

Study of all-solid state lithium/polyacenic semiconductor (PAS) battery

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Abstract

Some new polymer electrolytes, polyacrylonitrile-based lithium salt complexes, with high conductivity at ambient temperature have been developed. The electrical conductivity measurement, XRD and NMR results have been given. Solid-state lithium/polyacenic semiconductor (PAS) batteries using these polymer electrolytes have been constructed and tested. The charge and discharge behaviour has been studied, recycleability and the rate of self-discharge were measured at room temperature. When a battery cycled between 4.0 and 2.0 V, after 125 cycles the battery still has 97% capacity of the 10th cycle. The specific capacity was up to 58.6 mAh/g (based on the weight of PAS).

Keywords: Lithium batteries; Polymer electrolytes; Rechargeable batteries

1. Introduction

In the application of organic electrically conductive polymers to the electrodes of rechargeable batteries the polymer materials should possess stability and reversibility during the electrode reactions. Several kinds of conductive polymers such as polyacetylene [1], poly(*p*-phenylene) [2], polyaniline [3] and others [4] have been proposed for building up secondary batteries. On the other hand, polyacenic semiconductor (PAS) is one of the most stable materials among the conducting polymers and has exhibited excellent electrochemical reversibility as a positive electrode in non-aqueous electrolyte batteries [5–7] compared with any other conducting polymers. It was reported that PAS as positive electrode in lithium batteries with LiClO₄ in 1,4-butyrolactone (BL) and sulfolane (SL) (1:1 in volume) electrolyte showed a high open-circuit voltage [7]. This battery displayed excellent reversibility for electrochemical doping/undoping process and very small self-discharge and a high capacity density. It is expected that this battery would show a higher energy density than those of other polymer batteries. It was reported that the maximum capacity of Li/PAS battery was to be 220 Ah/kg [8] in contrast with that of a polyaniline 1,4-butyrolactone battery, 148 Ah/kg [9].

The development of ambient temperature rechargeable polymer batteries has remained a formidable chal-

lenge. The major problem is to find a suitable polymer electrolyte. The polymer electrolyte should not only has high ionic conductivity at ambient temperature but also exhibit good dimensional stability. It has been reported [10,11] that polyacrylonitrile (PAN)-based electrolyte can meet these requirements. In the paper, some highly conductive Li⁺ polymer electrolytes have been developed. The charge/discharge characteristics of Li/PAS secondary battery using these solid electrolytes has been described.

2. Experimental

PAS was prepared as follow [5]: under a nitrogen atmosphere and at a temperature-elevating rate of 30 °C/h phenol-formaldehyde resin was pyrolyzed in the presence of an appropriate amount of zinc chloride at 480, 580, 680 and 780 °C, respectively. The resultant powder was treated with hot 0.1 M hydrochloric acid and then washed with distilled water until no zinc ions were detected in the eluate. It was then dried and finally ground into powder. The product (pyrolysis temperature, $T_p = 580$ °C) was a black powder with a particle size of less than 60 μm, a surface area of ~1600 m²/g (BET method) and conductivity of 10⁻² S/cm at room temperature.

The PAN-based electrolytes were prepared by dissolving PAN in an appropriate amount of plasticizer and LiClO_4 at 110°C then casted to form a film. The thickness of the polymer electrolyte film was 0.1 to 0.15 mm. The conductivities of the electrolytes were obtained by analysis of the impedance spectra measured with 4192A LF impedance analyser. X-ray powder diffraction (XRD) patterns were obtained using a D/Max-VB X-ray diffractometer. The pulsed nuclear magnetic resonance (NMR) spectrograms of ^7Li were done using SXP4-100 pulse NMR equipment (Bruker). The test cells were constructed in a dry box filled with argon. The measurements of electrochemical characteristics of the cells were carried out at room temperature by using a potentiostat/galvanostat with a function generator and an x - y recorder.

