

## Characteristics of a lithium secondary battery using chemically-synthesized conductive polymers

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(Received September 6, 1990)

### Abstract

Several conductive polymers (polyacetylene, polypyrrole, polythiophene, polyiminodibenzyl, polycarbazole, polyfuran, polyphenothiazine) have been synthesized by a chemical polymerization method and examined for their suitability as positive electrode material for lithium secondary batteries. A test cell, using polypyrrole as a positive electrode, showed good charge/discharge characteristics. Oxidizing agents for the synthesis of polypyrrole have been investigated for further improvement, and polypyrrole prepared by a new method of synthesis using a  $\text{Cu}(\text{BF}_4)_2$ /nitrile system exhibited excellent performance.

### Introduction

Since polyacetylene was first employed as an electrode material for secondary batteries [1] much effort has been directed towards the development of this type of battery [2-7]. Polymer batteries are expected to have many advantages, such as lighter weight, higher voltage, multiple shape capabilities, and a pollution-free construction, owing to the nature of the polymers. Conductive polymers are synthesized by chemically or electrochemically polymerizing the corresponding monomers, but the former method is expected to allow more efficient mass-productivity and uniformity of the product.

In this paper, the properties and the charge/discharge characteristics of various chemically-synthesized conductive polymers are reported.

### Experimental

#### *Synthesis of conductive polymers*

Polyacetylene was synthesized by the Shirakawa method [8]. Other polymers were prepared by polymerizing corresponding monomers with

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various oxidizing agents. A solution of oxidizing agent was added dropwise to the monomer which was dispersed, or dissolved, in water or organic solvents. Crude polymers were purified by washing with water or organic solvents.

#### *Measurement of conductivity*

The conductivity of the polymers was measured by an a.c. 2-probe method. Polymers were made into pellets and gold plates were pressed on either side of each pellet. An LCR meter was used to measure the resistance of the sample.

#### *Charge/discharge test*

Conductive polymers in the form of pressed pellets were examined for their characteristics as positive electrode material for lithium secondary batteries.

Lithium or lithium-aluminum alloy was used as the negative electrode. The electrolyte comprised propylene carbonate containing  $\text{LiClO}_4$  or  $\text{LiBF}_4$ .

Charging and discharging was conducted at constant current over voltage ranges between 2.5 and 5.0 V (Li/polymer cell) or between 2.0 and 4.5 V (Li-Al/polymer cell).

## **Results and discussion**

#### *Screening of several conductive polymers*

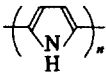
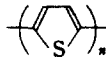
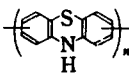
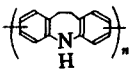
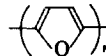
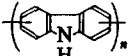
The chemical structure of the conductive polymers and the reagents used in their synthesis are given in Table 1. Polyacetylene was prepared by using Shirakawa's catalyst. Polymers other than polypyrrole were synthesized by nitrosonium tetrafluoroborate ( $\text{NOBF}_4$ ), a typical oxidizing agent. Polypyrrole was prepared using  $\text{FeCl}_3$ , since it was not obtained by use of  $\text{NOBF}_4$ .

Figure 1 shows the charge/discharge curves of the test cells with a charge capacity of  $17 \text{ mA h g}^{-1}$ . Polyacetylene, polypyrrole, polythiophene, polyiminodibenzyl and polycarbazole electrodes gave stable curves under this condition. In the cases of polyfuran and polyphenothiazine, however, the cell voltage reached 5.0 V immediately after charging started. This is thought to be due to the very low doping limit of these polymers.

Charge/discharge characteristics of these polymer electrodes were then examined under a larger charge capacity of  $33 \text{ mA h g}^{-1}$ . The resulting curves are presented in Fig. 2.

