Li|LiI|Iodine Primary Galvanic Cell and Zn|ZnI_2|Iodine Secondary Galvanic Cell using Poly(2,5-thienylene), Poly(2,5-pyrrolylene), and their Analogues as Positive Electrodes

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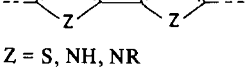
Abstract

Iodine adducts of chemically prepared poly(2,5-thienylene) show good electrical conductivity over a range of iodine content of 10–90 wt.%. The adducts serve as good active materials of positive electrodes of Li|LiI|iodine galvanic cells. Discharge curves of the galvanic cell at 500 kΩ load show stable voltage (2.8–2.3 V) until about 85% of added iodine is consumed in the cell reaction. Poly(2,5-thienylene), poly(2,5-pyrrolylene), and their derivatives prepared both chemically and electrochemically are useful as materials for positive electrodes of Zn|ZnI_2|cation-exchange membrane|ZnI_2|iodine secondary cells. The cells using the polymers show about 100% current efficiency and 85% energy efficiency, and are rechargeable more than 200 times.

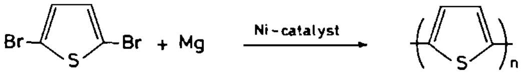
Utilization of electric conducting π-conjugated polymers as electrodes of primary and secondary cells is a subject of recent interest [1–7]. Among the electric conducting polymers, those constituted of recurring 5-membered heterocycles have high stabilities against air and heat. They show good electric conductivity when doped with electron acceptor or donor



Z = S, NH, NR

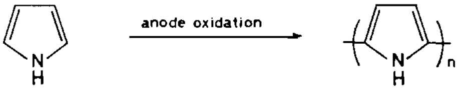
and are suitable as electrodes of the cells. Two methods have been developed for the preparation of the polymers.

Method 1: Transition metal catalyzed dehalogenation polycondensation of dihalo-compounds with magnesium or zinc [8–13]. e.g.,



(1)

Method 2: Anodic oxidation of thiophene, pyrrole, or their derivatives [14–21]. e.g.,



(2)

We now report utilization of the polymer as positive electrodes of Li|LiI|iodine primary and Zn|ZnI_2|cation-exchange membrane|ZnI_2|iodine (abbreviated as Zn|ZnI_2|iodine) secondary cells.

Experimental

Materials

Solvents were dried, distilled under N_2, and stored under N_2. Chemical preparation (Method 1) of poly(2,5-thienylene) [8], poly(3-methyl-2,5-thienylene) [8], and poly(*N*-methyl-2,5-pyrrolylene) [9] were carried out as reported in the literature. $CHCl_3$-insoluble fractions [8] of these polymers were used to prepare iodine-polymer adducts for the Li|LiI|iodine cell. On the other hand, $CHCl_3$-soluble fractions [8] were used to prepare electrodes for the Zn|ZnI_2|iodine cell. Electrochemical preparation (Method 2) of the polymers was carried out as follows.

Poly(2,5-thienylene)

A carbon fiber plate (Kureha KGF-100) was dipped in a dry nitrobenzene solution containing $[Bu_4N][BF_4]$ (0.10 M) and thiophene (0.25 M). The dimension of the carbon fiber plate dipped in the solution was 1.0 cm × 1.0 cm. The solution was electrolyzed by using Pt and the carbon fiber plates as the cathode and anode, respectively, for 2 h at 2 mA and 5 °C. A film of poly(2,5-thienylene) was formed

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on the carbon fiber plate. The electrochemical polymerization was carried out under N_2 by using a usual H-type cell.

Poly(2,5-pyrrolylene) and Poly(N-methyl-2,5-pyrrolylene)

An acetonitrile solution containing $[Bu_4N][BF_4]$ (0.10 M) and pyrrole (9.25 M) was electrolyzed by using Pt (cathode) and carbon fiber plates (anode, Kureha KGF-100, 1.0 cm X 1.0 cm) for 2 h at 2 mA and 5 °C to yield a film of poly(2,5-pyrrolylene) on the carbon fiber plate. Poly(*N*-methyl-2,5-pyrrolylene) was prepared analogously.

A roll of Li film (thickness = 0.5 mm), carbon powder (Ketjen black EC) and cation-exchange membrane (Selemion CMV) were donated from Mitsui Mining and Smelting Co. Ltd., Lion Co. Ltd., and Asahi Glass Co. Ltd., respectively.