3. Results and discussion

The conductivities as a function of temperature for PAN-EC-BL-SL- LiClO_4 (EC = ethylene carbonate) is shown in Fig. 1. It can be seen that this polymer

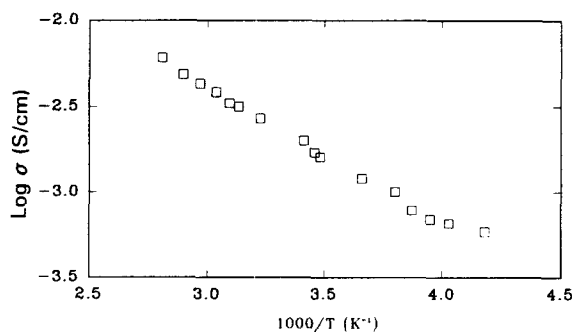


Fig. 1. Conductivity vs. temperature for 20PAN-30EC-32BL-13SL-5 LiClO_4 electrolyte in weight ratio.

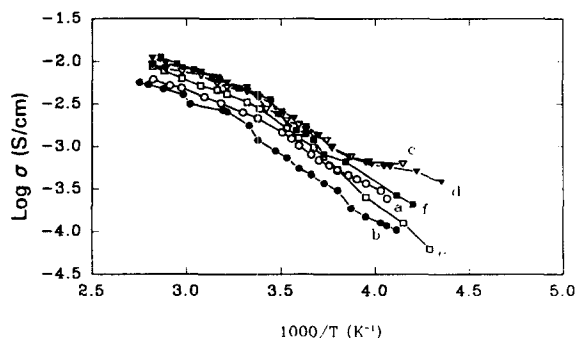


Fig. 2. Conductivity vs. temperature for PAN-based electrolyte in weight ratio: (a) 20PAN-35EC-40BL-5 LiClO_4 ; (b) 20PAN-26EC-35BL-14DL(dimethyl sulfoxide)-5 LiClO_4 ; (c) 20PAN-25EC-25PC-25DMF-5 LiClO_4 ; (d) 20PAN-37.5EC-37.5DMF-5 LiClO_4 ; (e) 20PAN-25EC-25PC-25BL-5 LiClO_4 , and (f) 20 PAN-25PC-25BL-25DMF-5 LiClO_4 .

Table 1

Discharge capacities and molar ratio of $[\text{H}]/[\text{C}]$ of polyacenic semiconductor pyrolyzed at various temperatures^a

T_p ($^\circ\text{C}$)	480	580	680	780
$[\text{H}]/[\text{C}]$	0.32	0.26	0.18	0.14
Capacity (mAh/g)	47.5	58.6	43.7	35.4

^a The Li/PAN-EC-BL-SL- LiClO_4 /PAS batteries cycled at $I_d = I_c = 0.1 \text{ mA/cm}^2$, and cutoff voltages of 4.0 to 2.0 V.

electrolyte possesses high conductivity even at -10°C . As shown in Fig. 2, all other polymer electrolytes based on PAN are highly conductive at room temperature (1×10^{-3} – $3.8 \times 10^{-3} \text{ } \sigma/\text{cm}$).

In order to understand the conduction behaviour of the new polymer electrolytes based on PAN, XRD and NMR experiments have been carried out. Fig. 3 shows the XRD patterns of PAN-EC-BL-SL- LiClO_4 and PAN-EC-PC-DMF- LiClO_4 (DMF = *N,N*-dimethylformamide) compared with pure LiClO_4 and PAN. It can be seen that PAN-based lithium salt complex is an amorphous phase. It is easy to understand that amorphous material has a higher ionic conductivity.

Some NMR spectra of ^7Li for two PAN-based lithium salt complexes at several temperatures are given in Fig. 4. The linewidth changed significantly between 210–220 K for PAN-EC-BL-SL- LiClO_4 and 200–210 K for PAN-EC-PC-DMF- LiClO_4 . Therefore, the glass transition temperatures (T_g) of the two polymer electrolytes are around 220 and 210 K, respectively. Above T_g the linewidth changed extremely little. The linewidth of the PAN-based lithium salt complex is almost the same as that of liquid electrolyte EC-PC-DMF- LiClO_4 as shown in Fig. 4. It means that the lithium-ion transport above T_g is similar to that in liquid electrolyte.

