

## Polyaniline used as a positive in solid-state lithium battery

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### Abstract

The composite film of polyaniline containing a complex of poly(ethylene oxide) (PEO) and lithium perchlorate was prepared and used as a positive in solid-state lithium rechargeable battery. The charge and discharge behaviour at constant current density of 0.1 and 0.2 mA/cm<sup>2</sup>, recycleability and the rate of self-discharge were measured at room temperature. The preliminary results showed that the composite positive of polyaniline exhibited a good compatibility with polymer solid-state electrolyte and its service life was up to 250 cycles at deep charge/discharge between 2.5 and 4.0 V. The coulombic efficiency and the capacity density of the Li/PAN solid-state rechargeable battery were 98% and 48.3 A h/kg, respectively (based only on positive active material).

### Introduction

Polyaniline (PAN) is one of the most stable materials among conducting polymers and has exhibited excellent electrochemical reversibility as a positive in either an aqueous or a nonaqueous electrolyte compared with any other conducting polymers. It was reported that PAN positive in Li battery with LiClO<sub>4</sub> in propylene carbonate (PC) electrolyte showed a high open-circuit voltage ( $V_{oc}$ ), operating voltage and capacity density as well as good recycleability [1-3].

The button cells of Li/PAN rechargeable batteries (models AL920, Al2016 and AL2032 with nominal capacities of 0.5, 2.0 and 8.0 mA h, respectively) with nonaqueous electrolyte were first produced by Seiko Electronic Components, Ltd., and its recycleability was up to 1000 cycles on the condition of a light charge/discharge [4].

Recently, many investigations have been concerned with the possibility to apply PAN to solid-state rechargeable Li batteries as a positive material. It has been found that PAN/PEO-LiClO<sub>4</sub> polymer electrolyte in a solid-state Li battery exhibited a good electrochemical reversibility and recycleability at 50-80 °C [5].

In this work, the composite positive film using chemical synthesized PAN powder with PEO-LiClO<sub>4</sub> complex was prepared in order to improve the interfacial contact between the electrode and the solid-state electrolyte during cell fabrication and on subsequent cycling; its electrochemical characteristics in a solid-state Li battery were measured at room temperature.

### Experimental

Polyaniline used as positive material was synthesized by either electrochemical or chemical method [3, 6]. The chemical synthesis of PAN powder has been described

in ref. 3. The composition and construction of synthesized PAN powder chemically were analysed by infrared, X-ray photoelectron spectroscopy, and elemental analysis. The composite positive film of PAN was prepared by mixing PAN powder with  $\text{LiClO}_4$ -PEO complex which was solved in a certain quantity of acetonitrile and was subsequently stirred for 24 h; then the mixed gel was cast onto a flat nickel foil. The composite positive film of PAN was finally formed by evaporating the solvent of acetonitrile under nitrogen atmosphere at room temperature for 48 h. The thickness of the composite film is about 0.1 to 0.2 mm.

The electrolyte was prepared by solving both poly(ethylene oxide) (average mol. wt.  $5 \times 10^6$ , Aldrich Chemical Company, Inc.) and lithium perchlorate into a suitable quantity of acetonitrile in a molar ratio of PEO:Li = 10:1. A small quantity of ethylene carbonate was added in order to improve the conductivity of solid-state electrolyte. The complex gel of  $\text{LiClO}_4$ -PEO was sufficiently stirred and then cast onto the surface of PAN composite positive film. Finally, it was slowly dried under nitrogen atmosphere, then dried in the vacuum oven for 48 h at room temperature. The thickness of the polymer electrolyte layer in the duplex film was about 0.1 mm and its conductivity was about  $10^{-4}$  to  $10^{-5}$  S/cm at room temperature.

Two types of Li/PAN solid-state Li batteries (button and plate cell) were constructed employing the duplex film of PAN/polymer electrolyte in a purified argon atmosphere box. The measurements of electrochemical characteristics of the cell were carried out at room temperature by using a potentiostat/galvanostat with function generator and  $x$ - $y$  recorder.

## Results and discussion

Typical charge and discharge curves of Li/PAN solid-state battery are illustrated in Fig. 1. Each curve was obtained during 3 to 6 h at a constant current density of  $I_c = 0.1 \text{ mA/cm}^2$  and  $I_d = 0.2 \text{ mA/cm}^2$ . The charge of the battery was stopped at the end voltage of 4.0 V, over which stage the potential began to rise rapidly and the polymer electrolyte began to decompose. During discharge under the above condition, the potential began to decrease slowly with time and as can be seen from the curve, discharge was complete at the cutoff voltage of 2.5 V with 98% coulombic recovery.