Charge and Discharge and Preparation of the Li–Iodine Cell

Discharge of the Li|LiI|iodine primary cell and charge and discharge of the $Zn|ZnI_2|$iodine secondary cell were controlled by a computer. Electric current for the charge and discharge was controlled with a Hokuto Denko potentiostat/galvanostat HA-301. A cell case (see Fig. 2 later), kindly donated by Japan Storage Batteries Co. Ltd., was placed in a glove box filled with pure argon. A lithium plate, gasket, the iodine–polymer adduct, and a cap to which a stainless steel net (collector) had been welded by spot-welding were placed in the cell case in this order, and the cell was packed by pressing it at about 100 kg/cm^2.

Preparation of Iodine–Polymer Adducts and Measurement of Electric Conductivity

Iodine adducts of the chemically prepared polymers (powder) were obtained by exposing the polymers to vapor of iodine at room temperature by using a vacuum line [8c] or by heating mixtures of the polymers and iodine for 15 h at 150 °C in sealed glass tubes; the former method was applied to preparation of the iodine–polymer adducts containing less than about 40 wt.% of iodine whereas the latter method was used in the preparation of the adducts containing more than about 50 wt.% of iodine. Electric conductivity was measured by a Takeda Riken TR-8651 electrometer with a 2-point probe method by pressing the iodine–polymer adduct at 100 kg/cm^2.

Preparation of Electrode for $Zn|ZnI_2|$Iodine Secondary Cell

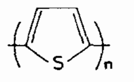
A $CHCl_3$ soluble fraction [8] of the chemically prepared polymer was dissolved in $CHCl_3$. To the $CHCl_3$ solution, carbon powder (Ketjen Black EC, 20 wt.% per polymer) was added with stirring. A part of the suspension thus obtained was taken out with a syringe and spread uniformly on a carbon fiber 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.

The electrochemically prepared polymer on the carbon fiber plate was used as the positive electrode of the secondary cell.

Results and Discussion

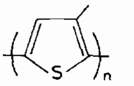
Li|LiI|Iodine Primary Cell

Of the polymers prepared by the two methods, the chemically prepared one (e.g., eqn. (1)) is more suitable for the Li|LiI|iodine galvanic cell, since the polymer can be easily prepared on a large scale and its iodine adduct is a powder suitable for the active materials of the galvanic cell. On the other hand, the electrochemically prepared polymer (e.g., eqn. (2)) is obtained as a thin film containing dopant (e.g., BF_4 and ClO_4) and seems to require additional processes to prepare its powdery adduct with iodine, which is suited for the active material of the galvanic cell. On this basis, we used iodine adducts of the chemically prepared polymers for the Li–iodine primary galvanic cell.



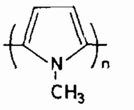
1a

chemically prepared poly(2,5-thienylene)



2a

chemically prepared poly(3-methyl-2,5-thienylene)



3a

chemically prepared poly(*N*-methyl-2,5-pyrrolylene)

Figure 1 shows the electrical conductivity (σ) of iodine adducts of powdery at various wt.% of iodine in the adduct. Electrical conductivity of the iodine adducts of poly(2-vinylpyridine) [22], which are now used as active materials in commercial Li|LiI|iodine galvanic cells, is also shown in Fig. 1. Other iodine adducts of non-conjugated polymers (e.g., nylon-6 [23] and poly(3-vinylpyrene) [24]) reportedly have similar electrical conductivity to that of the iodine-poly(2-vinylpyridine) adducts. It is seen from Fig. 1 that the iodine adducts of the π-conjugated polymers **1a**–**3a** show higher electrical conductivity than that of the iodine-poly(2-vinylpyridine) adducts, especially at

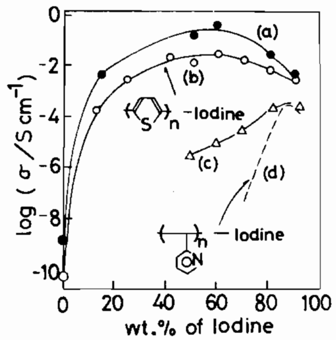
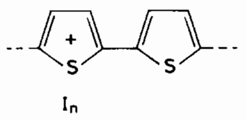


Fig. 1. Electrical conductivity of iodine adducts of chemically prepared **1a** (curve b), **2a** (a), **3a** (c) and poly(2-vinylpyridine) (d) [22] at 25 °C.

low wt.% of iodine. The iodine adducts of the π-conjugated polymers are considered to contain cationic centers in the polymer chain [25], e.g.,



Adduct A (**2a** + iodine)

and the move of the cationic center along the polymer chain is regarded to be responsible for the electrical conduction in the iodine-polymer adduct [8c, 25]. Mössbauer spectroscopy indicated that iodine in Adduct A exists mainly as I_5^- [25].