Fig. 5 gives the XRD patterns of PAS at different T_p . It indicates that PAS shows an amorphous structure. In fact, PAS was prepared by pyrolysis of phenol-formaldehyde resin moulded with ZnCl_2 [9]. ZnCl_2 used together with the resin serves not only as the pore-forming agent to form open pores, which grow into a three-dimensional network structure in the cured material, but also as the microstructure-controlling agent to form a loose structure dopable with bulky dopants such as PF_6^- , ClO_4^- and others [5].

Table 1 gives the characteristics of the Li/PAN-EC-BL-SL- LiClO_4 /PAS batteries at different T_p , from which we can see that the batteries show the highest specific capacity value (58.6 mAh/g) when $T_p = 580^\circ\text{C}$. The PAS mentioned in the following paragraphs was pyrolyzed at 580°C .

Fig. 6 gives a typical charge and discharge curves of Li/PAN-EC-BL-SL- LiClO_4 /PAS battery. The cutoff voltage of charge/discharge is 4.0–2.0 V at a constant-current density of $I_c = I_d = 0.1 \text{ mA/cm}^2$. It can be seen that the electrical capacity passed in the charge process is very close to that of discharge.

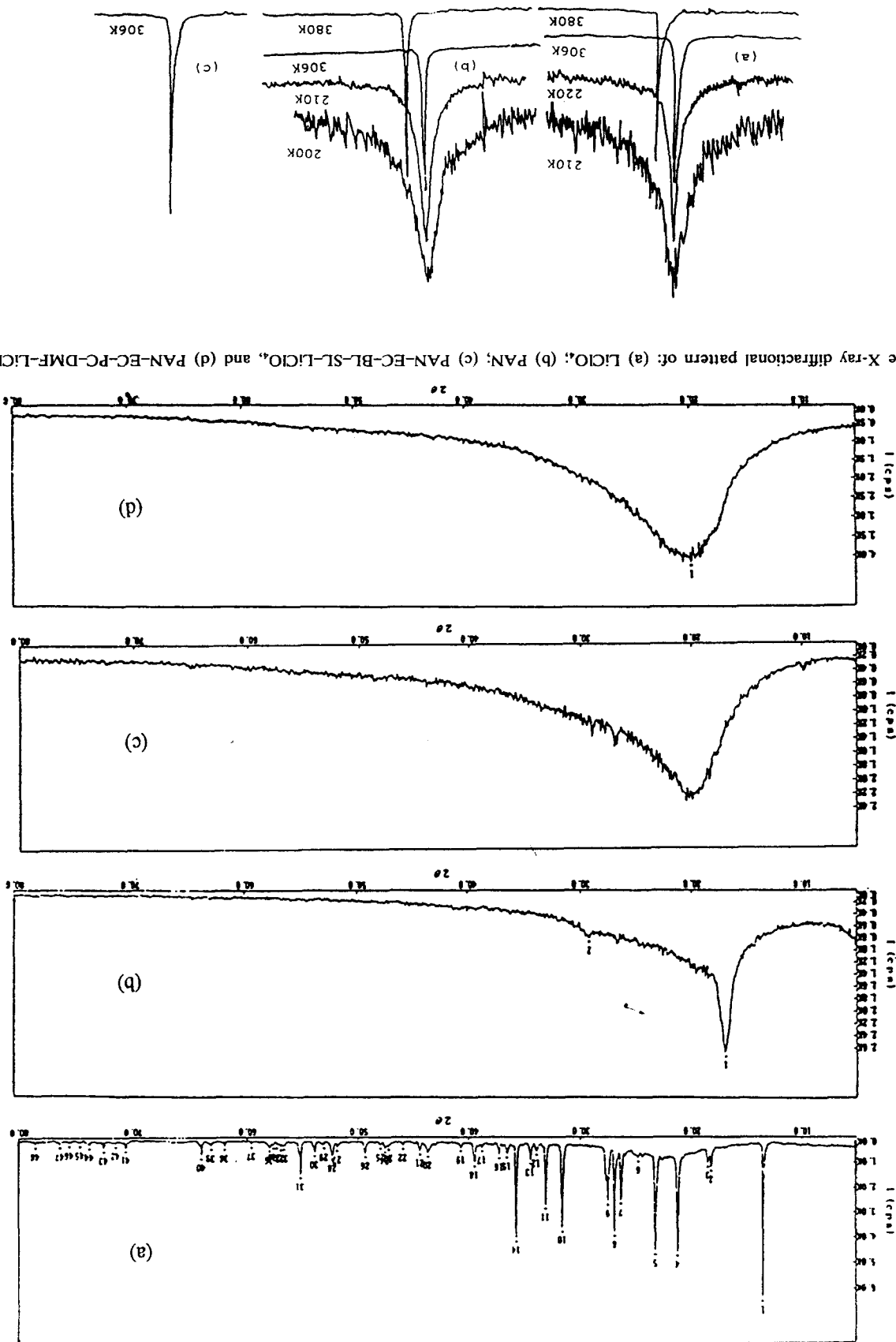
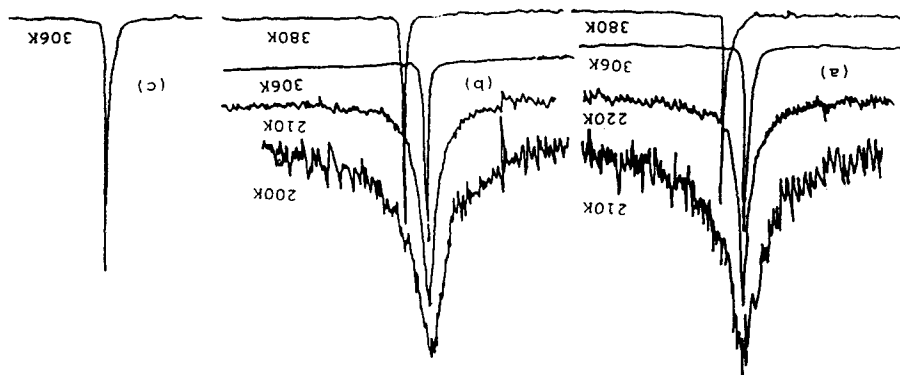


