

THE POLYANILINE/LITHIUM BATTERY

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Summary

Polyaniline (PAN), synthesized by electro-polymerization, has exhibited good reversibility in an LiClO_4 /propylene carbonate electrolyte. The reversible specific capacity reaches 120 A h kg^{-1} . PAN appears to be a candidate positive electrode for a secondary lithium battery because of its reversibility, high-rate discharge performance, and low self-discharge. The compatibility of the electrolyte between PAN and lithium electrodes is an important problem to be solved.

Introduction

Secondary lithium batteries using a conductive polymer as the positive electrode have attracted considerable attention since the demonstration of the electrochemical doping and undoping of polyacetylene (PA) by MacDiarmid and Heeger [1] in 1979. Diaz *et al.* [2] were the first to report that the conductive polymers, polypyrrole (PP), polythiophene (PT) and polyaniline (PAN), which have the same conjugated double bond as PA, can be synthesized by electro-polymerization. Since these conductive polymers are synthesized by oxidation of a solution containing each monomer, they are expected to be stable in an electrochemical oxidation environment. Hence, application of the polymers as the positive electrode of secondary batteries has been attempted by many research workers.

PAN is known to be the most stable of the conductive polymers. MacDiarmid *et al.* [3] suggested that PAN could find use as a positive electrode in the PAN/dil. H_2SO_4 aq./Pb system. Sasaki *et al.* [4] also pointed out the possibility of developing a secondary lithium battery using PAN as the positive electrode, since PAN was electrochemically active in the non-aqueous electrolyte and could be doped with 0.45 ClO_4^- anions per one aniline unit.

We have also conducted studies on PAN in order to clarify the redox mechanism in non-aqueous electrolytes. This work has involved *in situ* electrogravimetry, elemental analysis, XPS, EPMA, ESCA and charge/discharge capacity measurements of the redox process. It has been confirmed

[5] that the redox reaction of PAN is caused by the doping/undoping of ClO_4^- anions solvated with 3 - 4 propylene carbonate (PC) molecules, and that one ClO_4^- anion per one aniline unit could be doped in the polymer. This finding suggests that PAN has a considerably higher specific capacity than that predicted previously. In view of these results, PAN/Li batteries with LiClO_4/PC as the electrolyte have been fabricated and evaluated in comparison with other polymer batteries.

Experimental

Synthesis of conducting polymers

The PAN film was prepared by electro-polymerization onto a platinum electrode from a 2 M HClO_4 aqueous solution containing 1 M aniline. The total amount of electricity for the synthesis was about 20 coulomb cm^{-2} at a current density of 1 mA cm^{-2} . The resulting PAN film had a thickness of 300 μm . The film was washed with distilled water, dried at 100 °C under vacuum, and then assembled in the test cell. Other conducting polymers were synthesized as follows:

(i) PA by a method proposed by Shirakawa [6];

(ii) PP by an electro-polymerization from 0.2 M LiClO_4/PC containing 0.2 M pyrrole at a current density of 7 mA cm^{-2} [7];

(iii) PT by electropolymerization at 5 mA cm^{-2} from 0.2 M LiClO_4/PC containing 0.2 M thiophene.

The total amount of electricity used in the preparation of PP and PT was about 20 coulomb cm^{-2} .

Test cell

The conductive polymers were assembled in test cells in combination with non-woven cellulose separators and two lithium-foil anodes. The electrolyte was 1 M LiClO_4/PC . Charge/discharge tests were carried out in a dry box equipped with an argon gas recirculator.

Results and discussion

Specific capacity and coulombic efficiency

The charge and discharge characteristics of PAN at 1 mA cm^{-2} are given in Fig. 1. The quantity of electricity (A h) is referred to the weight (kg) of fully discharged PAN. The charging potential is seen to increase linearly with the charge passed until the value reaches 160 A h kg^{-1} . Further charging causes decomposition of the electrolyte at 5.4 V *versus* Li/Li^+ , which is higher than the value observed on a platinum electrode. This observation is due to the larger overpotential of PAN for the decomposition reaction of the electrolyte. The discharge curve of PAN shows the same linear, capacitor-like characteristics as those observed with the other conductive polymer elec-

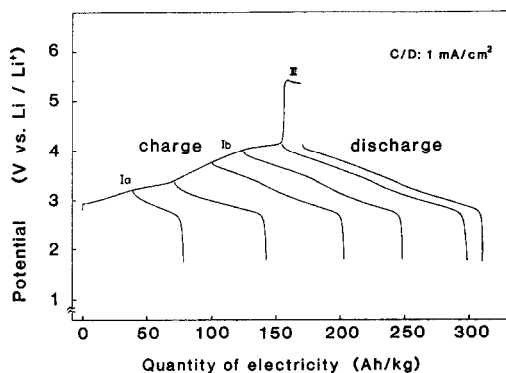


Fig. 1. Charge and discharge potential of PAn electrodes in 1.0 M LiClO_4/PC .

