

## Short Communication

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# A wound-type lithium/polyaniline secondary cell\*

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### Abstract

A wound-type cell with a polyaniline (PAn) positive electrode, a  $\text{LiClO}_4$ -propylene carbonate (PC) electrolyte, and a lithium foil negative electrode has been constructed. The two electrodes are separated by a polypropylene separator. The PAn is deposited on carbon felt from a  $\text{HClO}_4$  solution containing aniline by galvanostatic or potentiostatic electrolysis. Using cyclic voltammetry charge/discharge cycles and charge/retention tests, the following results have been obtained: (i) reversibility of the charge/discharge reaction of the PAn electrode is very good; (ii) more than 50 charge/discharge cycles at 80% charge/discharge efficiency and  $260 \text{ W h kg}^{-1}$  discharge energy density can be achieved at 50 mA between 2 and 4 V; (iii) the open-circuit voltage and the capacity retention of the battery after storage at open-circuit for 60 days are 3.4 V and 33%, respectively.

### Introduction

Polyaniline (PAn) is known to be the most stable of the conductive polymers. In addition PAn synthesized by electropolymerization has exhibited good reversibility in a  $\text{LiClO}_4$ -propylene carbonate (PC) electrolyte. Therefore, PAn can be used as the positive active material in secondary lithium cells and batteries [1–4]. A button-type Li–Al/PAn rechargeable cell has been made in Japan [5].

A large-capacity battery can be fabricated by increasing the electrode area. Achieving a good contact between the metal current-collector and the electrode is, however, difficult when a wound PAn electrode with a large surface area is used. The electrical conductivity of polyacrylonitrile carbon felt is very good; it can be used not only as a substrate material for electrochemical deposition of PAn, but also as a current collector for the PAn electrode.

In this work, studies have been conducted on the cyclic voltammetric properties, charge/discharge behaviour and charge/retention ability of cells using PAn deposited on carbon felt.

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## Experimental

### *Preparation of PAN carbon-felt electrode*

A separator type electrolyzer [6] was employed for deposition of PAN on the carbon felt. A 1 M HClO<sub>4</sub> solution containing 0.5 M aniline served as the electrolyte. A carbon-felt (thickness: 2 mm) and a graphite plate were used as the anode and the cathode, respectively. The reference electrode was a standard calomel electrode (SCE). All potentials are reported with respect to this electrode. The PAN was deposited on carbon felt by galvanostatic (2 to 10 mA cm<sup>-2</sup>) or potentiostatic (0.8 to 0.9 V) electrolysis. The electrode was treated with acetonitrile for 24 h in order to eliminate excess acid and water and to remove the PAN of low molecular weight. The PAN was then dried under vacuum. The resulting PAN carbon-felt electrodes are denoted as PANc. A carbon felt (area: 2 cm<sup>2</sup>) with about 20 mg PAN was used as the working electrode in cyclic voltammetric studies, while a carbon felt (area: 204 cm<sup>2</sup>) with about 1.4 g PAN served as the positive electrode in cells employed in other electrochemical investigations.

### *Assembly of test cell*

A PANc electrode, a polypropylene separator and a lithium foil (thickness: 0.3 mm) electrode were wound together in a glove box under an atmosphere of flowing dry argon. The assembly was then placed in a cylindrical polyethylene container. A 1 M solution of LiClO<sub>4</sub>-PC was added and the cell sealed with a polyethylene cover. The PANc electrode was connected to the positive terminal with six nickel tabs; the lithium electrode was connected to the negative terminal in a similar fashion.

### *Electrochemical measurements*

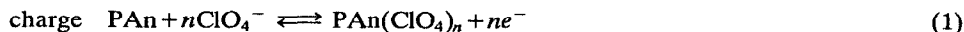
Cyclic voltammetric studies were conducted using a three-electrode glass cell. The electrolyte was 1 M LiClO<sub>4</sub>-PC. The working electrode consisted of PAN deposited on to carbon felt, while the counter and reference electrodes each comprised a lithium plate. The voltammetric curves were obtained with a model DH-1 potentiostat. The scan rate was 2 mV s<sup>-1</sup>. The charge/discharge tests were performed at a constant current of 50 mA. All experiments were carried out in a dry container at room temperature.

Aniline and PC were purified by distillation. Lithium perchlorate was dried at 150 to 160 °C under vacuum for 30 h. Other chemicals were analytical grade and were not subjected to further purification.

## Results and discussion

The cyclic voltammogram for a PANc electrode in 1 M LiClO<sub>4</sub>-PC solution is given in Fig. 1. The oxidation peak appearing at ~3.8 V (versus Li/Li<sup>+</sup>) is due to doping of ClO<sub>4</sub><sup>-</sup> anions into PAN; it corresponds to a charging reaction for the cell. Conversely, the reduction peak observed at ~2.9 V (versus Li/Li<sup>+</sup>) is the release of ClO<sub>4</sub><sup>-</sup> anions from PAN and corresponds to the cell discharge reaction.

It is generally considered that the charge/discharge reactions in the cell (or battery) are:



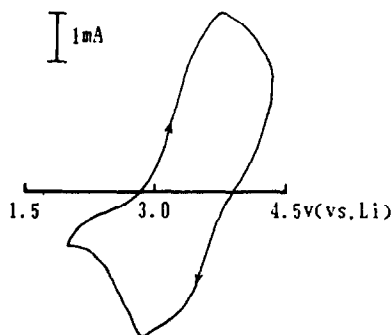


Fig. 1. Cyclic voltammogram for a PANc electrode in  $\text{LiClO}_4\text{-PC}$ ; scan rate:  $2 \text{ mV s}^{-1}$ .

