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SECONDARY CELLS USING POLY(2,5-THIENYLENE)S AND POLY(2,5-PYRROLYLENE)S AS MATERIALS FOR POSITIVE ELECTRODES. Zn|ZnI_2|I_2 SECONDARY CELL

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Poly(2,5-thienylene), poly(2,5-pyrrolylene), and their derivatives are useful as materials for positive electrodes of Zn|ZnI_2|cation-exchange membrane|ZnI_2|I_2 secondary cells, which show about 100% current efficiency and 85% energy efficiency and are rechargeable more than 200 times.

Utilization of electric-conducting π-conjugated polymers as materials for electrodes of primary and secondary cells is the subject of recent interest.1-4) As for the preparative methods of poly(2,5-thienylene), poly(2,5-pyrrolylene), and their derivatives, the following two methods have been developed.

Method A: Ni-catalyzed dehalogenation polycondensation of 2,5-dihalothiophene, its derivatives, and N-substituted 2,5-dihalopyrrole.5)

Method B: electrochemical oxidation of thiophene, pyrrole, and their derivatives.6)

We previously reported that poly(2,5-thienylene) prepared by Method A served as materials for primary and secondary cells using metal iodides as electrolytes.1) We now report charge-discharge profiles of Zn|ZnI_2|cation-exchange membrane|ZnI_2|I_2 (hereafter denoted as Zn|ZnI_2|I_2) secondary cells using the polymers prepared by Methods A and B as materials for positive electrodes. The polymers absorb $I_2$5) to form positively charged polymer and I_n^- (I_5^- for poly(2,5-thienylene)7)) and iodine-polymer adducts thus formed are electrically conductive. Therefore, the iodine-polymer adducts serve as good active materials of positive electrodes. The positive electrodes were prepared as described below.

Electrode using polymer prepared by Method A: A $CHCl_3$-soluble fraction5) of the polymer was dissolved in $CHCl_3$. To the $CHCl_3$ solution, carbon powder (Kejen Black EC, 20 wt-% per polymer) was added with stirring. A part of the suspension thus obtained was taken out with a syringe and spread uniformly on a carbon fiber plate (Kureha carbon fiber KGF 100, 10 mm x 10 mm), and $CHCl_3$ was removed by evaporation. The amount of polymer overlaid on the carbon fiber plate was 10 mg.

Electrode using polymer prepared by Method B: An anhydrous $C_6H_5NO_2$ solution containing 0.2 mol/dm^3 of monomer (thiophene, pyrrole, or N-methylpyrrole) and 0.1 mol/dm^3 of $[Bu_4N][BF_4]$ was electrolyzed for 2 h at 5 °C at constant electric current (1 mA/cm^2) by using the carbon fiber plate (10 mm x 10 mm) and platinum plate as anode and cathode, respectively. The electrolysis gave a film of polymer (3-5 mg) on the surface of the carbon fiber plate. The polymer-coated carbon fiber plate was used as the positive electrode of the secondary cell.

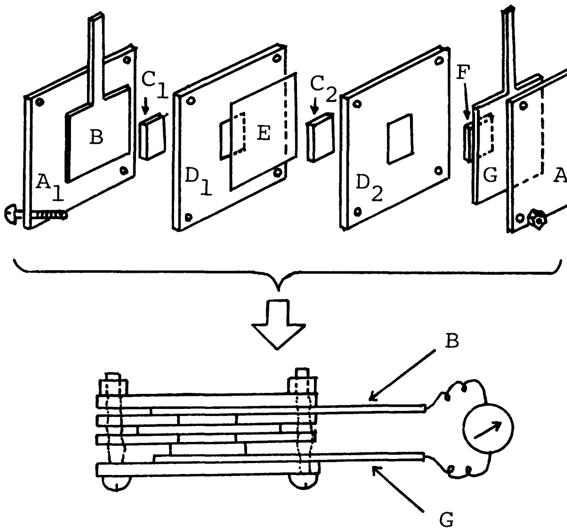
Figure 1 shows a sketch of the Zn|ZnI_2|I_2 secondary cell. An aqueous solution of ZnI_2 (0.5 mol/dm^3) is used as catholyte (C_1 in Fig. 1) and anolyte (C_2), and the catholyte and anolyte are separated by a cation-exchange membrane (Selemion CMV, thickness = 0.13 mm, E in Fig. 1). When the cell is charged, I^- ion in the anolyte loses its charge at the polymer-coated positive electrode (F) and I_2 thus formed is trapped by the polymer. A part of I_2 not trapped by the polymer exists as pure I_2 or I_3^- (formed by the reaction of I^- and I_2) in the anode compartment (C_2).