In this sense, the mechanism of electrical conduction in the iodine adduct of the π-conjugated polymer is considered to be different from that in the iodine adduct of conventional non-conjugated polymers. The high electrical conductivity of the iodine adducts of the π-conjugated polymers suggests that the adducts serve as better active materials for the lithium–iodine galvanic cells than the iodine adducts of the non-conjugated polymers. The iodine adducts of polymers **1a**–**3a** have high stability in air and their electrical conductivity virtually did not vary after having been stored 3 years under air. In contrast to the high chemical stability of the iodine adduct of polymers **1a**–**3a**, iodine adducts of poly(acetylene) [26] which show very high electrical conductivity are unstable and seem not to be suited for the active material for the lithium–iodine galvanic cell.

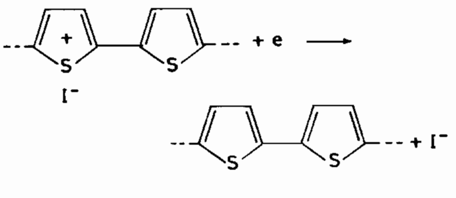
Figure 2 shows the sketch of a test cell. A layer of the solid electrolyte, LiI, was formed between the positive and negative electrodes by a reaction of Li and iodine.

Figure 3 shows discharge curves of the Li|LiI|-iodine–**1a** adduct (Adduct A) galvanic cell. As shown in Fig. 3, about 85% of iodine added is used in the cell reaction:

$\frac{1}{2}I_2 + e \rightleftharpoons I^-$ (positive electrode)

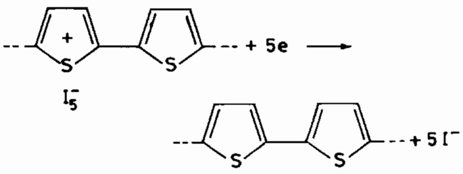
$Li \rightleftharpoons Li^+ + e$ (negative electrode)

Since Adduct A contains the ion-pair shown above, the discharge reaction at the positive electrode may be written like



(3a)

or



(3b)

The discharging behavior shown in Fig. 3 is much better than the discharging behavior of Li|LiI|-iodine–nylon-6 adduct galvanic cell [7g] in which 51% of iodine added is used for the cell reaction. The

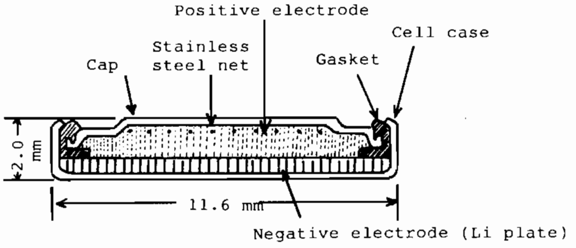


Fig. 2. Constitution of the Li|LiI|iodine galvanic cell.

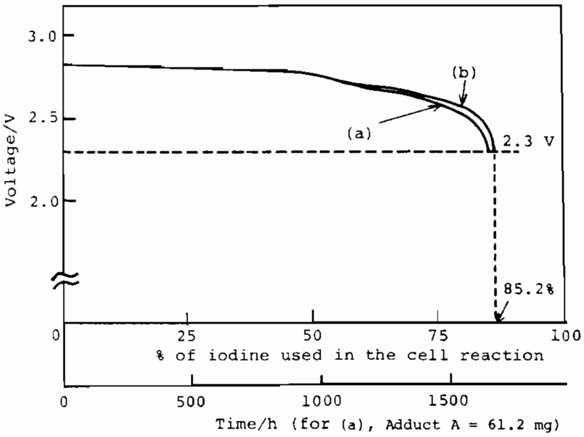


Fig. 3. Discharge curves of the Li|LiI|Adduct A galvanic cell at 25 °C. Wt.% of iodine in Adduct A: (a) 75 and (b) 50.

