FIBROUS POLYANILINE AS POSITIVE ACTIVE MATERIAL IN LITHIUM SECONDARY BATTERIES

SATOSHI TAGUCHI and TOSHIHIKO TANAKA

Takatsuki Research Laboratory, Sumitomo Chemical Co., Ltd., 2-10-1, Tsukahara, Takatsuki, Osaka 569 (Japan)

Summary

Fibrous polyaniline (f-PANI) has displayed a maximum discharge capacity of 164 A h kg^{-1}, a low rate of self-discharge, and a long life as a positive active material in a secondary lithium battery.

Introduction

Since the discovery of rechargeable batteries using polyacetylene (PA) as an electroactive material, several other organic-based batteries have attracted much attention. Various kinds of conducting organic polymers have been examined as electrode materials, *e.g.*, PA [1], poly(*p*-phenylene) [2], PANI [3, 4], polythiophene [5], etc.

PANI has been shown to be a promising material for secondary batteries [3], and in particular for secondary lithium batteries [4]. When obtained by an electrochemical process, PANI has been found to have several morphologies depending on the polymerization conditions of the aniline. However, little is known concerning the influence of the morphology of PANI on battery performance.

This paper reports studies of the characteristics of fibrous polyaniline (f-PANI) when serving as the positive active material in a secondary lithium battery.

Experimental

The PANI was prepared from an aqueous acidic solution of aniline by electro-polymerization. Two platinum sheets (each 4 cm^2 in area) were used as the working and counter electrodes. The f-PANI was obtained with a fine fibrous structure and a smooth surface by constant-current (5 mA cm^{-1}) electrolysis in 1 M $HClO_4$ containing 0.5 M aniline at room temperature; 6 coulombs cm^{-2} were consumed. Granular PANI (g-PANI) was prepared under similar conditions but by using 0.5 M H_2SO_4. The PANI deposited on the platinum

plate was first washed with water and then with methanol, and finally dried under vacuum at room temperature.

The test cell was of beaker-type with a positive electrode consisting of PANI deposited on a platinum plate, a negative electrode consisting of a lithium rod, and an electrolyte of 1 M $LiClO_4$ in propylene carbonate (PC). The lithium and $LiClO_4$ were used in large excess compared with the stoichiometric amount of PANI so that these materials did not limit the capacity of the cell. The PC was distilled under vacuum and the $LiClO_4$ was dried under vacuum at 160 °C. Other chemicals were used in the state in which they were purchased.

The cell was constructed and operated in an argon-filled dry box; the charge/discharge cycles were performed under constant current at room temperature. The cell was removed from the dry box for studies of the effect of temperature, and was placed in either an ice or water bath.
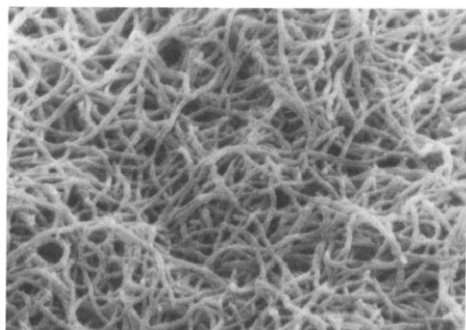
The weight of PANI, from which the charge and discharge capacities were calculated, was determined from the difference between the weight of the electrochemically deposited PANI and the equivalent weight of undoped dopants calculated from the discharge curve in which PANI was first discharged to a cell voltage of 1.5 V. This weight contained polymer chains and residual dopants after first discharge.

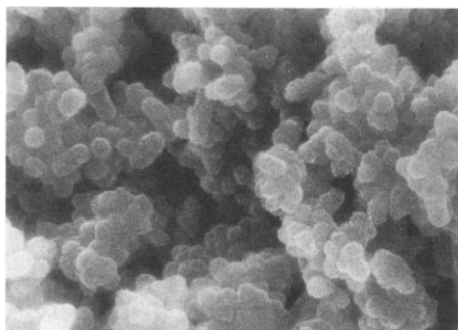For IR analysis, PANI was treated with 1 M NaOH to remove dopants.

Surface area measurements were determined using the conventional BET process.

Results and discussion

Figures 1 and 2 show electron micrographs of f-PANI and g-PANI, respectively. It can be seen that f-PANI consisted of fine fibrils with diam-

Fig. 1. Electron micrograph of f-PANI prepared from 0.5 M aniline/1 M $HClO_4$ at 5 mA cm^{-2}.

Fig. 2. Electron micrograph of g-PANI prepared from 0.5 M aniline/0.5 M H_2SO_4 at 5 mA cm^{-2}.

eters ~0.1 μm. On the other hand, g-PANI was composed of fine particles with diameters ~0.5 μm. No significant differences were found between f-PANI and g-PANI from IR analysis. However, f-PANI had a large specific surface area of ~10 $m^2 g^{-1}$, which was 2.5 times as large as that of g-PANI.