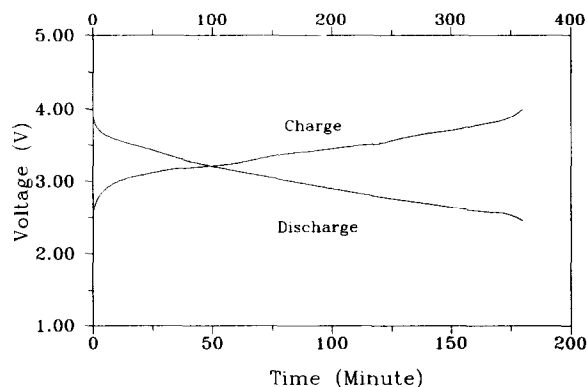


Fig. 1. Typical charge/discharge curves of a Li/PEO- $\text{LiClO}_4$ /PAN cell at room temperature:  $I_c = 0.1 \text{ mA/cm}^2$ , and  $I_d = 0.2 \text{ mA/cm}^2$ .

It can be seen that the coulomb passed in charge process is very close to that of during the following discharge process.

Figure 2 shows the discharge curves of solid-state Li battery cell employing positive of PAN at the constant current density of  $0.2 \text{ mA/cm}^2$  at different cycles at room temperature. It can be seen from Fig. 2 that the experimental capacity at the 240th cycle is about 95% of that at the 120th cycle and is about 90% of that at the 10th cycle. It indicated that the decline rate of the capacity of this Li/PAN solid-state cell is significantly low. It was found that during charge/discharge processes the capacity of the cell can be completely recovered by charging, even the battery was overdischarged below 1.0 V. It is indicated that this Li/PAN battery can tolerate the misuse of an overdischarge. The characteristics exhibited above in the Li/PAN solid-state cell are significantly better than those in vanadium oxide/Li solid-state cell.

The discharge capacity of the Li/PEO-LiClO<sub>4</sub>/PAN cell varied with cycle number as shown in Fig. 3. It was found from Fig. 3 that the discharge capacity of solid-state Li cell using composite positive of PAN maintained a stable value of 25 mA h before the 240th cycle.

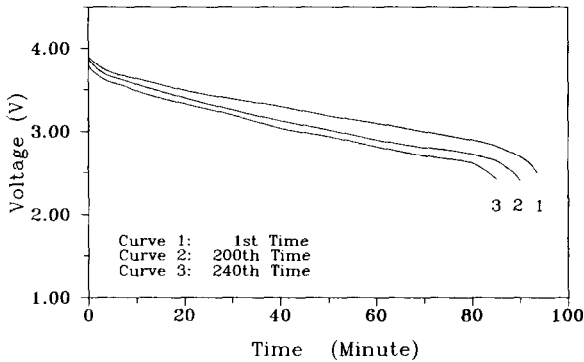


Fig. 2. Discharge curves of a Li/PEO-LiClO<sub>4</sub>/PAN cell at the rate of  $0.2 \text{ mA/cm}^2$  at room temperature at the different cycle number; electrode area:  $40 \text{ cm}^2$ , curve 1: 10th cycle; curve 2: 120th cycle, and curve 3: 240th cycle.

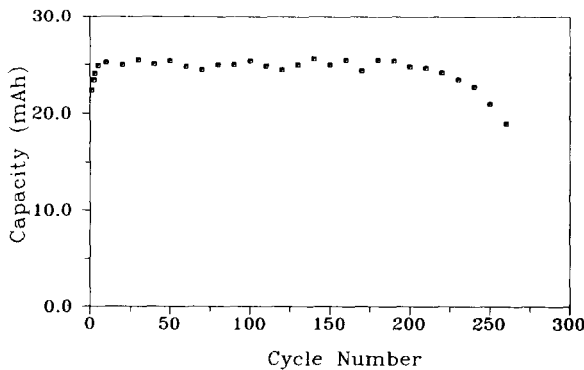
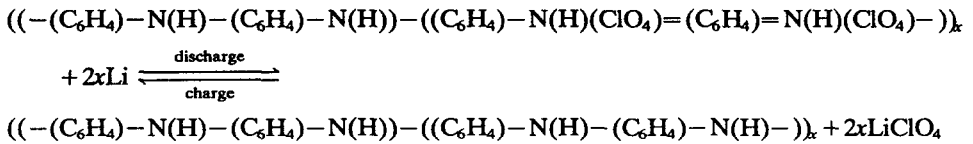


Fig. 3. Discharge capacity vs. cycle number of a Li/PEO-LiClO<sub>4</sub>/PAN cell at  $0.2 \text{ mA/cm}^2$  between 4.0 and 2.5 V at room temperature; electrode area:  $40 \text{ cm}^2$ .