Fig. 3. The X-ray diffraction pattern of: (a) LiClO_4 ; (b) PAN; (c) PAN-EC-BL-SL- LiClO_4 ; and (d) PAN-EC-PC-DMF- LiClO_4 .

Fig. 4. ^7Li NMR spectra of: (a) PAN-EC-BL-SL- LiClO_4 ; (b) PAN-EC-PC-DMF- LiClO_4 ; and (c) EC-PC-DMF- LiClO_4 ; frequency: 34.984 MHz, at various temperatures.



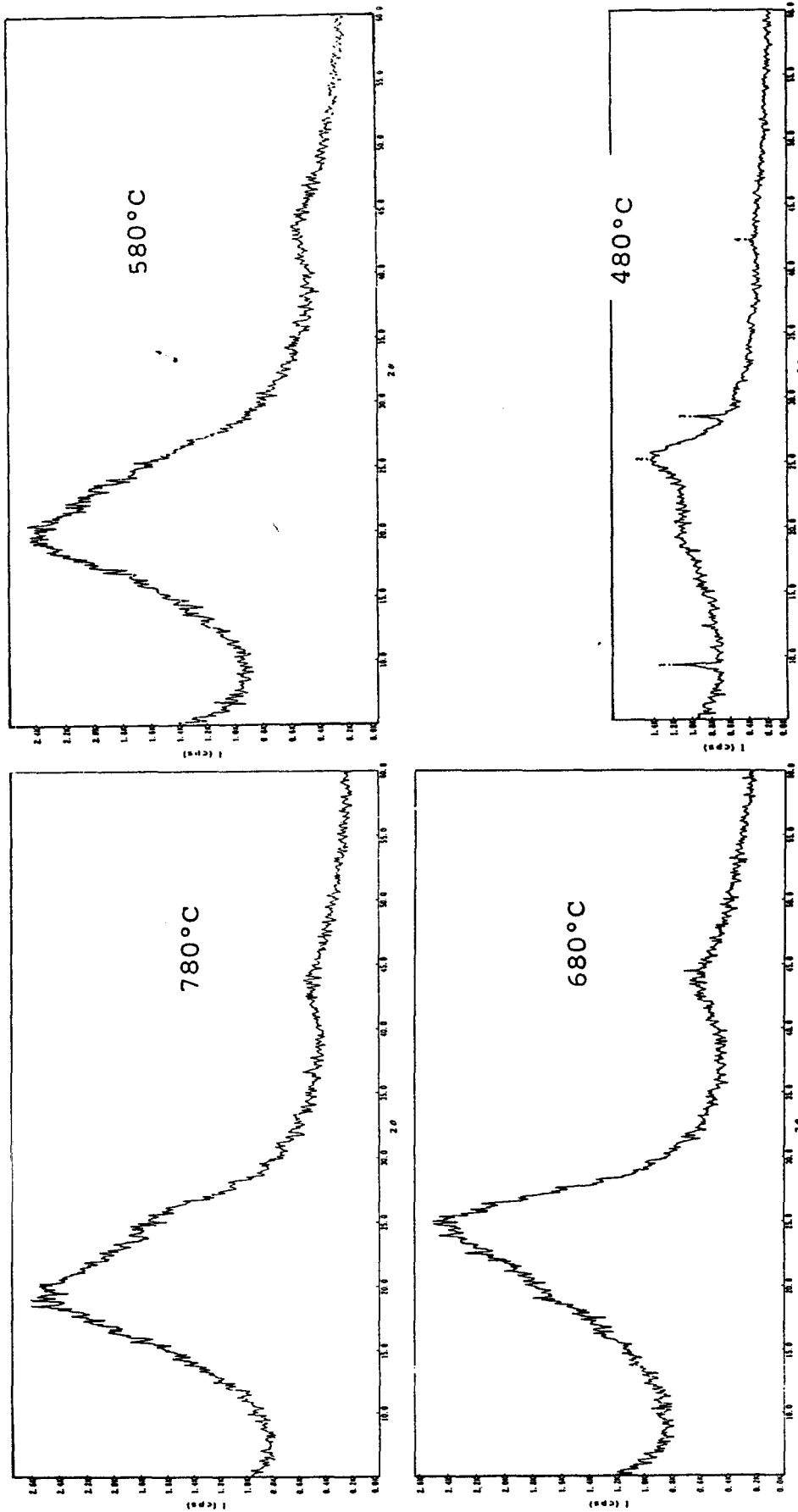


Fig. 5. The X-ray diffractogram of PAS of samples pyrolyzed at various temperatures (T_p).

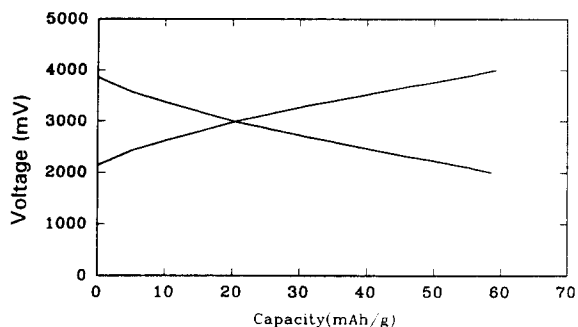


Fig. 6. Typical charge/discharge profiles of Li/PAN-EC-BL-SL-LiClO₄/PAS cell at room temperature, cycled at $I_d = I_c = 0.1$ mA/cm².