The charge/discharge coulombic efficiency is summarized in Table 2. Under a charge capacity of  $17 \text{ mA h g}^{-1}$ , polypyrrole exhibits the highest efficiency, viz., 98%. The corresponding efficiencies for polyacetylene, polythiophene, polyiminodibenzyl and polycarbazole are 86, 96, 96 and 91%, respectively. Under the larger charge capacity of  $33 \text{ mA h g}^{-1}$ , polypyrrole maintained a coulombic efficiency of 98%, but those of other polymers were reduced.

TABLE 1  
Various chemically-synthesized conductive polymers

| Compound          | Chemical constitution  | Catalyst or oxidizing agent                              |
|-------------------|--|--|
| Polyacetylene     | $\text{-(CH=CH)-}_n$   | $\text{Ti(OC}_4\text{H}_9)_4\text{-Al(C}_2\text{H}_5)_3$ |
| Polypyrrole       |   | $\text{FeCl}_3$  |
| Polythiophene     |   | $\text{NOBF}_4$  |
| Polyphenothiazine |   | $\text{NOBF}_4$  |
| Polyiminodibenzyl |   | $\text{NOBF}_4$  |
| Polyfuran         |   | $\text{NOBF}_4$  |
| Polycarbazole     |  | $\text{NOBF}_4$  |

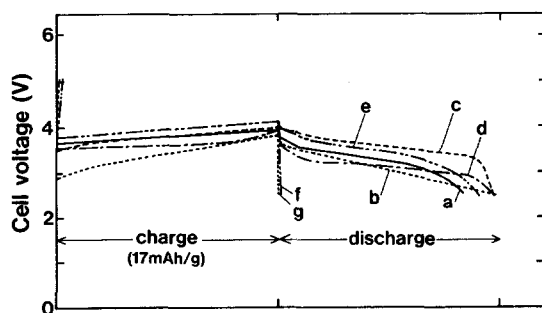


Fig. 1. Charge/discharge curves of Li/polymer cells using chemically-synthesized conductive polymers. Charge capacity:  $17 \text{ mA h g}^{-1}$ . (a) Polyacetylene, (b) polypyrrole, (c) polythiophene, (d) polyiminodibenzyl, (e) polycarbazole, (f) polyfuran, (g) polyphenothiazine.

### *Synthesis of high-performance polypyrrole*

Oxidizing agents, which are the dominant factors in the chemical synthesis of polymers, were investigated in order to obtain polypyrrole with improved charge/discharge characteristics.

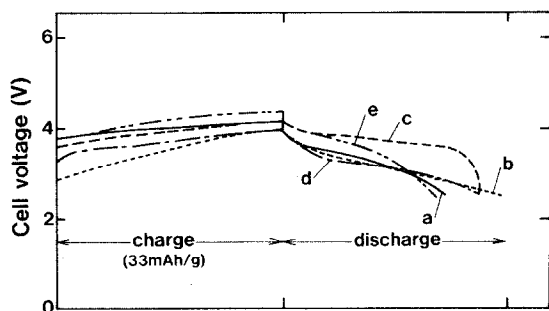


Fig. 2. Charge/discharge curves of Li/polymer cells using chemically-synthesized conductive polymers. Charge capacity:  $33 \text{ mA h g}^{-1}$ . (a) Polyacetylene, (b) polypyrrole, (c) polythiophene, (d) polyiminodibenzyl, (e) polycarbazole.

TABLE 2

Charge/discharge efficiency of cells using various chemically-synthesized conductive polymers

| Conductive polymer | Coulombic efficiency (%)         |                                  |
|--------------------|----------------------------------|----------------------------------|
|                    | Charge: $17 \text{ mA h g}^{-1}$ | Charge: $33 \text{ mA h g}^{-1}$ |
| Polyacetylene      | 86                               | 74                               |
| Polypyrrole        | 98                               | 98                               |
| Polythiophene      | 96                               | 87                               |
| Polyiminodibenzyl  | 96                               | 88                               |
| Polycarbazole      | 91                               | 68                               |