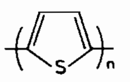
discharging behavior of the present cell is even better than the Li|LiI|iodine–poly(2-vinylpyridine) adduct galvanic cell. The good discharging behavior of the present cell seems to be attributable to the high electrical conductivity of Adduct A, especially at low wt.% of iodine. Actually initial internal resistance (1.2 kΩ, 1.5 kΩ, 1.3 kΩ, and 2.8 kΩ for the cells using Adducts A containing 50, 60, 70, and 90 wt.% of iodine, respectively) of the Li|LiI|Adduct A galvanic cell is smaller than that (*ca.* 4 kΩ) of the Li|LiI|iodine–nylon-6 adduct galvanic cell [7g].

The Li|LiI|Adduct A galvanic cell showed somewhat lower utility of iodine when it was discharged at 100 kΩ load. When Adduct A containing 50 wt.% of iodine was added, 65% of the iodine was used until the closed circuit voltage dropped to 2.0 V in the discharging at 100 kΩ. The utility, however, is better than that (49%) of the Li|LiI|iodine–nylon-6 adduct galvanic cell discharged at 100 kΩ load.

Use of iodine adducts of polymer **2a** as the active material gave a similar cell. However, the cell showed self-discharge at a relatively high rate, and the Li|LiI|iodine–polymer **2a** adduct cell showed about 40% of utility of iodine when discharged at 500 kΩ. Iodine adducts of polymer **3a** were also usable as the active material, however the discharging profile of the cell using this adduct was not good.

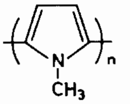
Zn|ZnI₂|Iodine Secondary Galvanic Cell

Polymers **1a**, **2a**, **3a**, and



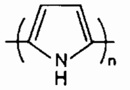
1b

electrochemically prepared poly(2,5-thienylene)



3b

electrochemically prepared poly(*N*-methyl-2,5-pyrrolylene)



4b

electrochemically prepared poly(2,5-pyrrolylene)

were used as positive electrodes of Zn|ZnI_2|cation-exchange membrane|ZnI_2|iodine secondary galvanic cells. As described above, the π-conjugated polymer electrodes absorb iodine to form electrically conducting materials.

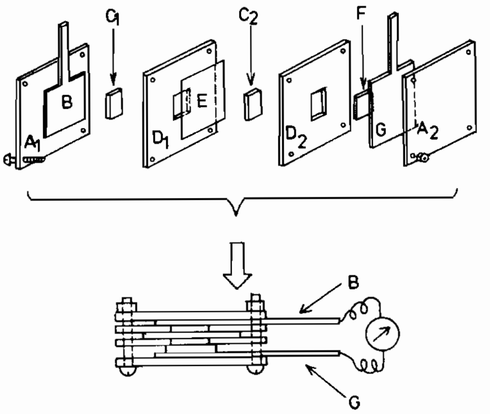


Fig. 4. Sketch of the Zn|ZnI_2|cation exchange membrane|ZnI_2|iodine secondary cell. A: board, B: zinc plate, C_1 and C_2: glass fiber (Toyo Roshi type GA100, 10 mm × 10 mm) impregnated with an aqueous solution (0.1 cm^3) of ZnI_2 (0.5 mol/dm^3), D: board with hole (10 mm × 10 mm), E: cation-exchange membrane, F: polymer-coated carbon fiber plate (10 mm × 10 mm), and G: Pt-plate.

Figure 4 shows the constitution of the test cell. An aqueous solution of ZnI_2 (0.5 mol/dm^3) was used as catholyte (C_1 in Fig. 4) and anolyte (C_2), and the catholyte and anolyte were separated by a cation-exchange membrane (Selemion CMV, thickness = 0.13 mm, E in Fig. 4). 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).

$$\text{Charge (positive electrode): } I^- \longrightarrow (1/2)I_2 + e^- \quad (4)$$

$$I_2 + \text{polymer} + \text{iodine–polymer adduct} \quad (5)$$

$$I_2 + I^- \rightleftharpoons I_3^- \quad (6)$$

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^- ($Zn + I_3^- \rightarrow ZnI_2 + I^-$) is prevented. The negative electrode reaction is expressed as follows

$$\text{Charge (negative electrode): } Zn^{2+} + 2e^- \longrightarrow Zn \quad (7)$$