$$\text{Charge (positive electrode): } I^- \longrightarrow (1/2)I_2 + e^- \qquad (1)$$

$$I_2 + \text{polymer} \rightleftharpoons \text{iodine-polymer adduct} \qquad (2) \qquad I_2 + I^- \rightleftharpoons I_3^- \qquad (3)$$

The cation-exchange membrane prevents moving of I_3^- to the negative electrode side, and thus the self-discharge of the cell by the reaction of Zn and I_3^- ($Zn + I_3^- \longrightarrow ZnI_2 + I^-$) is prevented. The negative electrode reaction is expressed as follows:

$$\text{Charge (negative electrode): } Zn^{2+} + 2\,e^- \longrightarrow Zn \qquad (4)$$



A_1 and A_2: board, B: negative electrode (Zn), C_1 and C_2: glass fiber (Toyo Roshi type GA 100, 10 mm x 10 mm) impregnated with an aqueous solution (0.1 cm^3) of ZnI_2 (0.5 mol/dm^3), D_1 and D_2: board with hole (10 mm x 10 mm), E: cation-exchange membrane, F: polymer-coated carbon fiber plate (10 mm x 10 mm), G: Pt-plate.

Fig. 1. Sketch of secondary cell.

At the stage of discharge, reactions reverse to those expressed by Eqs. 1 and 4 take place. Figure 2 shows charge and discharge curves of the Zn|ZnI_2|I_2 secondary cell using poly(2,5-thienylene) prepared by Method A. Charge and discharge are performed at constant electric current (2 mA/cm^2). As seen in Fig. 2, the charging starts with initial voltage of 1.36 V, and after about 48 min the charging voltage reaches 1.50 V, where the charging is stopped. After 1 min of pause time, the cell is discharged with 1.32 V of initial voltage. After 48 min

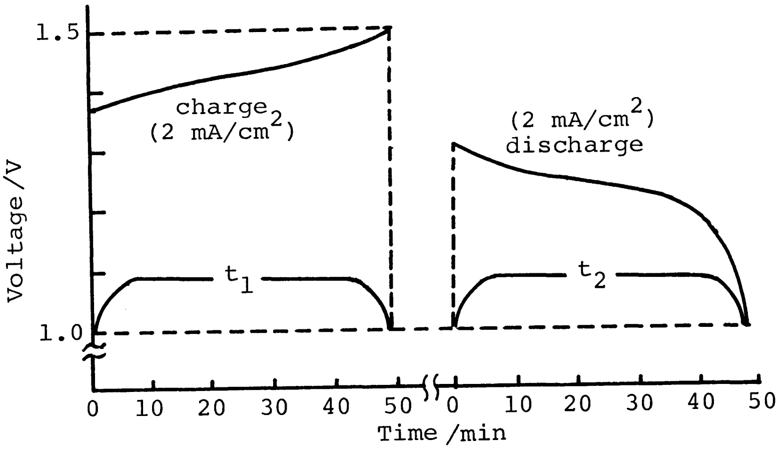


Fig. 2. Charge and discharge curves (1st cycle) of the Zn|ZnI_2|I_2 secondary cell using poly(2,5-thienylene) (10 mg) prepared by Method A.

of discharging time, the voltage drops to 1.0 V, where the discharging is stopped. Elongation of the pause time to 10 h does not affect the discharge curve. The agreement of the discharging time with the charging time indicates about 100% current efficiency of the present secondary cell. Energy efficiency is calculated as 85% from average charging and discharging voltages (1.43 and 1.22 V, respectively). The current and energy efficiencies as well as the current density (2 mA/cm^2) of the present secondary cell are much larger than those of reported secondary cells using other π-conjugated polymers (e.g., poly(acetylene) and poly(p-phenylene)) and/or other electrolyte (e.g., $LiClO_4$ and $LiAsF_6$).[2-4]

As the number of the charge-discharge cycle increases, the charging and discharging times decrease presumably due to degradation of the polymer (Fig. 3).

