechargeability. In these batteries, p-type and n-type conducting polymers are usually used as the cathode and the anode, respectively.¹ In general, n-type conducting polymers are unstable and their durability has been in question. Therefore, metal (*e.g.* Li) electrodes have often been used as the anode,² as well as neutral polymers, prepared by reduction of p-type conducting polymers.³ For polypyrrole, only p-type and no n-type polymers have been prepared previously. We now describe a polymer battery composed of an electrochemically reduced PPy–PA anode and an oxidized PPy–Cl[−] (PPy doped with Cl[−]) cathode.

We have already reported that the incorporated macromolecular PA (so-called polymer dopant) was not released when PPy–PA was electrochemically reduced, owing to its large molecular size, and penetration of electrolyte cations into the PPy matrix occurred to conserve the electroneutrality of the PPy–PA (pseudo-cathodic doping).⁴ This pseudo-cathodic doping enabled electrochemical deionization to occur from electrolyte solutions.⁵ Here, we use the electrochemically reduced PPy–PA as the anode of a polymer battery. Interestingly, the redox potential ($E_{1/2}$) of PPy–PVS[−] (polyvinyl sulphate; M 1.8×10^5) was lower than that of PPy–Cl[−]. The $E_{1/2}$ values for PPy–Cl[−], PPy–PS[−] (pentanesulphonate; M 151), and PPy–PVS[−] in H₂O (each dopant anion as supporting electrolyte; 0.1 M) were +165, −510, and −370 mV respectively *vs.* S.C.E. (standard calomel electrode).⁴ PPy–Cl[−], PPy–PS[−], and PPy–PVS[−] were prepared by electrochemical polymerization (4.9 mC) of pyrrole in H₂O containing 0.1 M KCl, Na⁺PS[−], and K⁺PVS[−], respectively. Figure 1 shows cyclic voltammograms of PPy–Cl[−], PPy–PS[−], and PPy–PVS[−] in H₂O containing 0.1 M KCl. The $E_{1/2}$ value for PPy–PVS[−] hardly changed on successive potential sweeps (−900 to +400 mV), whereas $E_{1/2}$ for PPy–PS[−] shifted to an

anodic potential corresponding to the $E_{1/2}$ for PPy–Cl[−] on successive cyclic sweeps. This suggests that PPy doped with small anions is not suitable for use as the anode of a rechargeable battery owing to the exchange reaction of the dopant anion (PPy–PS[−] → PPy–Cl[−]), but that PPy–PVS[−] could be used as anode since its electrochemical properties are unchanged. Thus, we constructed a rechargeable battery using electrochemically reduced PPy–PVS[−] as the anode and oxidized PPy–Cl[−] as the cathode.

The doping–undoping process in H₂O containing KCl, corresponding to charge–discharge of the battery, can be described by equations (1) and (2), where i (5.99) and j (6.06) denote the reciprocals of the doping ratios (ratios of sulphate and Cl[−] to pyrrole unit) for PPy–PVS[−] (0.167) and PPy–Cl[−] (0.165), which were estimated from elemental analyses.

Anode:



Cathode:

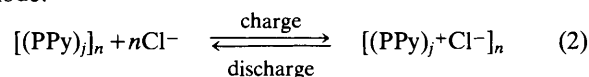


Figure 2 shows the charge–discharge properties of the battery using PPy–PVS[−] as anode and PPy–Cl[−] as cathode. In this experiment, PPy–PVS[−] and PPy–Cl[−] were prepared by

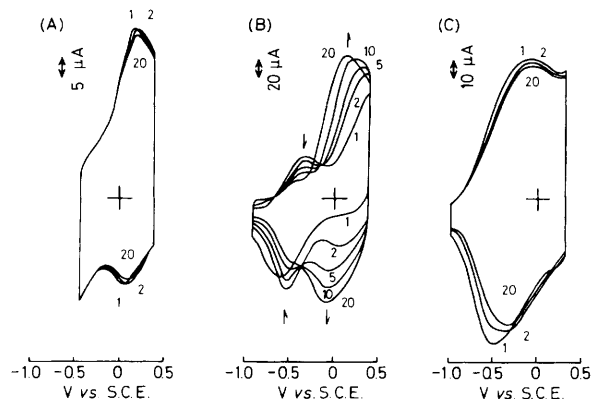


Figure 1. Cyclic voltammograms of (A) PPy–Cl[−], (B) PPy–PS[−], and (C) PPy–PVS[−] in H₂O containing 0.1 M KCl. The numerals denote the number of sweeps.

