

Li|LiI|IODINE GALVANIC CELLS USING IODINE-POLY(2,5-THIENYLENE)  
ADDUCTS AS ACTIVE MATERIALS OF POSITIVE ELECTRODES

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Iodine adducts of poly(2,5-thienylene) serve as good active materials of positive electrodes of Li|LiI|iodine galvanic cells. Discharge curves of the galvanic cells at 500 k $\Omega$  load show stable voltage (2.8-2.3 V) until about 85% of iodine added is consumed in the cell reaction.

Utilization of electric-conducting  $\pi$ -conjugated polymers as electrodes of primary and secondary galvanic cells is the subject of recent interest.<sup>1-6)</sup> As for the preparative methods of poly(2,5-thienylene) and its derivatives, the following two methods have been developed,

Method A: Ni-catalyzed dehalogenation polycondensation of 2,5-dihalothiophene and its derivatives.<sup>7)</sup>

Method B: electrochemical oxidation of thiophene and its derivatives.<sup>8-10)</sup>

The polymer prepared by Method A has been used as positive electrodes of primary galvanic cells using an aqueous system<sup>1)</sup> and the polymer prepared by Method B as a positive electrode of a secondary galvanic cell using a non-aqueous medium.<sup>6)</sup> We now report utilization of iodine adducts of the polymer prepared by Method A as electrodes of Li|LiI|iodine solid electrolyte galvanic cells. Of the polymers prepared by the two methods, the one prepared by Method A is more suitable for the Li|LiI|iodine galvanic cell, since the polymer can be easily prepared in a large scale and its iodine adduct is a powder suitable for the active material of the galvanic cell. On the other hand, the polymer prepared by Method B is obtained as a thin film containing dopant (e.g., BF<sub>4</sub> and ClO<sub>4</sub>) and seems to require additional processes to prepare its powdery adduct with iodine, which is suited for the active material of the galvanic cell.

The iodine-poly(2,5-thienylene) and -poly(3-methyl-2,5-thienylene) adducts (abbreviated as Adduct A and Adduct B, respectively) containing more than 50 wt-% of iodine were prepared by leaving mixtures of iodine and the polymers sealed in evacuated glass ampoules in a thermostated oil bath at 150 °C for 15 h. As shown in Table 1, the adducts have electric conductivity of  $2.1 \times 10^{-3} \text{ S cm}^{-1}$  through  $7.0 \times 10^{-2} \text{ S cm}^{-1}$ , and are suitable for active materials for the Li|LiI|iodine galvanic cells.

Figure 1 shows a sketch of the Li|LiI|iodine-polymer adduct galvanic cell which was prepared under an atmosphere of argon. A layer of the solid electrolyte, LiI, was formed between the positive and negative electrodes by a reaction of Li and iodine.<sup>11)</sup> Figure 2 shows discharge curves of the Li|LiI|Adduct A galvanic

cells at 500 k $\Omega$  load at 25 °C.

Table 1. Electric conductivity ( $\sigma$ ) of iodine-poly(2,5-thienylene) and -poly(3-methyl-2,5-thienylene) adducts.

	Electric conductivity/S cm <sup>-1</sup>					
	0	50	60	70	80	90
Adduct A	<10 <sup>-12</sup>	1.2 x 10 <sup>-2</sup>	3.5 x 10 <sup>-2</sup>	2.0 x 10 <sup>-2</sup>	7.7 x 10 <sup>-3</sup>	2.1 x 10 <sup>-3</sup>
Adduct B	<10 <sup>-12</sup>	5.3 x 10 <sup>-2</sup>	7.0 x 10 <sup>-2</sup>	4.2 x 10 <sup>-2</sup>	2.2 x 10 <sup>-2</sup>	5.3 x 10 <sup>-3</sup>