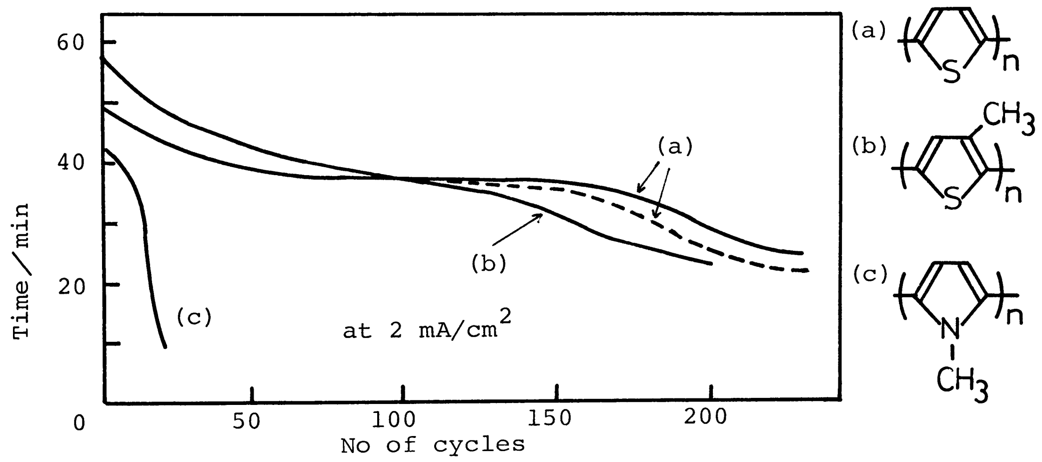


Fig. 3. Change of charging (——) and discharging (------) times of the Zn|ZnI_2|I_2 secondary cells using polymers (10 mg) prepared by Method A. When the discharging time coincides with the charging time, only the charging time is shown. The cell depicted in Fig. 1 was used at room temperature.

Use of polymers prepared by Method B as the material for the positive electrode gives charge and discharge curves similar to those shown in Fig. 2. Figure 4 shows change of the charging and discharging times of the secondary cell using the polymer prepared by Method B.

As described above, the present results indicate that poly(2,5-thienylene), poly(2,5-pyrrolylene) and their derivatives prepared by the two methods serve as good materials for the positive electrodes of the secondary cells. Among the polymers, poly(2,5-thienylene), especially the one prepared by Method B, shows the best charge-discharge profile. The better charge-discharge profile of the secondary cell using poly(2,5-thienylene) prepared by Method B than that of the cell using poly(2,5-thienylene) prepared by Method A may be attributed to higher electrical conductivity of poly(2,5-thienylene) prepared by Method B than that of poly(2,5-thienylene) prepared by Method A.[5,6]

Since the polymers are insensitive to air and thermally stable and the electrolyte is neither air-sensitive nor toxic, construction and handling of the present secondary cell are easy compared with the other secondary cells using other π-conjugated polymers (e.g, poly(acetylene) is air-sensitive) and/or electrolyte (e.g., $LiAsF_6$ is toxic). Due to the advantages of the present cell, it may find practical use.

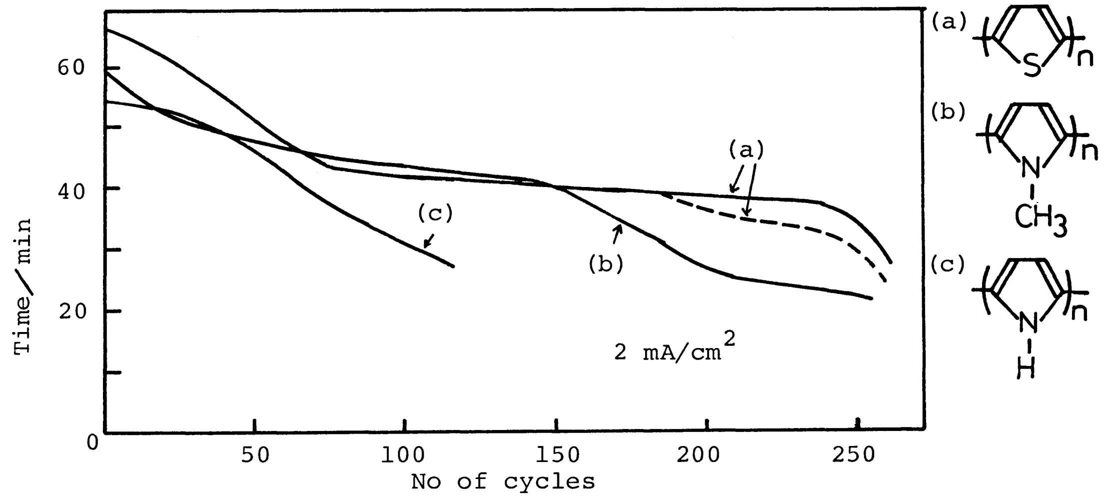


Fig. 4. As in Fig. 3 but for the use of polymers prepared by Method B.

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