

## Zn|ZnI<sub>2</sub>|Iodine Secondary Battery Using Iodine-Nylon-6 Adduct as Positive Electrode, and Its Charge–Discharge Performance

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Use of  $\pi$ -conjugated polymers such as poly(acetylene) [1], poly(*p*-phenylene) [2], and poly(thienylene) [3] as materials for positive electrodes of rechargeable batteries has been recently reported. However, the batteries so far have not found practical use; high air-sensitivity of poor processibility of the  $\pi$ -conjugated polymer, use of toxic electrolyte (e.g., LiAsF<sub>6</sub>), or poor charge–discharge performance of the battery has prevented practical use.

Previously we reported that I<sub>2</sub> adducts of nylon-6, which is one of the most widely used polymers and can be handled easily, serve as good positive electrodes of galvanic cells such as Zn|ZnI<sub>2</sub>|iodine [3] and Li|LiI|iodine [4]. We now report that the Zn|ZnI<sub>2</sub>|iodine primary cell is applicable to the rechargeable battery if one uses an appropriate ion exchanger as a separator of battery and carbon powder as conductor of electric current generated in the electrochemical cell reaction. The present battery shows good charge–discharge performance and may find considerable practical use.

Figure 1 shows a sketch of the battery. When a positive ion exchanger film, Selemion CMV from Asahi Glass Co. Ltd., was used as the separator (E in Fig. 1) and a carbon black, Ketjen Black EC from AKZO Chemle CO. Ltd., was used to make the nylon-6-carbon powder composite electrode (G in Fig. 1), the secondary cell showed good charge–discharge performance.

Figure 2 shows typical charge–discharge profile of the battery, which is charged at a constant electric current (2 mA/cm<sup>2</sup>) until the charging voltage reaches 1.50 V and then discharged at a constant electric current (2 mA/cm<sup>2</sup>) until the discharging voltage (closed circuit voltage) drops to 1.00 V. The charge and discharge were controlled with a potentiostat/galvanostat HA-301 from Hokuto Denko Co. Ltd. At the stage of charging, the following electrochemical reactions take place in the battery.

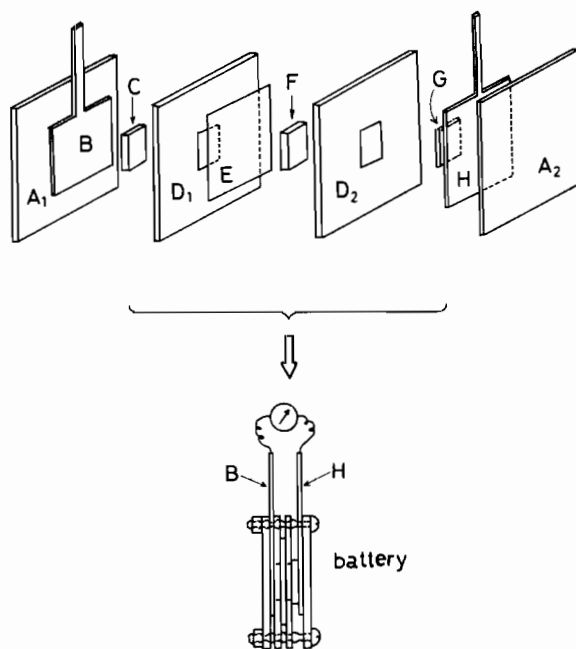


Fig. 1. Sketch of the secondary battery. A: board made of glass fiber-epoxy resin composite, B: negative electrode (Zn plate), C: glass fiber filter impregnated with an aqueous solution (100  $\mu$ l) of ZnI<sub>2</sub> (1 N), D: board made of Teflon, E: separator, F: glass fiber filter impregnated with an aqueous solution (100  $\mu$ l) of ZnI<sub>2</sub> (1 N), G: nylon-6(2 mg)-carbon powder (0.4 mg) composite overlaid on carbon fiber plate (Kureha carbon fiber KCF-100), H: Pt plate. C and F fit the holes (10 mm  $\times$  10 mm) of D<sub>1</sub> and D<sub>2</sub>.