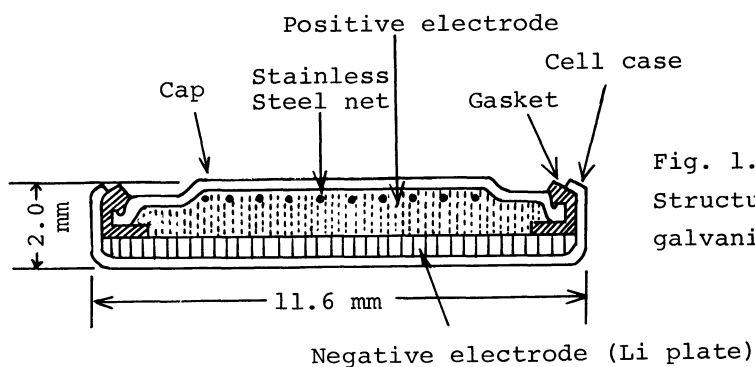


Fig. 1. Structure of the galvanic cell.

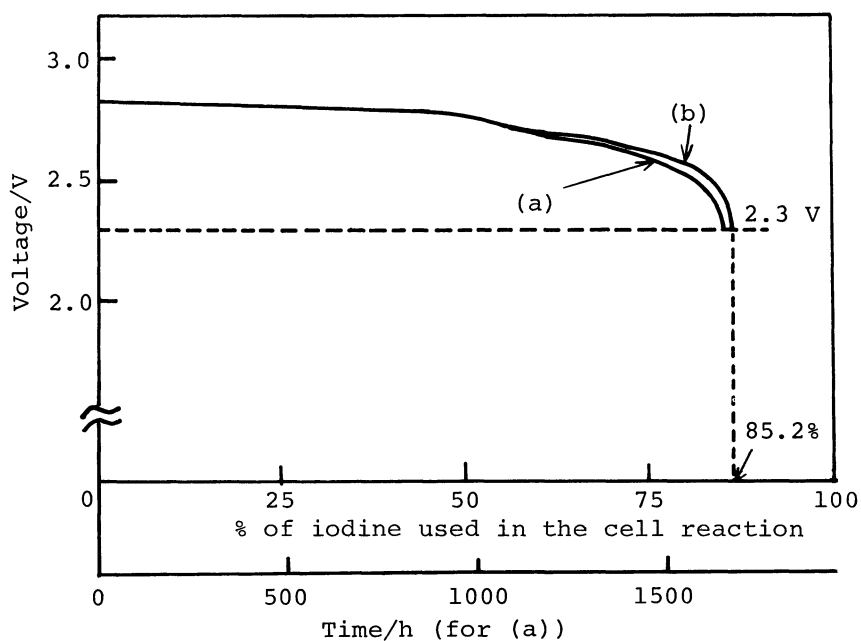
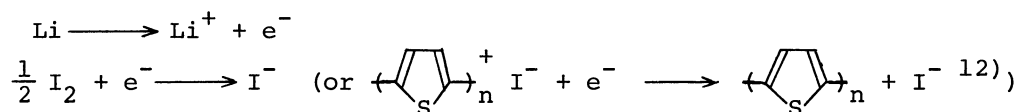


Fig. 2. Discharge curves of Li|LiI|Adduct A at 500 k $\Omega$  load. (a) Wt-% of iodine = 75% (weight of Adduct A = 61.2 mg); (b) Wt-% of iodine = 50%.

As shown in Fig. 2, about 85% of iodine is used in the cell reaction,



This discharge behavior is much better than the previously reported discharge behavior of a Li|LiI|iodine-nylon-6 adduct galvanic cell where 41% of iodine added is used for the cell reaction<sup>13)</sup> and even better than commercialized Li|LiI|iodine-poly(2-vinylpyridine) adduct galvanic cell.<sup>14)</sup> This excellent discharge behavior seems to be attributable to higher electric conductivity of Adduct A than the other iodine-polymer adducts, especially at low wt-% of iodine; e.g.,  $\sigma = 10^{-5} \text{ S cm}^{-1}$  for Adduct A containing 10 wt-% of iodine<sup>7)</sup> whereas  $\sigma < 10^{-12} \text{ S cm}^{-1}$  for the iodine-nylon-6<sup>13)</sup> and iodine-poly(2-vinylpyridine)<sup>14)</sup> adducts containing 10 wt-% of iodine. Actually initial internal resistance (1.2-2.8 k $\Omega$ ) of the Li|LiI|Adduct A galvanic cell is smaller than that (ca. 4 k $\Omega$ ) of the Li|LiI|iodine-nylon-6 adduct galvanic cell<sup>13)</sup> (Table 2).