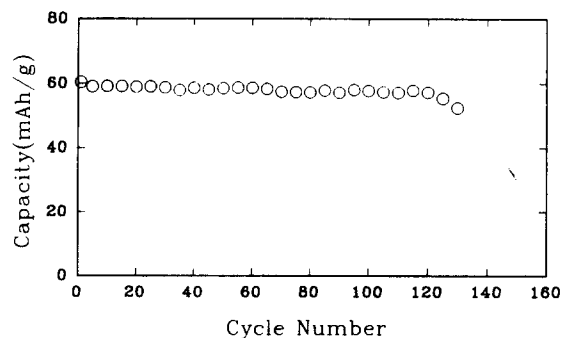


Fig. 7. Discharge capacity vs. cycle number of Li/PAN-EC-BL-SL-LiClO₄/PAS cell at 0.1 mA/cm² between 4.0 and 2.0 V at room temperature.

The capacity of the test cell after 125 cycles is about 97% of that of 10th cycle as shown in Fig. 7. It indicates the decline rate of the capacity of this battery is extremely low. It is also found from Fig. 7 that the discharge capacity of the battery maintained a stable value of 58.6 mAh/g (based on the weight of PAS). When the battery was charged to 4.0 V, after storage at room temperature for 60 days (shown in Fig. 8), the voltage

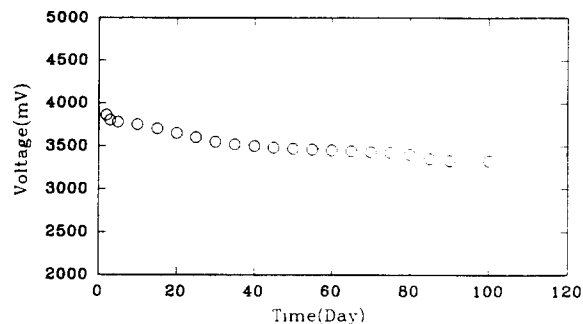


Fig. 8. Self-discharge behaviour of Li/PAN-EC-BL-SL-LiClO₄/PAS cell.

of this battery still stays at 3.45 V. This voltage change indicates a small self-discharge in an Li/PAN-EC-BL-SL-LiClO₄/PAS battery.

References

- [1] P.J. Nigrey, D. Macinnes, Jr., D.P. Nairns, A.G. MacDiarmid and A. Heeger, *J. Electrochem. Soc.*, **128** (1981) 1651.
- [2] L.W. Shacklette, J.E. Toth, N.S. Murthy and R.H. Baughman, *J. Electrochem. Soc.*, **132** (1985) 1529.
- [3] A.G. MacDiarmid, S.L. Mu, N.L. Somasiri and W. Wu, *Mol. Cryst. Liq. Cryst.*, **121** (1985) 1987.
- [4] A.G. MacDiarmid and R.B. Kaner, in T.A. Skotheim (ed.), *Handbook of Conducting Polymers*, Vol. 1, Marcel Dekker, New York, 1986, p. 689.
- [5] S. Yata, Y. Hato, K. Sakurai, H. Satake, K. Mukai, K. Tanaka and T. Yamabe, *Synth. Met.*, **38** (1990) 169.
- [6] S. Yata (Kanebo Ltd.), *US Patent No. 4 625 960* (Oct. 1986).
- [7] S. Yata, Y. Hato, K. Sakurai, T. Osaki, K. Tanaka and T. Yamabe, *Synth. Met.*, **18** (1987) 645.
- [8] A.G. MacDiarmid, L.S. Yang, W.S. Huang and B.D. Humphrey, *Synth. Met.*, **18** (1987) 393.
- [9] S. Yata, Y. Hato, T. Osaki and K. Sakurai (Kanebo Ltd.), *US Patent No. 4 753 717* (June 1988).
- [10] K.M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, **137** (1990) 1657.
- [11] H. Huang, L.Q. Chen, X.J. Huang and R.J. Xue, *Electrochim. Acta*, **37** (1992) 1671.