

## Short Communication

---

# An all-solid-state lithium/polyaniline rechargeable cell\*

Li Changzhi\*\*, Peng Xinsheng, Zhang Borong and Wang Baochen

*Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022 (China)*

(Received March 2, 1992)

### Abstract

The performance of an all-solid-state cell having a lithium negative electrode, a modified polyethylene oxide (PEO)–epoxy resin (ER) electrolyte, and a polyaniline (PAn) positive electrode has been studied using cyclic voltammetry, charge/discharge cycling, and polarization curves at various temperatures. The redox reaction of the PAn electrode at the PAn/modified PEO–ER interface exhibits good reversibility. At 50–80 °C, the Li/PEO–ER–LiClO<sub>4</sub>/PAn cell shows more than 40 charge/discharge cycles, 90% charge/discharge efficiency, and 54 W h kg<sup>-1</sup> discharge energy density (on PAn weight basis) at 50 μA between 2 and 4 V. The polarization performance of the battery improves steadily with increase in temperature.

### Introduction

Several studies have been reported [1–4] on the use of polyaniline (PAn) as the positive electrode material in lithium organic-electrolyte cells and batteries. Some of the problems found with these units include a high rate of self-discharge, poor chemical stability, and leakage of solution. These short-comings could be overcome by substituting a solid polymer electrolyte for the organic electrolyte. Since polymer electrolytes can be fabricated in the form of thin films, the possibility of developing a new type of rechargeable lithium cell has been proposed. Although investigations have been published [5–8] on polymer-electrolyte lithium cells and batteries, no study of an all-solid-state Li/PAn rechargeable system has been reported. As is well known, the conductivity of polyethylene oxide (PEO) electrolytes is quite low at room temperature. In general, the operation temperature of cells using polymer electrolytes is in the range 100 to 120 °C. Therefore, the practical application of such cells could encounter difficulties. Using a modified polyethylene oxide–epoxy resin (PEO–ER) electrolyte developed in our laboratories, an all-solid-state Li/PAn rechargeable cell has been constructed. This can operate at a temperature of 50 to 80 °C and exhibits promising performance as discussed in this paper.

---

\*Paper presented at the 5th International Meeting on Lithium Batteries, Beijing, China, May 28–June 2, 1990.

\*\*Author to whom correspondence should be addressed.

## Experimental

### *Electrochemical synthesis of polyaniline powder*

A separator type electrolyzer [9] was used to obtain a polyaniline (PAn) powder by electrochemical polymerization. Platinum or graphite plates were employed as the anode and the cathode, respectively. The reference electrode was a saturated calomel electrode (SCE). All potentials are reported with respect to this electrode. The PAn powder was synthesized by galvanostatic (2 to 10 mA cm<sup>-2</sup>) or potentiostatic (0.8 to 0.9 V) electrolysis in 1 M HClO<sub>4</sub> containing 0.5 M aniline. The resulting PAn powder was extracted with acetonitrile for 24 h to eliminate excess acid and water and to remove the PAn of low molecular weight. It was then dried under vacuum at 100 °C.

### *Fabrication of polyaniline electrode*

The treated PAn powder was mixed thoroughly with 3% PEO and 10 wt.% graphite powder or acetylene black; 10 mg this mixture was then pressed on nickel mesh, in a die, to give disc electrodes of geometric area 1.4 cm<sup>2</sup>.

### *Preparation of polymeric electrolyte films*

Cross-linking amorphous copolymers were prepared by reacting ER with PEO. The PEO-ER-LiClO<sub>4</sub> complexes were formed by treating the copolymers with LiClO<sub>4</sub>. Simultaneously, a thin film (100–200 μm thick) of polymeric electrolyte was prepared by a standard cast procedure. The conductivity of the latter was ~10<sup>-6</sup> S cm<sup>-1</sup> at room temperature.

