A Novel Type of Polymer Battery with a High Energy Density

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A novel type of polymer battery in which an electrolytic solution does not essentially contribute to charge and discharge processes has been developed, by using a polypyrrole-polymer anion composite cathode.

We report here that a polypyrrole-polymer anion (PPy/PA) composite electrode can be used as the cathode in a conducting polymer-metal rechargeable battery, and that the battery should have a high energy density, since the electrolytic solution does not really contribute to the reaction. Many types of polymer battery have been reported.[1] We have

reported that the PPy/PA composite electrode could be used as the anode of a polymer-only battery.[2] However, from a practical point of view, a battery composed of a p-type polymer cathode and a metal anode, which has a high electromotive force and is stable, is most advantageous.

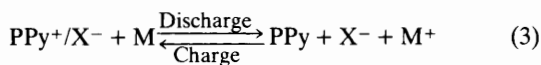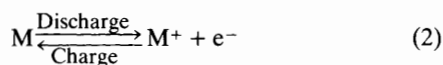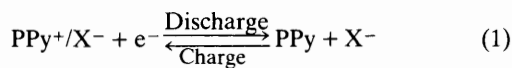A rechargeable battery composed of a p-type polymer
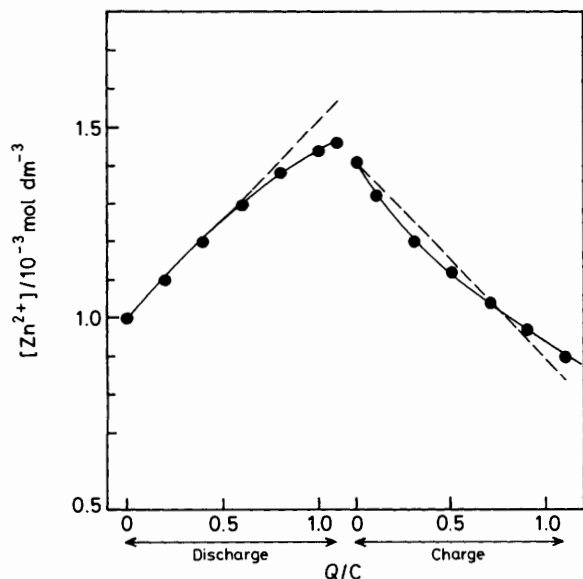
Figure 1. Change of Zn^+ concentration with a 1 kΩ load discharge and constant current charge for the $Zn|ZnSO_4$(aq. soln.)$|PPy/Cl^-$. The dashed line indicates the concentration of Zn^{2+} estimated in reactions (3).
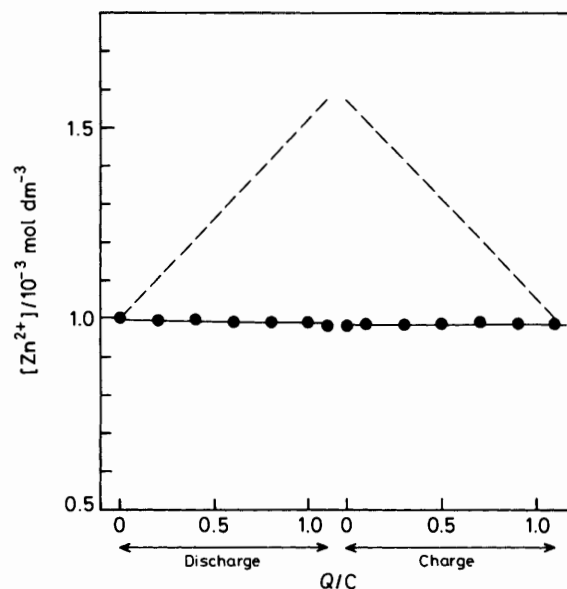
Figure 2. Change of Zn^{2+} concentration with a 1 kΩ load discharge and constant current charge for the $Zn|ZnSO_4$(aq. soln.)$|PPy/PVS^-$. The dashed line indicates the concentration of Zn^{2+} estimated in reaction (3).

cathode and a metal anode has an essential problem that a large amount of electrolytic solution is required in its construction.[3] The electrochemical reactions for a battery composed of a PPy/X^- (X^- is a small anion) cathode and metal anode are shown in reactions (1)—(3) [where reaction (1) is the reaction on the polymer electrode, reaction (2) is the reaction on the metal electrode and reaction (3) is the total process].

$$PPy^+/X^- + e^- \underset{Charge}{\overset{Discharge}{\rightleftarrows}} PPy + X^- \qquad (1)$$

$$M \underset{Charge}{\overset{Discharge}{\rightleftarrows}} M^+ + e^- \qquad (2)$$

$$PPy^+/X^- + M \underset{Charge}{\overset{Discharge}{\rightleftarrows}} PPy + X^- + M^+ \qquad (3)$$
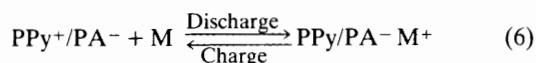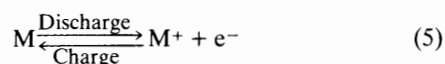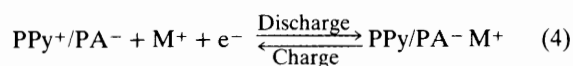
In reaction (3), a large amount of solvent is required to dissolve X^- and M^+ in the discharging process. Clearly the concentration of ions in the electrolytic solution increases during the discharging and decreases during the charging process. The large amount of electrolytic solution makes the real energy density of the polymer battery decrease.