At the stage of discharge, reactions reverse to those expressed by eqns. (4) and (7) take place. Figure 5 shows charge and discharge curves of the Zn|ZnI_2|iodine secondary cell using poly(2,5-thienylene) prepared by Method 1. Charge and discharge are performed at constant electric current (2 mA/cm^2). As seen in Fig. 5, the charging started with an initial voltage of 1.36 V, and after about 48 min the charging voltage reached 1.50 V, where the charging was stopped. After 1 min of pause time, the cell was discharged with 1.32 V of initial voltage. After 48 min of discharging time, the voltage dropped to 1.0 V, where the discharging was stopped. Elongation of the pause time to 10 h did 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

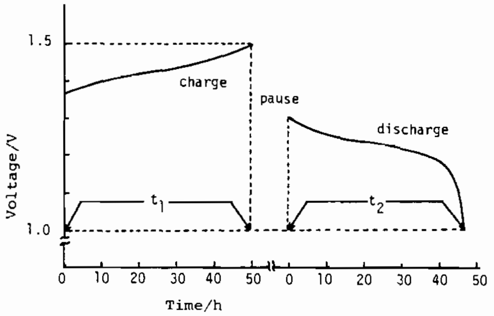


Fig. 5. Charge–discharge curve of the secondary cell using polymer **1a** (10 mg) at 25 °C at constant electric current (2 mA).

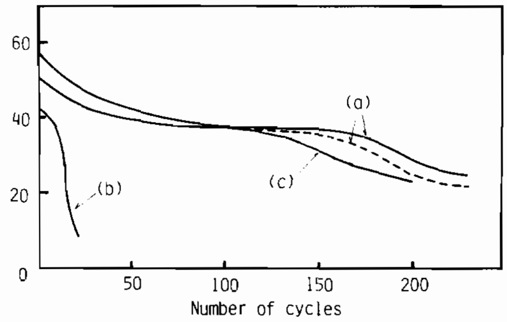


Fig. 6. Change of charging (——) and discharging (– – –) times of the Zn|ZnI$_2$|iodine secondary cells using (a) **1a**, (b) **2a**, or (c) **3a**. Amount of polymer = 10 mg. At 25 °C. When the discharging time coincides with the charging time, only the charging time is shown.

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 electrolytes (e.g., LiClO$_4$ and LiAsF$_6$).

As the number of the charge–discharge cycle increases, the charging and discharging times decreased presumably due to degradation of the polymer (Fig. 6).

Use of polymers prepared by Method 2 as the material for the positive electrode gave charge and discharge curves similar to those shown in Fig. 5. Figure 7 shows change of the charging and discharging times of the secondary cell using the polymer prepared by Method 2.

As described above, the present results indicated that poly(2,5-thienylene), poly(2,5-pyrrolylene) and their derivatives prepared by the two methods served as good materials for the positive electrodes of the secondary cells. Among the polymers, poly(2,5-thienylene)s (**1a**) and (**1b**) showed the best charge–discharge profile. The better charge–discharge profile of the secondary cell using poly(2,5-thienylene) prepared by Method 2 than that of the cell using poly(2,5-thienylene) prepared by Method 1 may be attributed to higher electrical conductivity of poly(2,5-thienylene) prepared by Method 2 than that of poly(2,5-thienylene) prepared by Method 1 [8, 15].

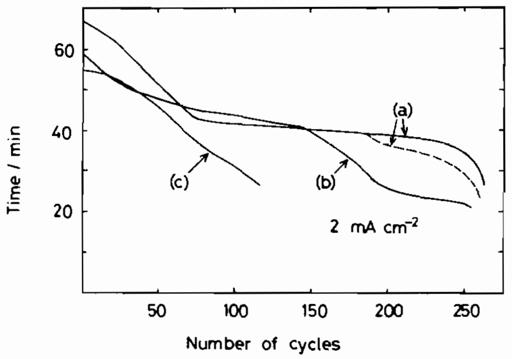


Fig. 7. Change of charging and discharging times of the Zn|ZnI$_2$|iodine secondary cells using (a) **1b**, (b) **3b** and (c) **4b**. As in Fig. 6.

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 –conjugated polymers. Due to the advantages of the present cell, it may find practical use.

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