Table 2. Initial internal resistance of the galvanic cell.<sup>a)</sup>

Positive electrode	Internal resistance/k $\Omega$			
	Iodine content/wt-%			
	50	60	70	90
Adduct A	1.2	1.5	1.3	2.8
Adduct B	0.57	-	0.80	0.90

a) Calculated from difference between open circuit voltage and closed circuit voltage. -: not measured.

The internal resistance of the Li|LiI|Adduct B galvanic cell (Table 2) is smaller than that of the Li|LiI|Adduct A galvanic cell. However, discharge performance of the Li|LiI|Adduct B galvanic cell is not so good as that of the Li|LiI|Adduct A galvanic cell; only about 40% of iodine was consumed in the cell reaction at 500 k $\Omega$  load. This may be attributed to occurrence of self discharge in the galvanic cell.

The Li|LiI|Adduct A galvanic cell shows somewhat lower current efficiency at 100 k $\Omega$ . However, its discharge performance at 100 k $\Omega$  is much better than that of a previously reported similar galvanic cell using the iodine-nylon-6 adduct. Table 3 shows the percentage of utilization of iodine of the adducts A and B having different iodine contents in the discharge process of the constructed cells. The percentage was determined as the ratio of the amount of charges obtained in the discharge of the cell to the theoretically usable one which was predicted from the iodine content in the adducts. The discharge of the cell was continued until the cell voltage dropped to 2.3 V under a 500 k $\Omega$  load and to 2.0 V under a 100 k $\Omega$  load.

Table 3. Percentage of utilization of iodine.

Positive electrode	Load/k $\Omega$	Percentage of utilization		
		Iodine content/wt-% <sup>a)</sup>		
		50	75	90
Adduct A	500	85.2	84.1	-
	100	64.9	-	-
Adduct B	500	-	-	40.3
	100	-	-	28.2

a) -: not measured.

At 10 k $\Omega$  load, both types of the galvanic cells give low percentage of utilization of iodine due to relatively higher internal resistance compared with the load. For example, the closed circuit voltage of the Li|LiI|Adducts A (iodine content = 75 wt-%) galvanic cell drops to 2.0 V after 2.5 h discharge at 10 k $\Omega$  load. Addition of 5 wt-% of carbon black (Kejen Black) to poly(2,5-thienylene) increases the electric conductivity of the active material of the positive electrode, thus increasing the discharge time to about 5 h. Iodine adducts of poly(2,5-pyrrolylene) and its derivatives having a similar  $\pi$ -conjugation system are also usable as active materials of similar Li solid electrolyte galvanic cells.

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- 11) LiI has low electric conductivity (ca.  $10^{-7}$  S cm $^{-1}$  at room temperature) and the internal resistance of the Li|LiI|iodine galvanic cell usually increases on leaving the cell at room temperature due to the direct reaction of Li and iodine (T. Yamamoto and M. Hishinuma, unpublished result). However, the discharge performances at 100 k $\Omega$  and 500 k $\Omega$  are slightly affected by the leaving time of the cell (the present and other<sup>13,14</sup> cells), since most part of the internal resistance originates from the iodine-polymer adduct if the cell is discharged to certain extent.
- 12) A part of iodine in Adduct A seems to exist as I $^-$  or I $_n^-$  with  $\{2,5-C_4H_2S\}_n^+$  due to migration of electron from poly(thienylene) to iodine (H. Sakai, M. Mizota, Y. Maeda, T. Yamamoto, and A. Yamamoto, *J. Phys. Chem.*, submitted).
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