We have already reported that the incorporated macromolecular PA (so-called polymer dopant) was not released when the 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] We utilized this property of PPy/PA to construct a novel type of rechargeable battery with a high energy density. Thus, electrochemical reactions for a battery composed of a PPy/PA cathode and a metal anode are shown in reactions (4)—(6).

Where reaction (4) is the reaction on the polymer electrode, reaction (5) is the reaction on the metal electrode, and reaction (6) is the total process.
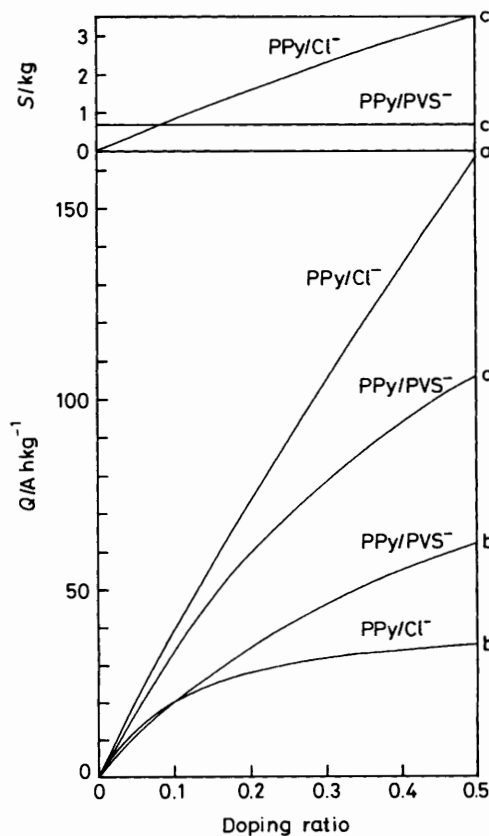
Figure 3. Relationship between theoretical charge density (Q) and weight of electrolytic solution (S), and doping ratio for the $Zn|ZnSO_4$(aq. soln.)$|PPy/Cl^-$ and the $Zn|ZnSO_4$(aq. soln.)$|PPy/PVS^-$ batteries. (a) Q was calculated for the weight of PPy/Cl^- or PPy/PVS^-. (b) Q was calculated for the weight of PPy/anion plus that of the electrolytic solution. (c) Weight of electrolytic solution.

$$PPy^+/PA^- + M^+ + e^- \; \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} \; PPy/PA^- M^+ \qquad (4)$$

$$M \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} M^+ + e^- \qquad (5)$$

$$PPy^+/PA^- + M \; \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} \; PPy/PA^- M^+ \qquad (6)$$

In reaction (6), although the electrolytic solution is necessary as an electron carrier between the two electrodes, it does not contribute to the reaction and consequently the concentration of ions in the electrolytic solution does not change in the discharging and the charging processes.

Figures 1 and 2 show changes of concentration of Zn^{2+} in solution for the $Zn|ZnSO_4(aq. soln.)|PPy/Cl^-$ and for the $Zn|ZnSO_4(aq. soln.)|PPy/PVS^-$ batteries, respectively. [PVS^- = poly(vinylsulphate); m.w. = 1.8×10^5.] The PPy/Cl^- and the PPy/PVS^- were prepared by electrochemical polymerization (18C) of pyrrole in H_2O, containing KCl and the potassium salt of PVS^- respectively. In these charging–discharging experiments, large volumes (10 ml) of dilute (10^{-3} mol dm^{-3}) electrolytic solutions were used to estimate the change of concentration of Zn^{2+} accurately. A 1 k Ω load discharge and a constant current charge of 1.1 C were used. The open-circuit voltages were 1.5 V and 1.3 V for the PPy/Cl^--Zn and the PPy/PVS^--Zn batteries, respectively. The concentration of Zn^{2+} in solution increased with discharging and decreased with charging in the PPy/Cl^--Zn battery. However the concentration of Zn^{2+} in solution did not change during discharging and the charging processes for the PPy/PVS^--Zn battery. This result implies that the PPy/PVS^--Zn

battery has an advantage in the construction of rechargeable batteries. Figure 3 shows theoretical charge density (Q; ampere hour per kg) of the $Zn|ZnSO_4(aq. soln)|PPy/Cl^-$ and the $Zn|ZnSO_4$ (aq. soln)$|PPy/PVS^-$ batteries. The values were calculated by assuming: i, the concentration of electrolyte in the PPy/Cl^--Zn battery changes within the range 1.0—2.0 mol dm^{-3} during the discharging and the charging processes; ii, the concentration of electrolyte in PPy/PVS^--Zn battery is constant (1 mol dm^{-3}) and the 0.7 kg of the electrolytic solution is used for 1 kg of PPy/PVS^-. In the PPy/Cl^--Zn battery, the amount of the electrolytic solution increases with the doping ratio since the amount of dopant anion to be dissolved increases with doping ratio. Taking into account the weight of the electrolytic solution Q for the PPy/PVS^- is higher than that for the PPy/Cl^- at a higher doping ratio, although Q for the PPy/Cl^- only is much higher than that for PPy/PVS^-.

References

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