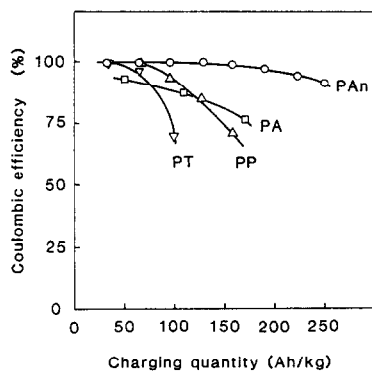


Fig. 2. Coulombic efficiencies of PAn and other conducting polymers.

trodes. Coulombic efficiencies *versus* charge capacity curves for the four polymer electrodes at the same current densities are presented in Fig. 2. The data show that PAn yields 100% coulombic efficiency until the charging capacity reaches about 120 A h kg^{-1} , while the other polymer electrodes exhibit a sharp decrease in coulombic efficiency with increase in the charging capacity.

Figure 3(a) shows the dependence of the charging potential and the discharge capacity of a PA positive electrode on the quantity of electricity (A h kg^{-1}) used in charging. The charging potential can be divided into three regions (I \rightarrow III). In the lower plot, the dotted line represents the boundary where the coulombic efficiency is 100%. The coulombic efficiency is nearly 100% at a small A h kg^{-1} in region I. However, the coulombic efficiency gradually decreases with increase in charging and the dischargeable capacity begins to deviate from the dotted line even in region I. In region II, the dischargeable capacity decreases further with charging while the charging potential remains constant. It is therefore suggested that decomposition of the polymer takes place in this region. If PA is charged to region III, PA suffers severe damage. Figure 3(b) provides the corresponding data for PP. It can be seen that, compared with PA, PP shows 100% efficiency over a larger

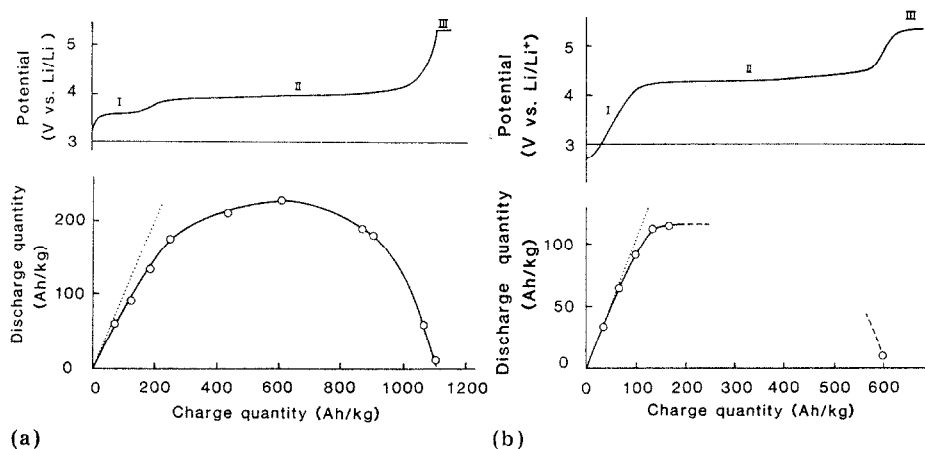


Fig. 3. (a) Charging curve of PA and discharge quantity in various charge quantities; (b) Charging curve of PP and discharge quantity in various charge quantities.

charging period in region I, but charging in region III again causes degradation of the polymer to an undischageable state.

As mentioned above, the coulombic efficiency is an index of the stability of the polymers. PAN maintains an efficiency of 100% up to 120 A h kg⁻¹ charging throughout region II. This suggests that PAN is more stable towards oxidation than the other conducting polymers. In the PA and PP II regions, two-phase reaction occurs because a flat potential is observed in the process. This potential will correspond to a decomposition reaction of the polymers. PAN seems to have a higher decomposition potential than PA and PP, since a flat potential is not observed for PAN in the charging process. This stability of PAN in the charging process results in a higher coulombic efficiency compared with other polymers, which appears to be closely related to a different doping mechanism of the imine/amine change in the N atom of PAN [5].