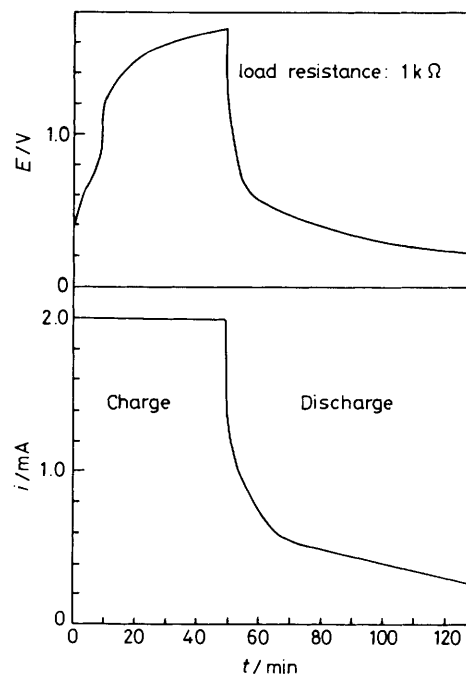


Figure 2. Charge–discharge voltage and current as a function of time for the PPy–PVS[−]|KCl(aq. soln.)|PPy–Cl[−] battery system. Charging: 2.0 mA galvanostatic electrolysis (50 min); discharging: 1 kΩ load resistance.

galvanostatic electrochemical polymerization (10 mA for 5.6 h, 200 C) of pyrrole on platinum plate electrodes (7 cm²). The PPy-Cl⁻ electrode was treated by potentiostatic electrochemical reduction (-1.0 V vs. S.C.E.) in H₂O containing 0.3 M KCl prior to the charge-discharge experiment to make up the discharged cathode. The potential between the PPy-Cl⁻ and PPy-PVS⁻ electrodes was gradually increased and reached 1.7 V under galvanostatic conditions (2.0 mA) in H₂O containing 0.3 M KCl. When the battery was discharged through a 1 kΩ load resistance, an initial discharge current of 1.4 mA and an initial voltage of 1.3 V were observed. The potential of this battery was attained at a lower redox potential of the PPy-PA composite electrode with pseudo-cathodic doping. After 80 min, the current and the voltage had decreased to 0.3 mA and 300 mV. This battery was easily recharged, and it then showed the original capacity. It is considered to be a p-type-p'-type battery and is thus different from p-type-n-type and p-type-metal batteries. The PPy-PA composite anode (*e.g.* PPy-PVS⁻) could also be combined with other p-type conducting polymer electrodes, *e.g.*, poly-(thiophene) *etc.*, which have higher redox potentials than PPy-Cl⁻, and this should lead to a more effective battery.

This study thus provides a novel type of polymer battery with a PPy-PA composite anode, which has specific properties different from those of small anion-doped PPy.

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References

- 1 D. MacInnes, Jr., M. A. Druy, P. J. Nigrey, D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1981, 317.
- 2 P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, and A. J. Heeger, *J. Electrochem. Soc.*, 1981, **128**, 1651.
- 3 G. J. Waltman, A. F. Diaz, and J. Bargon, *J. Electrochem. Soc.*, 1984, **131**, 1452.
- 4 T. Iyoda, A. Ohtani, T. Shimidzu, and K. Honda, *Chem. Lett.*, **1986**, 687; T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Electroanal. Chem.*, submitted for publication.
- 5 T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Chem. Soc., Chem. Commun.*, 1986, 1415.