

Development of cylindrical secondary lithium/polyaniline batteries

Li Changzhi*, Zhang Borong and Wang Baochen

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

Abstract

The cylindrical 'D'-size batteries were fabricated by polyaniline paste cathode and lithium foil anode sandwiched with microporous polypropylene separator. The electrolyte used was LiClO_4 dissolved in a mixed solvent of propylene carbonate and dimethoxyethane. The results of charge/discharge curves, charge/discharge cycles, the short-circuit current, the open-circuit voltage storage and the change of discharge capacity with temperature, discharge current are reported.

Introduction

Among the conductive polymers, polyaniline (PAn) is the most stable one. PAn synthesized by electropolymerization has exhibited good reversibility in organic electrolyte containing LiClO_4 . Therefore, attempts have been made to use PAn as rechargeable cathode material in secondary lithium batteries [1-4]. Coin-type Li-Al/PAn rechargeable cell were made in Japan [5]. We have developed a wound-type Li/PAn secondary battery using carbon felt as the substrate material of PAn electrode [6], but the energy density of such battery was comparatively low. Shinozaki *et al.* [7] have assembled a cylinder-type "AA"-size Li/PAn battery with capacity of 180 mA h.

A larger capacity Li/PAn battery using stainless-steel mesh as current collector was fabricated in this work. We have conducted the studies on the charge/discharge behaviour, cycle and short-circuit discharge characteristics, charge-retention ability and the effect of the discharge current, cutoff voltage, temperature on the discharge capacity of the battery.

Experimental

A separator-type electrolyzer [8] was used to obtain a PAn powder by galvanostatic (2 to 10 mA cm^{-2}) or potentiostatic (+0.8 to +0.9 V) electrolysis in 1.0 M HClO_4 solutions containing 0.5 M aniline. A stainless-steel plate and a graphite plate were used as anode and cathode, respectively. As reference electrode a saturated calomel electrode has been used. Flexible PAn sheet electrodes were fabricated by coating a fine stainless-steel mesh, which also served as current collector, with a PAn paste containing 5% graphite powder and 10% polytetrafluoroethylene (PTFE). PAn-coated

*Author to whom correspondence should be addressed.

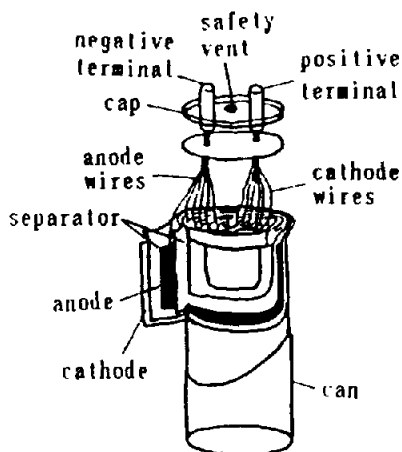


Fig. 1. Exploded view of a cylindrical 'D'-size Li/PAn battery.

electrodes were extracted with acetonitrile for 24 h, to remove the low mol. wt. PAN, and then dried under vacuum.

Figure 1 shows an exploded view of the cylindrical 'D'-size Li/PAn battery. The anode was a 0.2 to 0.3 mm thick lithium foil. PAN-coated electrode containing 7.0 g polyaniline was used as cathode. The electrolyte used was 1 M LiClO_4 /propylene carbonate (PC)–1,2-dimethoxyethane (DME) (1:1) solution. In a glove box with flowing dry argon, a positive electrode, with microporous polypropylene separators and a negative electrode were wound together, and put into a cylindrical polyethylene container, 1.0 M LiClO_4 /PC–DME was added, then a polyethylene cover was used to seal the battery. PAN electrode and lithium electrode were connected to the positive terminal and the negative terminal with stainless-steel wires, respectively.

PC, DME and aniline were purified by distillation. LiClO_4 was dried at 150–160 °C under vacuum for 32 h. Other chemicals used were analytical grade without further purification.

Results and discussion

Figure 2 shows charge/discharge curves of cylindrical Li/PAn battery at 0.2 A between 2 and 4 V. It can be seen that the charge curve increases slowly with time until the charging voltage reaches 4 V, while the discharge curve has a flat region. The average discharge voltage of the battery is about 2.9 V. The coulombic efficiency and the discharge energy density, estimated from the charge/discharge curves, were about 95% and 260 Wh kg^{-1} on PAN weight base, respectively. The observed charge/discharge behaviour of cylindrical Li/PAn battery is similar to that found in an all solid-state Li/PAn rechargeable battery [9].

The discharge capacity of cylindrical Li/PAn battery as a function of cycle numbers is shown in Fig. 3. It will be seen that the discharge capacity was still sustained 0.53 A h when the battery was cycled more than 30 cycles at 0.2 A (charge) and 0.4 A (discharge) between 2 and 4 V.

Figure 4 shows the change of discharge capacity of a cylindrical Li/PAn battery with temperature. The battery was charged up to 4 V at 0.2 A and then was discharged

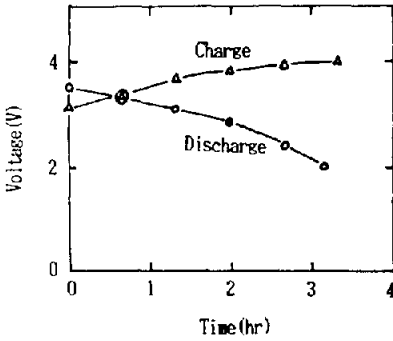


Fig. 2. Charge/discharge curves of a cylindrical Li/PAN battery at 0.2 A between 2 and 4 V.