### *Battery assembly and electrochemical measurements*

Using a glove box with flowing dry argon, a lithium electrode, the modified PEO-ER-LiClO<sub>4</sub> electrolyte film and a PAn electrode were pressed into a stainless-steel case that was then hermetically sealed with polytetrafluoroethylene (PTFE) foil. Charge/discharge cycles and polarization curves were performed using a two-electrode cell (i.e., to model the button-cell structure). A three-electrode cell (semicircle lithium foils served as the counter and reference electrodes, respectively) was used for cyclic voltammetric tests.

The electrochemical measurements were conducted with standard electronic equipment. This comprised a potentiostat (model DH-1), an X-Y recorder (model LZ3-204), and a galvanostat (model JY-10A). The measurements of cyclic voltammetry, charge/discharge cycles and polarization curves were carried out under the various conditions specified below.

## Results and discussion

Figure 1 illustrates the trends in cyclic voltammetric curves for the electrochemical reaction at the PAn/modified PEO-ER interface at 60 and 70 °C. The shape of voltammetric curves is similar to that for polypyrrole [8]. The cyclic voltammogram is that for an electrochemical couple with well-defined peaks. The oxidation charge passed during the anodic cycle is very close to the reduction charge released during the following cathodic cycle. This indicates that the conductivity of modified PEO-ER-LiClO<sub>4</sub> electrolyte is relatively high, and that the reversibility of the redox reaction of the PAn electrode at a PAn/PEO-ER-LiClO<sub>4</sub> interface is very good. It is generally believed that the P-doping, oxidation process of PAn, i.e.,

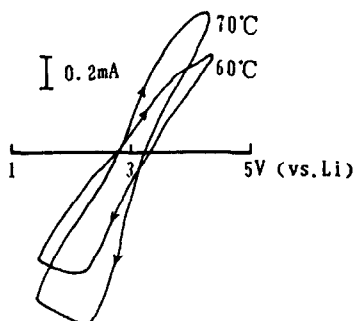


Fig. 1. Cyclic voltammograms for a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell at 60 and 70 °C; scan rate: 2 mV s<sup>-1</sup>.

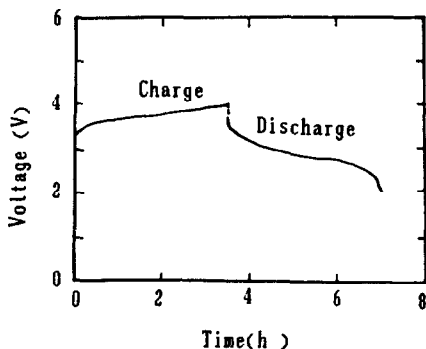


Fig. 2. Charge/discharge curve for a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell at 50 μA; voltage limits: 2 and 4 V.

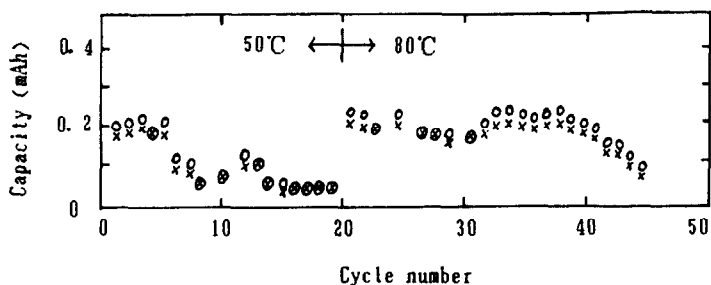


Fig. 3. Charge (O) and discharge (X) capacity of a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell as a function of cycle number at 50 and 80 °C.



may proceed easily and reversibly as indicated by the cyclic voltammetric curves obtained at 60 and 70 °C.

Typical charge/discharge curves for a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell at 50 °C are given in Fig. 2. The charge/discharge process was performed at a constant current of 50 μA between 2 and 4 V. The charging voltage of the battery increases slowly with time, while the discharge curve has a plateau. The mean discharge voltage of the battery is ~3 V. The coulombic efficiency and the discharge energy density, estimated from the charge/discharge curves, are about 90% and 54 W h kg<sup>-1</sup> (on a PAN weight basis), respectively.