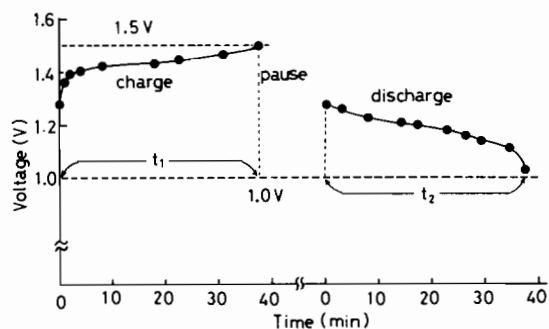


Fig. 2. Charge–discharge curve at constant electric current (2 mA). Charging and discharging were continued until the voltage of the cell reaches 1.50 V and 1.00 V, respectively. The first cycle is shown. Measured at room temperature (about 15 °C).

Positive electrode:



or (after charging to some extent)



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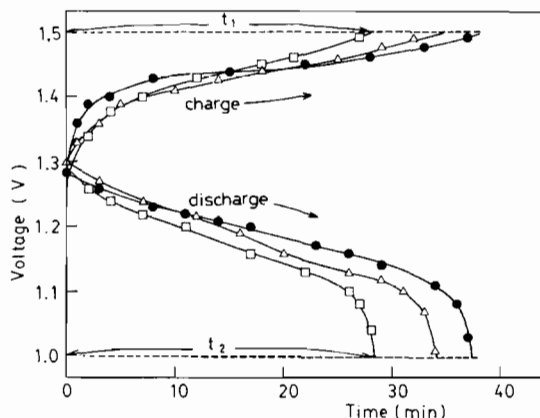


Fig. 3. Charge-discharge curves at the 1st (●), 160th (△), and 260th (□) cycles. At room temperature (about 15 °C).

Negative electrode:



$\text{I}_2$  thus formed in the positive electrode solution (F in Fig. 1) is absorbed by nylon-6 in G in Fig. 1 to form  $\text{I}_2$ -nylon-6 adduct [5]. During this charging of the battery,  $\text{Zn}^{2+}$  in the positive electrode solution moves to the negative electrode side through the positive ion exchanger (E in Fig. 1) and loses its positive charge at the negative electrode (eqn. 2), whereas  $\text{I}_3^{-}$  in the positive electrode solution in F remains in the solution and consequently self-discharge of battery by the chemical reaction between Zn (negative electrode) and  $\text{I}_3^{-}$  is avoided. In the first charging of the battery (Fig. 2), about 47% of  $\text{ZnI}_2$  in the positive electrode solution in F participates in the electrochemical reactions (eqns. 1 and 2), as estimated from the charging electric current, charging time, and the amount of  $\text{ZnI}_2$  in F.

In the stage of discharge,  $\text{I}_2$  absorbed by nylon-6 is consumed in the cell reaction, and the reverse reactions to those expressed by eqns. 1 and 2 occur. The present secondary battery shows an excellent charge-discharge performance with the following features.

1) Charging time ( $t_1$  in Fig. 2) virtually coincides with discharging time ( $t_2$ ), indicating 100% current efficiency (depth of discharge = 100%) of the

\*Iodine-nylon-6 adduct without mixing carbon powder has only low electric conductivity of  $\sigma = 4 \times 10^{-9} \text{ S cm}^{-1}$ , but the galvanic cell using this iodine-nylon-6 adduct as the positive electrode shows much smaller internal resistance than that calculated from its electric conductivity in the dry state and shape of the positive electrode [3] indicating that the iodine-nylon-6 adduct has high electric conductivity in an aqueous medium. The present iodine-nylon-6-carbon powder composite has much higher electric conductivity than the iodine-nylon-6 adduct in the dry state and seems to have only minor electric resistance in the aqueous medium.