High-rate discharge characteristics

The test cell, charged up to 50 A h kg⁻¹ of the polymer at 1 mA cm⁻², was short circuited and the resulting current measured. The discharge current of the PAN electrode reached about 50 mA cm⁻² at the initial stage. The capacity was totally discharged in less than 6 min. The cumulative discharge capacity *versus* time is shown in Fig. 4. PA gives a poor high-rate discharge performance compared with PAN. However, this difference in performance cannot be associated with polymer morphology as scanning electron microscopic studies show the polymers to have similar fibril network structures. The discharge reaction has been identified [5] as the undoping of ClO₄⁻ anions from the polymer solvated with 3 - 4 PC molecules per anion. Hence, a sponge-like porous polymer, permeable to the solvated anion, is suggested as a model for the high-rate dischargeable polymers.

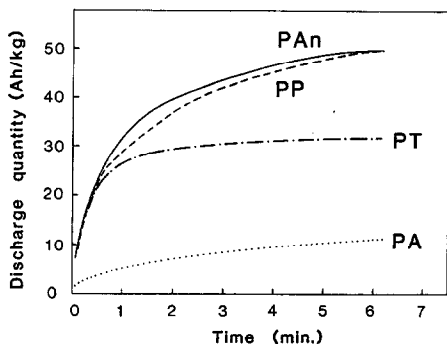


Fig. 4. Discharge quantity at the short circuit tests after 50 A h kg⁻¹ charging.

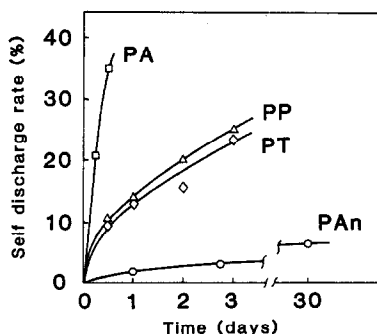


Fig. 5. Self-discharge rates of PAN and other conducting polymers. Charging quantity: 120 A h kg⁻¹ for PAN; 30 A h kg⁻¹ for PA, PP, and PT.

Self-discharge characteristics

Figure 5 shows self-discharge data of the PAN cell, which was charged up to 120 A h kg⁻¹ at 1 mA cm⁻² and then set aside at room temperature. The retained capacity after 30 days was 93% of the original value. The results obtained on PA, PP, and PT cells are also given in the Figure. The charging amount for these polymers before standing was 30 A h kg⁻¹. The more the cell is charged, the greater the self discharge of these polymers. As the self-discharge of an Ni/Cd battery is around 30%/month, PAN appears to be a practical material for positive electrodes. Although the mechanism of self discharge in the polymers has not been completely clarified, it may be closely related to the stability of the polymers towards oxidation and to a local cell effect caused by impurities formed during the synthetic process. Sufficient evidence for the latter has still to be obtained, but the former has been confirmed by the stability of PAN in the charging process.

Button-type cells

Button-type R2020 cells were fabricated and tested using a PAN positive electrode synthesized at 30 coulomb cm⁻². The capacity and the surface area were 2.6 mA h and 1.77 cm², respectively. An 80% Li-Al alloy foil

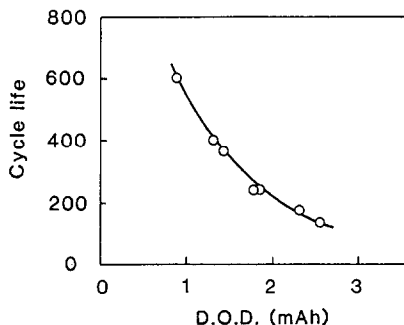


Fig. 6. Cycle life and DOD of button type cells (R2020).

was used for the negative electrode. The capacity of the negative electrode was about 60 times larger than the positive electrode. Cycle tests were carried out to different values of the depth-of-discharge (DOD) at a constant current density of 0.56 mA cm^{-2} for both charge and discharge. The results are shown in Fig. 6. The cycle life is strongly dependent on the DOD; at 100% DOD, the life was about 150 cycles. Cell autopsy revealed that the failure was not due to the PAN electrode, but was caused by a passivation of the lithium negative electrode. PC is not generally used as the electrolyte solvent for lithium secondary batteries, since PC reacts with Li to form Li_2CO_3 [8]. However, PC is a good electrolyte solvent for a longer life and a lower self-discharge performance of PAN. Further research efforts are required to find a new electrolyte system that is compatible with PAN and lithium.

Conclusions

Polyaniline (PAN) shows promise as a material for positive electrodes in lithium secondary batteries, since a PAN electrode synthesized by electropolymerization exhibits good specific capacity, stability, reversibility, and low self-discharge in an LiClO_4/PC electrolyte. However, better compatibility of the electrolyte with PAN and Li is required.

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