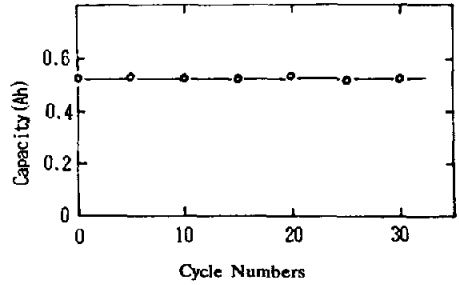


Fig. 3. Discharge capacity of a cylindrical Li/PAN battery as a function of cycle number; charge/discharge current: 0.2 A/0.4 A, voltage limits: 2 V and 4 V.

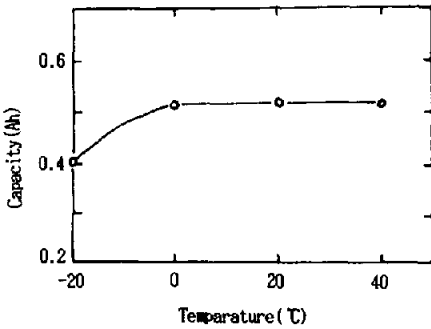


Fig. 4. Change of discharge capacity of a cylindrical Li/PAN battery with temperature; charge/discharge current: 0.2 A/0.4 A, voltage limits: 2 V and 4 V.

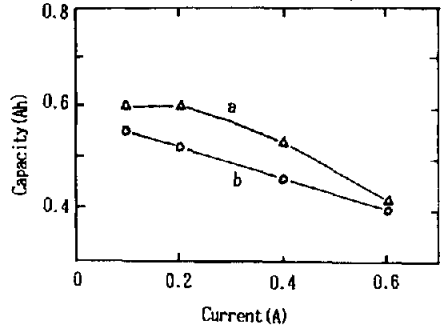


Fig. 5. Effect of discharge current and cutoff voltage on discharge capacity of a cylindrical Li/PAN battery; discharge cutoff voltage: (a) 2 V and (b) 2.5 V.

to 2 V at 0.4 A. A discharge capacity of 0.53 A h was obtained at 0, 20, 40 °C compared with 0.42 A h at -20 °C. It is quite evident that discharge performance of the battery is relatively good at low temperature.

The effect of discharge current and cutoff voltage on discharge capacity of cylindrical Li/PAN battery was given in Fig. 5. The battery was charged up to 4 V at 0.2 A and then was discharged to 2 V or 2.5 V at room temperature. It can be seen that discharge capacity of 0.63 A h can be derived when discharge current less than 0.2 A and discharge cutoff voltage of 2 V (curve a), but discharge capacity gradually decreases when discharge current were more than 0.2 A or discharge cutoff voltage of 2.5 V (curve b). The effect of discharge cutoff voltage on discharge capacity is not large at discharge current of 0.6 A.

The battery was charged up to 4 V at a constant current of 0.2 A and then was discharged at the short-circuit current. As shown in Fig. 6, the short-circuit current first reached 3 A, then gradually decreased to 0.6 A in about 30 min, while the wall temperature rose from room temperature to a steady value of 34.5 °C in about 25 min; but no explosion was observed.

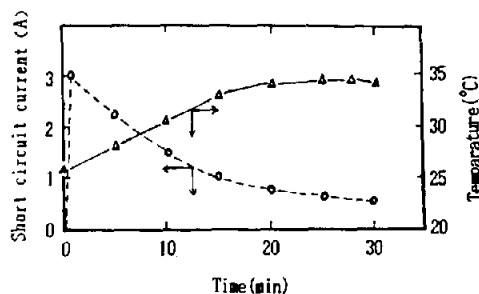


Fig. 6. The short-circuit discharge characteristics of a cylindrical Li/PAN battery.

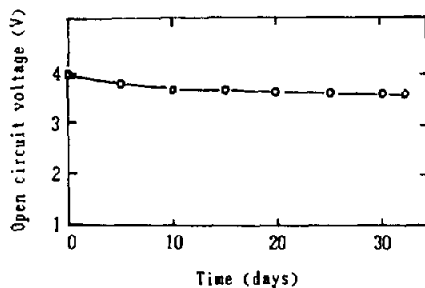


Fig. 7. The change of the open-circuit voltage with the storage time.

The cylindrical Li/PAN battery was charged up to 4 V at 0.2 A and then was stored at room temperature. Figure 7 illustrates the change in the open-circuit voltage of a charged Li/PAN battery with the storage time. The open-circuit voltage decays slowly with time. After storing for 30 days, the open-circuit voltage of a charged battery has dropped from 4 to 3.6 V. Although the voltage-retention ability is very good, the capacity suffered much greater losses. In general, the majority of the polymer electrodes show poor charge retention in organic electrolytes. A high rate of self-discharge may be related to a spontaneous undoping process of the doping anions within the bulk of PAN. Therefore, it is necessary to solve the problem of self-discharge in polymer 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. Vieil, *Synth. Methods*, 18 (1987) 631.
- 4 F. Goto, K. Abe, K. Okabayashi, T. Yoshida, H. Morimoto, *J. Power Sources*, 20 (1987) 243.
- 5 H. Daifuka, T. Kawagoe and T. Mataunaga, *Denki Kagaku*, 57 (1989) 557.
- 6 L. Changzhi, Z. Borong and W. Baochen, *J. Power Sources*, 39 (1992) 259.
- 7 K. Shinozaki, A. Kabumoto, Y. Tomizuka, H. Sato, K. Watanabe, H. Umemura and K. Tanemhira, *Denki Kagaku*, 58 (1990) 753.
- 8 L. Changzhi and W. Baochen, *Chin. Patent No. 88 207 383.4*(1988).
- 9 L. Changzhi, P. Xinsheng, Z. Borong and W. Baochen, *J. Power Sources*, 39 (1992) 255.