Figure 3 shows the change in charge/discharge capacity of a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell with cyclic number and temperature. The battery was cycled at a constant current of 50 μA between 2 and 4 V. Clearly, the charge/discharge capacity of the battery gradually decreases after the first few cycles at 50 °C. The initial capacity at 50 °C is restored when the operating temperature is increased to 80 °C. Nevertheless, the charge/discharge capacity again decreases after 20 cycles at 80 °C. This change might be associated with a progressive decrease in the conductivity of the

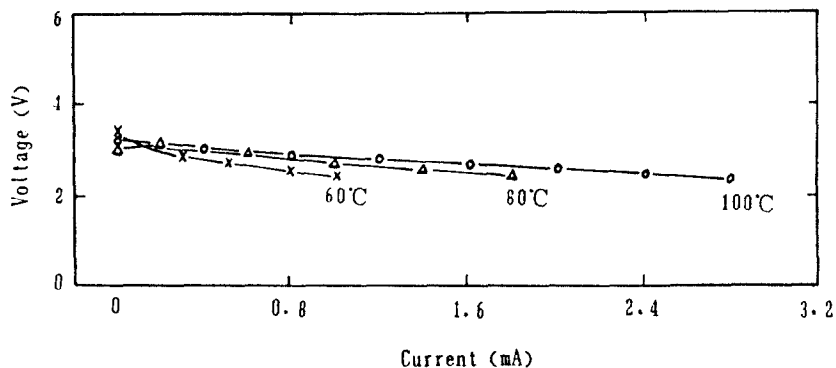


Fig. 4. Polarization curves of a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell at various temperatures.

PEO-ER-LiClO<sub>4</sub> electrolyte with time. This is confirmed by measurements of the polarization performance of the battery at various temperatures.

Figure 4 presents the polarization curves of a Li/PEO-ER-LiClO<sub>4</sub>/PAN cell at 60, 80 and 100 °C. It is quite evident that the polarization performance improves steadily with increase in temperature. This is due mainly to an increase in the conductivity of the PEO-ER-LiClO<sub>4</sub> electrolyte and the faster diffusion of ClO<sub>4</sub><sup>-</sup> anions in both the electrode and the electrolyte materials.

In order to attain a practical cell, it is necessary to improve further the manufacturing technology of the PAN electrode and to increase the conductivity of the PEO-ER-LiClO<sub>4</sub> electrolyte film in all-solid-state Li/PAN rechargeable cells and batteries.

## References

- 1 A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, *Mol. Cryst. Liq. Cryst.*, **121** (1985) 187.
- 2 A. Titani, M. Kaya, Y. Hiromoto and K. Sasaki, *Denki Kagaku*, **53** (1985) 592.
- 3 E. M. Genies, M. Lapkowski, C. Santier and E. Viel, *Synth. Met.*, **18** (1987) 631.
- 4 F. Goto, K. Abe, K. Okabayashi, T. Yoshida and H. Morimoto, *J. Power Sources*, **20** (1987) 243.
- 5 M. Gauthier, D. Fouteux, G. Vassort, A. Belanger, M. Duval, P. Ricoux, J.-M. Chabagno, D. Muller, P. Rigaud, M. B. Armand and D. Derou, *J. Electrochem. Soc.*, **132** (1985) 1333.
- 6 K. West, B. Zachau-Christiansen, T. Jacobsen and S. Atlung, *J. Power Sources*, **14** (1985) 235.
- 7 P. Novak, O. Lnganas and R. Bjorklund, *J. Electrochem. Soc.*, **134** (1987) 1341.
- 8 S. Panero, P. Prospero and B. Scrosati, *Electrochim. Acta*, **31** (1986) 1597; **32** (1987) 1461.
- 9 Li Changzhi and Wang Baochen, *Chin. Patent*, **88 207 383**, 4(1988).