A typical charge/discharge curve of the cell containing f-PANI at a constant current of 0.2 mA cm^{-2} is given in Fig. 3. The voltage of the cell changes with time. Since the potential of lithium was constant throughout the charge/discharge cycle, the change in the cell voltage was due solely to the change in potential of f-PANI. As with other conducting polymers, the charge and the discharge of f-PANI proceeds via the doping and the undoping of ClO_4^-. Figure 4 shows the relationship between the discharge and charge capacity of f-PANI. When the charge capacity was <130 A h kg^{-1}, the coulombic efficiency of f-PANI was nearly 100%, thus indicating that doping and undoping had proceeded reversibly. When the charge capacity was >130 A h kg^{-1}, the coulombic efficiency was found to fall. At the same time, the electrolyte became coloured around the surface of f-PANI and thus indicated that the f-PANI was destroyed by the excess charge. The maximum value of the discharge capacity was 164 A h kg^{-1}.

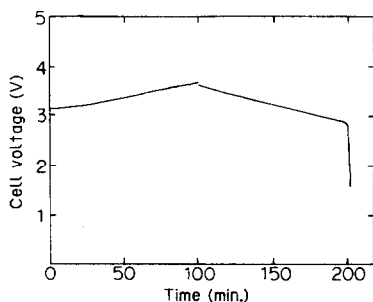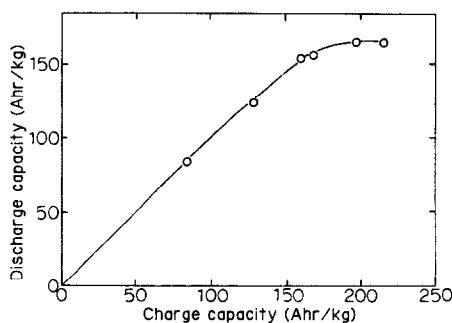Fig. 3. Charge/discharge curve of f-PANI/Li cell at 0.2 mA cm^{-2}.

Fig. 4. Relationship between charge and discharge capacities of f-PANI at 0.2 mA cm^{-2}.

According to an elemental analysis, the molar ratio of the dopants to the nitrogen atom (N) of f-PANI after polymerization was ~0.35, whereas the molar ratio of dopants undoped at the first discharge to N of f-PANI was ~0.25. Therefore, discharged f-PANI still contained 10 mol% dopants per monomer unit. At the maximum discharge capacity, the undoped dopants were equivalent to ~60 mol%. That is to say, the maximum doping level of f-PANI was 70 mol%, although Kitani et al. [4] have shown that the doping level of ClO_4^- was 45 mol%. This discrepancy can be explained in terms of a difference in polymer morphology. Since f-PANI consists of fine fibrils, as shown in Fig. 1, it is likely that ClO_4^- will permeate into this material more readily and more homogeneously than into PANI with a different morphology.

The charge/discharge cycle was examined at 0.1 mA cm^{-2} at a charge capacity of 83 A h kg^{-1}, i.e., about one half the maximum capacity. From
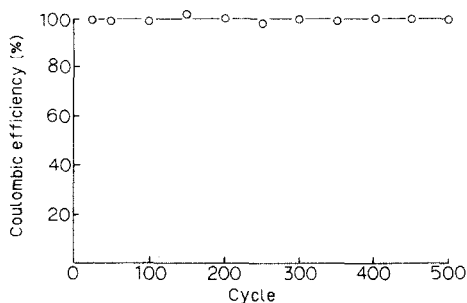
Fig. 5. Coulombic efficiency of f-PANI/Li cell as a function of change/discharge cycle number. Charge capacity = 83 A h kg^{-1}; current density = 0.1 mA cm^{-2}.
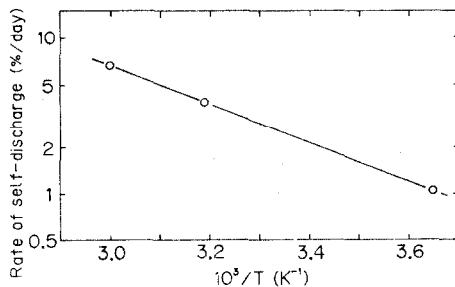
Fig. 6. Relationship between self-discharge rate and f-PANI/Li cell temperature. Charge capacity = 110 A h kg^{-1}; current density = 0.1 mA cm^{-2}.

the date given in Fig. 5, it can be seen that the coulombic efficiency is maintained at nearly 100% over 500 cycles without any degradation of the f-PANI.

The self-discharge rate was calculated from the relationship between the coulombic efficiency and the open-circuit time. Figure 6 shows the linear relationship between the self-discharge rate and the cell temperature when the charge capacity was 110 A h kg^{-1}. From the slope of this line, the activation energy of self-discharge was calculated to be 5.7 kcal mol^{-1}. The self-discharge rate was less than 2%/day at room temperature.

These observed characteristics demonstrate that f-PANI is a suitable material for a polymer battery.

References

1 D. MacInnes, Jr., M. A. Druy, P. J. Nigrey, D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (1981) 317.
2 L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, J. M. Sowa, D. W. Ivory, G. G. Miller and R. H. Baughman, *J. Chem. Soc., Chem. Commun.*, (1982) 3417.
3 A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, *Mol. Cryst. Liq. Cryst.*, *121* (1985) 187.
4 A. Kitani, M. Kaya, Y. Hiromoto and K. Sasaki, *Denki Kagaku*, *53* (1985) 592.
5 K. Kaneto, K. Yoshino and Y. Inuishi, *Jpn. J. Appl. Phys.*, *22* (1983) L567.