It can be also found from both Figs. 2 and 3 that the solid-state Li battery employing composite positive of PAN exhibited an excellent recycleability and stability during 250 cycles at deep charge and discharge between 2.5 to 4.0 V at 0.2 mA/cm<sup>2</sup> at room temperature.

The experimental capacity at above discharge condition is 25 mA h for plate cell and is 2.4 mA h for button cell, respectively. The capacity density of the PAN positive in solid-state battery at the discharge rate of 0.2 mA/cm<sup>2</sup> is 48.3 mA h/g based only on the weight of PAN used in the cell. The utilization of PAN active material in the solid-state Li cell is about 30% of the theoretical capacity density of 148 mA h/g, if the charge and discharge reactions are given as follow:



The utilization of positive active material is 30% in solid-state electrolyte which is much lower than that of over 60% in nonaqueous electrolyte at the same rate of discharge at room temperature. It is essential for most batteries to be stored for a long period without high self-discharge and significant loss of performance. Therefore, it is necessary to test the rate of self-discharge during the stand time. The button cell of PAN was charged to 4.0 V and was then permitted to stand for 180 days at room temperature.

The  $V_{oc}$  of a completely-charged button cell as a function of stand time is given in Fig. 4. After being charged to 4.0, the  $V_{oc}$  fell to 3.6 V after 1 h, and then slowly decreased from 3.6 to 3.4 V within 30 days and was kept at a value of 3.4 V for 140 days from then on. Thus, for the conducting polymer battery, the reserve capacity of the cell may be estimated from the value of the  $V_{oc}$ . From the preliminary experimental results is believed that the rate of self-discharge in solid-state electrolyte is significantly lower than that in nonaqueous electrolyte [7].

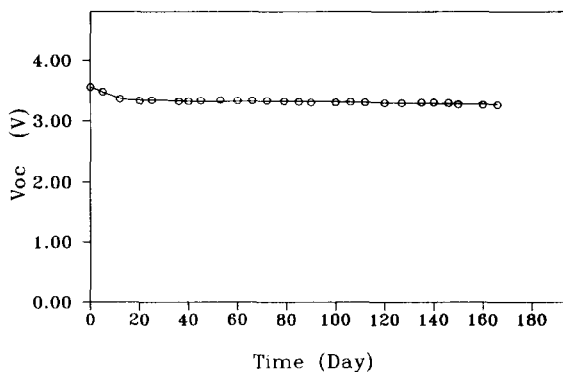


Fig. 4. Open-circuit voltage ( $V_{oc}$ ) of a 100% charged Li/PEO-LiClO<sub>4</sub>/PAN cell as a function of stand time.

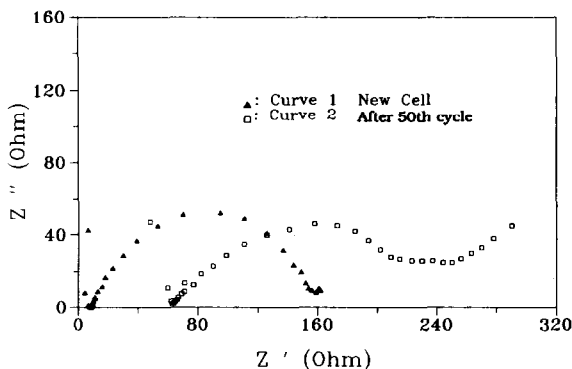


Fig. 5. Complex impedance plots of a Li/PEO-LiClO<sub>4</sub>/PAN button cell; (▲) new cell, and (□) after 50 cycles.

The complex impedance plots of Li/PEO-LiClO<sub>4</sub>/PAN button cell at different stage (curve 1: new cell, curve 2: after the 50th cycle) are given in Fig. 5. The impedance spectra of the cell were measured in the frequency range from 0.1 Hz to 999.9 kHz under open-circuit condition. It can be seen that it shows only a change at the starting point of the plot without any change on the diameter of the semicircle. We can consider that the resistance of the interface between the PAN electrode and solid-state polymer electrolyte does not change apparently during a long period of cycle by comparing with the impedance spectra in Fig. 5 because the impedance semicircle 1 is similar to that of curve 2 and the resistance of anodic interface may be negligible. This composite positive shows a good property on interfacial contact and a good compatibility with solid-state electrolyte for a long time.

## References

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