TABLE 3

Effect of oxidizing agents on characteristics of polypyrroles

| Oxidizing agent                         | Conductivity ( $\text{S cm}^{-1}$ ) | Coulombic efficiency (%) | FT-IR (Observed peaks) |
|---|-------------------------------------|--------------------------|------------------------|
| $\text{Fe}(\text{ClO}_4)_3$             | $3 \times 10^{-1}$                  | 100                      | 1                      |
| $\text{FeCl}_3$                         | $1 \times 10^{-4}$                  | 98                       | 1                      |
| $\text{Fe}(\text{NO}_3)_3$              | $7 \times 10^{-4}$                  | 98                       | 1                      |
| $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ | $1 \times 10^{-3}$                  | 65                       | 2                      |
| $\text{Fe}_2(\text{SO}_4)_3$            | $1 \times 10^{-5}$                  | **                       | 2                      |

1, Peaks attributed to polypyrrole.

2, Peaks attributed to polypyrrole and carbonyl group.

\*\* Charging was impossible.

Ferric perchlorate ( $\text{Fe}(\text{ClO}_4)_3$ ), ferric nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), ammonium iron(III) sulfate ( $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ ), and ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) were used as oxidizing agents and were compared with  $\text{FeCl}_3$ . The conductivity and charge/discharge coulombic efficiency of the test cells, as well as FT-IR data, are given in Table 3.

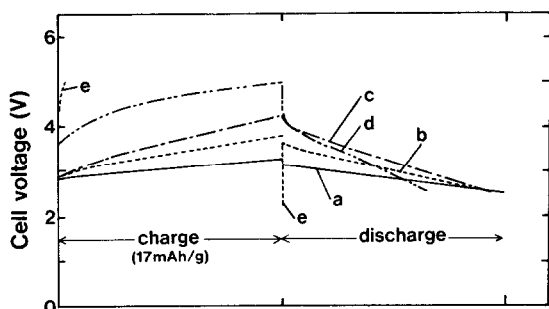


Fig. 3. Charge/discharge curves of Li/polypyrrole cells. Oxidizing agent for polypyrrole synthesis: (a)  $\text{Fe}(\text{ClO}_4)_3$ , (b)  $\text{FeCl}_3$ , (c)  $\text{Fe}(\text{NO}_3)_3$ , (d)  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ , (e)  $\text{Fe}_2(\text{SO}_4)_3$ .

The charge/discharge curves of the test cells are shown in Fig. 3. Polypyrrole prepared by  $\text{Fe}(\text{ClO}_4)_3$  exhibited a very flat curve and the highest coulombic efficiency (100%). Polypyrrole prepared by  $\text{FeCl}_3$  and  $\text{Fe}(\text{NO}_3)_3$  also yielded a high coulombic efficiency of 98%, but in the case of  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ , the value was only 65%. A test cell using polypyrrole synthesized by  $\text{Fe}_2(\text{SO}_4)_3$  gave a rapid rise in cell voltage after the initiation of charging, and charge/discharge was hardly possible.

In the FT-IR spectra of polymers synthesized by  $\text{Fe}_2(\text{SO}_4)_3$  and  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ , a peak was observed at  $1790\text{ cm}^{-1}$ . This is attributed to the carbonyl group and is thought to be formed by oxidation of the pyrrole ring. Such a finding indicates that these two polymers are not complete polypyrroles and therefore exhibit inferior performance, as stated above. On the other hand, the FT-IR spectra of polypyrrole synthesized by  $\text{Fe}(\text{ClO}_4)_3$ ,  $\text{FeCl}_3$  and  $\text{Fe}(\text{NO}_3)_3$  did not display peaks attributable to the carbonyl group and, accordingly, a high coulombic efficiency was obtained. In the latter three polypyrroles, flatness of the charge/discharge curve was best for the  $\text{Fe}(\text{ClO}_4)_3$  method, which showed the highest conductivity.