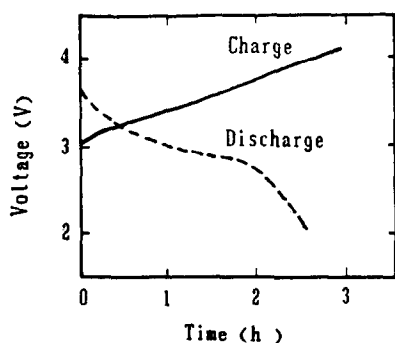


Fig. 2. Charge/discharge curves for  $\text{Li/LiClO}_4\text{-PC/PANc}$  cell at  $50 \text{ mA}$ ; voltage limits:  $2$  and  $4 \text{ V}$ .

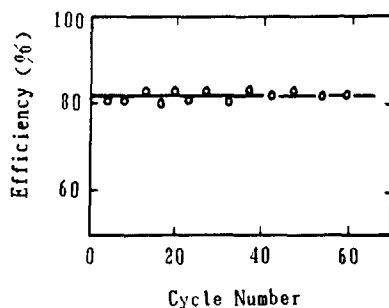
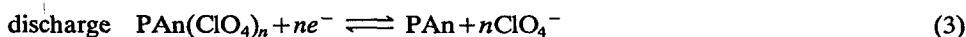


Fig. 3. Charge/discharge efficiency of  $\text{Li/LiClO}_4\text{-PC/PANc}$  cell as a function of cycle number.



The integrated charge of the anodic peak is almost equal to that of the cathodic peak and the coulombic efficiency is therefore close to 100%. This indicates that the redox reaction of the PAn electrode is virtually reversible.

Figure 2 shows the charge/discharge curves of a  $\text{Li/LiClO}_4\text{-PC/PANc}$  cell at  $50 \text{ mA}$  between  $2$  and  $4 \text{ V}$  (versus  $\text{Li/Li}^+$ ). It can be seen that the charge curve increases slowly with time until the charge voltage reaches  $4 \text{ V}$ . By contrast, the discharge curve has a flat region. From the charge/discharge data, the charge/discharge efficiency and discharge energy density are estimated to be  $>80\%$  and  $260 \text{ W h kg}^{-1}$ , respectively.

The charge/discharge efficiency of the  $\text{Li/LiClO}_4\text{-PC/PANc}$  cell is given in Fig. 3 as a function of the cycle number. Under the same charge/discharge conditions, the efficiency is still  $>80\%$  after 50 cycles.

The  $\text{Li/LiClO}_4\text{-PC/PANc}$  cell was charged up to  $4 \text{ V}$  at a constant current of  $50 \text{ mA}$ , and then stored at room temperature. The resulting change in the open-

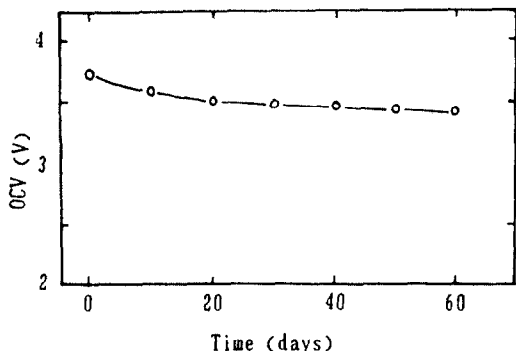


Fig. 4. Change in open-circuit voltage (OCV) of Li/LiClO<sub>4</sub>-PC/PAnC cell with storage time.

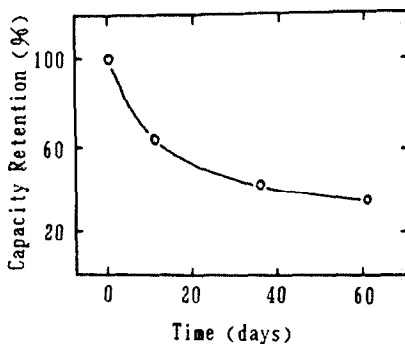


Fig. 5. Capacity retention of charged Li/LiClO<sub>4</sub>-PC/PAnC cell as a function of storage time.

circuit voltage (OCV) is given in Fig. 4. Although the OCV is seen to decay, steadily, the overall change is very small. After 60 days, the value is still 3.4 V. Therefore, it can be concluded that the cell exhibits good the voltage retention.

Figure 5 shows the capacity retention of a charged Li/LiClO<sub>4</sub>-PC/PAnC cell with storage time. Under the above-mentioned conditions, the capacity retention after open-circuit storage for 10, 35 and 60 days was 64, 42 and 33%, respectively. In general, most polymer electrodes exhibit poor charge retention in organic electrolytes that contain lithium salts. This self-discharge may be closely related to a spontaneous release of the doping ClO<sub>4</sub><sup>-</sup> anions within the bulk of the PAn.

In order for the PAn electrode to serve as a practical material for positive electrodes in wound-lithium cells and batteries, it is necessary to improve the adherence of the PAn to the carbon felt and to use thinner carbon felt.

## References

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