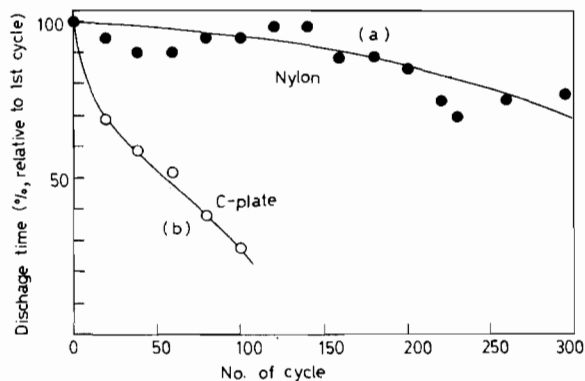


Fig. 4. Discharge time ( $t_2$  in Fig. 3) vs. number of cycles. At room temperature (about 15 °C).

present battery. The ratio of the energy recovered to the energy charged is calculated as 83% from the average charging and discharging voltage.

2) The discharging voltage is considerably flat compared with the other recently developed batteries based on other polymers (e.g., poly(acetylene) [1], poly(*p*-phenylene [2], and poly(thienylene) [3]).

3) The charge-discharge cycle can be repeated more than 300 times. Although the efficiency of the battery estimated from the charging and discharging times is lowered as the number of the charge-discharge cycles increases (Fig. 3), the extent of the lowering of the efficiency is not large. Reason for the shortening of the charge-discharge time with repeated charge-discharge cycles has not been clarified, but loss of the cell solution by evaporation of water and partial degradation or corrosion of the positive and negative electrodes account for the cause.

4) The closed circuit voltage of the battery is lower by about 0.10 V than the open circuit voltage during the course of the discharge. This is attributable to internal resistance of the battery. Preliminary studies indicate that the iodine-nylon-6 adduct has only low electric resistance in the aqueous medium as previously reported [3], and most of the internal resistance is attributable to membrane resistance of the positive ion exchanger\*. By forming a battery having larger electrode area, the internal resistance of battery can be lowered.

Since nylon-6 is one of the most widely used commercial polymers, and the preparation and handling of the iodine-nylon-6 electrode is much easier than those with a recently developed polymer electrode using air-sensitive poly(acetylene) or the poisonous  $\text{AsF}_6$ -poly(*p*-phenylene) adduct, the present rechargeable battery seems to be potentially usable on commercial basis.

When the carbon fiber plate in G in Fig. 1 itself is used without coating with the nylon-6-carbon powder composite, the Zn|positive ion exchanger

TABLE I. Zn|NH<sub>4</sub>Cl (1 N)|Iodine Primary Galvanic Cells Using Iodine-Polymer Adducts as Active Materials for Positive Electrodes.<sup>a</sup>

Polymer <sup>b</sup>	V <sub>0</sub> (V) <sup>c</sup>	I <sub>0</sub> (mA) <sup>d</sup>
poly(methyl methacrylate)	1.43	430
poly(acrylonitrile)	1.68	440
poly(vinyl acetate)	1.47	230
poly(vinyl chloride)	1.55	94
poly(styrene)	1.43	43

<sup>a</sup>The positive electrode was prepared by mixing iodine (40 mg), polymer (40 mg), and carbon powder (Ketjen Black, 10 mg) in a solution, spreading the mixture uniformly on a carbon fiber plate (20 mm × 20 mm), and evaporation of the solvent. Negative electrode: 20 mm × 20 mm zinc plate. Measured at room temperature (about 15 °C).

<sup>b</sup>Polymer with which the iodine-polymer adduct is formed.

<sup>c</sup>Initial short circuit voltage of the cell. <sup>d</sup>Initial short circuit current of the cell. When nylon-6 is employed, I<sub>0</sub> is about 500–700 mA.

|ZnI<sub>2</sub>|C fiber plate|Pt battery still works to some extent. However, in this case, efficiency of the battery is steeply lowered with the increase in the number of the charge-discharge cycles presumably due to degradation of the carbon fiber plate (Fig. 4).

Other nylons (e.g., nylon-6,6) and other polymers having affinity toward I<sub>2</sub> also seem to be usable as the coating polymer on the carbon fiber plate, since they serve as positive electrodes of primary galvanic cells [3a]. Among the other polymers tested, poly(methyl methacrylate), poly(acrylonitrile), and poly(vinyl acetate) are the candidates for making good positive electrodes, since I<sub>2</sub> adducts of these polymers serve as good positive electrodes of the primary galvanic cells, as shown in Table I.

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