Good solubility of  $\text{ClO}_4^-$  ions in propylene carbonate is considered to be another reason for the high performance of polypyrrole synthesized by  $\text{Fe}(\text{ClO}_4)_3$  [9]. On the other hand, the flatness of the charge/discharge curves of polypyrrole electrodes containing  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$ , which have low solubility in propylene carbonate, was worse. Oxidizing agents containing  $\text{BF}_4^-$  ions, which are highly soluble in electrolyte solution, were therefore investigated. Ferric tetrafluoroborate ( $\text{Fe}(\text{BF}_4)_3$ ) was tried first, but polypyrrole with good charge/discharge characteristics was not obtained. Copper tetrafluoroborate ( $\text{Cu}(\text{BF}_4)_2$ ) was then examined. Pyrrole was added to a water solution of  $\text{Cu}(\text{BF}_4)_2$ , but no progress in the form of a polymerization reaction was observed within 24 h. We believe this is due to the poor affinity between pyrrole and water, and, therefore, an attempt was made to improve this affinity through the addition of organic solvents. When acetonitrile was added, a black substance was immediately obtained and identified as polypyrrole by elemental analysis. On the other hand, no polymer product was obtained by the addition of methanol.

As summarized in Table 4, when  $\text{Cu}(\text{BF}_4)_2$  was used as an oxidizing agent, a high yield of polypyrrole was obtained only in the presence of a nitrile compound.  $\text{Cu}(\text{BF}_4)_2/\text{nitrile}$  is a new system for conductive polymer synthesis in which nitrile has a ligand effect and induces the polymerization reaction.

Polypyrrole synthesized by  $\text{Fe}(\text{ClO}_4)_3$ ,  $(\text{Fe}(\text{ClO}_4)_3\text{-PPY})$ , and  $\text{Cu}(\text{BF}_4)_2$ ,  $(\text{Cu}(\text{BF}_4)_2\text{-PPY})$ , were examined under high doping levels of 44, 67, and 89  $\text{mA h g}^{-1}$ . Lithium–aluminum alloy was employed as a negative electrode. The charge/discharge characteristics are shown in Fig. 4. The rise in cell voltage during charging was more rapid with  $\text{Fe}(\text{ClO}_4)_3\text{-PPY}$  than with  $\text{Cu}(\text{BF}_4)_2\text{-PPY}$ . The coulombic efficiency declined above 44  $\text{mA h g}^{-1}$ , showing 95% at 67  $\text{mA h g}^{-1}$  and 85% at 89  $\text{mA h g}^{-1}$ . Using  $\text{Cu}(\text{BF}_4)_2\text{-PPY}$ , a high coulombic efficiency of 100% was obtained at 67  $\text{mA h g}^{-1}$ , but declined to 91% at 89  $\text{mA h g}^{-1}$ .

TABLE 4

Influence of solvents on polymerization of aniline (using  $\text{Cu}(\text{BF}_4)_2$  as oxidizing agent)

| Solvent  | Product                              |
|--|--------------------------------------|
| Acetonitrile, Acrylonitrile, Adiponitrile, Butyronitrile   | Polypyrrole                          |
| Nitromethane, 1,4-Dioxane, Dimethyl sulfoxide, Water, Tetrahydrofuran, Methanol, <i>N,N</i> -Dimethylformamide | None                                 |
| Acetone, Acetic acid   | None, but colour change was observed |

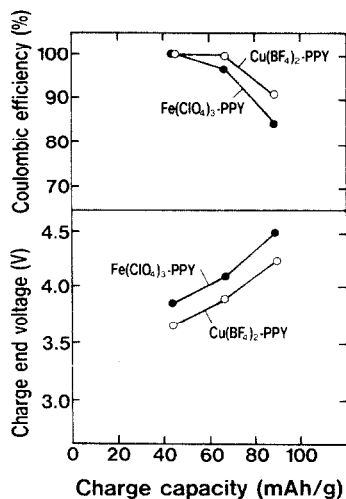


Fig. 4. Relationship between coulombic efficiency, charge end voltage, and charge capacity of Li–Al/polypyrrole cells.

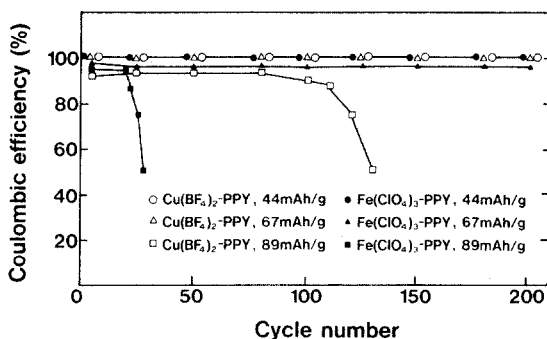


Fig. 5. Cycle characteristics of Li–Al/polypyrrole cells.

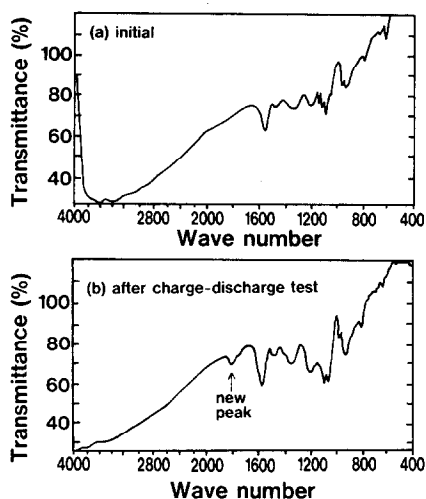


Fig. 6. FT-IR spectra of polypyrrole ( $\text{Fe}(\text{ClO}_4)_3\text{-PPY}$ ) before, and after, charge/discharge test.

Charge/discharge cycling performance was tested for these two polypyrroles under a charge capacity of 44, 67, and  $89 \text{ mA h g}^{-1}$ . The cycle test was stopped at 200 cycles, or when the coulombic efficiency reached 50%. The relation between coulombic efficiency and cycle number is shown in Fig. 5. At a charge capacity of 44 and  $67 \text{ mA h g}^{-1}$ , neither polypyrrole showed any deterioration in cell performance up to 200 cycles. At  $89 \text{ mA h g}^{-1}$ ,  $\text{Fe}(\text{ClO}_4)_3\text{-PPY}$  and  $\text{Cu}(\text{BF}_4)_2\text{-PPY}$  gave 28 and 130 cycles, respectively. These two polypyrrole electrodes were examined after the cycle test by the FT-IR method. A peak at  $1790 \text{ cm}^{-1}$ , which is attributed to the carbonyl group, was observed for  $\text{Fe}(\text{ClO}_4)_3\text{-PPY}$ , as shown in Fig. 6(b). Deterioration of charge/discharge performance is considered to be caused by oxidation of the  $\beta$ -position of the pyrrole ring and the consequent interception of  $\pi$ -electron conjugation. In the FT-IR spectra of  $\text{Cu}(\text{BF}_4)_2\text{-PPY}$ , no such carbonyl peaks were observed. Other factors, such as decomposition of the electrolyte solution, are also thought to be the cause of degradation in cell performance.

## Conclusions

Several chemically-synthesized conductive polymers have been examined for their characteristics as positive electrode material for lithium secondary batteries. The polypyrrole electrode was found to have good charge/discharge characteristics.

Oxidizing agents for polypyrrole synthesis have been investigated because they greatly influence the charge/discharge characteristics of polypyrrole electrodes. A new oxidizing agent, the  $\text{Cu}(\text{BF}_4)_2/\text{nitrile}$  system, has been

developed. Polypyrrole synthesized by this method exhibits excellent performance, with high doping levels and stable charge/discharge cycle characteristics.

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