Li|LiI|I_2 Galvanic Cells Using I_2–Nylon-6 Adducts as Positive Electrodes

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Iodine is used as one of many active materials for cathodes of dry Li galvanic cells. Iodine in this Li|LiI|I_2 galvanic cell is usually employed as adducts with electron donors such as poly(2-vinylpyridine) [1] and thiophene [2], since such adducts show higher electric conductivities than pure iodine and thus the internal resistance of the galvanic cells is lowered.

It is known that nylon-6, one of the most popular polymers, forms stable adducts with iodine [3]. However, use of the iodine-nylon-6 adduct as the cathode of the Li galvanic cell has not been reported. We previously reported the I_2–nylon-6 adducts as being positive electrodes of wet cells (*e.g.*, Zn|ZnI_2(aq)|I_2–nylon-6) [4]. As an extension of our previous research, we have examined the I_2–nylon-6 adduct as the cathode of the dry Li galvanic cell, and now wish to report the results.

When a mixture of 2.7 g of I_2 and 0.3 g of nylon-6 was heated in a sealed glass tube under vacuum at 115 °C for 16 h, a black solid adduct (3.0 g) of iodine with nylon-6 was obtained. Since purple vapor of I_2 was scarcely observed in the sealed tube, most of I_2 is regarded to be taken into the black adduct. Although I_2–nylon-6 adducts containing less than about 60 wt-% of I_2 have been prepared by dipping nylon-6 films into solutions containing I_2 [3, 4], the I_2–nylon-6 adduct containing as much as 90 wt-% of I_2 has not been reported. Figure 1 shows a sketch of the dry Li galvanic cell using the I_2–nylon-6 adduct as the positive electrode. As the negative electrode, a lithium plate (thickness = 0.5 mm, from Mitsui Mining & Smelting Co., Ltd.) was used.

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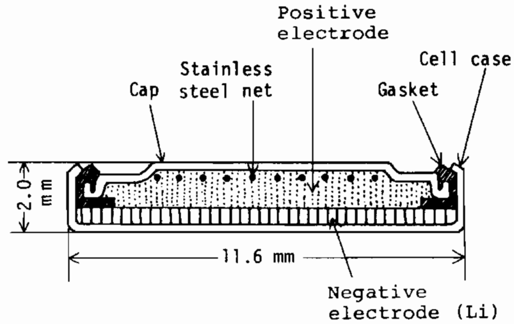

Fig. 1. Structure of the galvanic cell. Cell case and cap are made of stainless steel (SUS 304).

Closed-circuit voltage (C.C.V.) and discharge time of the Li galvanic cell strongly depend on the wt-% of I_2 in the adduct as shown in Table I. When the wt-% of I_2 is lower than 69 corresponding to 1 mol of I_2 per monomer unit of nylon-6 (R-value = 1), the galvanic cell shows only minor C.C.V. Use of the adduct containing more than 82 wt-% of iodine gives initial C.C.V. of 2.8 V when discharged at 500 kΩ. These observations seem to be related to decrease in electric resistance of the I_2–nylon-6 adduct with increase in the I_2 content. A preliminary study indicates that the I_2–nylon-6 adduct containing 69 wt-% of I_2 is an insulator whereas the adduct containing more than 82 wt-% of I_2 shows electric conductivity of a range of semiconductors.

Figure 2 shows discharge curves of the Li galvanic cells listed in Table I at 500 kΩ load at 25 °C. Figure 3 shows the dependence of the internal complex impedance of the Li galvanic cell (No 4 in Table I) on

TABLE I. Characterization of Li|LiI|I_2–nylon-6 Galvanic Cells.

No	I_2 wt-%	R-value[a]	Weight of cathode mg	O.C.V.[b] V	$(C.C.V.)_0$ at 500 kΩ[c] V	$(C.C.V.)_0$ at 10 kΩ[d] V	Discharge time[e] h
1	50	0.5	44	(0)	0	0	0
2	69	1.0	66	2.8	1.5	0	0
3	82	2.0	88	2.8	2.8	2.6	1100
4	87	3.0	105	2.8	2.8	2.2	1650
5	90	4.0	123	2.8	2.8	2.4	2000

[a] R = (mol of I_2)/(mol of monomer unit of nylon-6). [b] Open circuit voltage measured by Takeda Riken TR-8651 electrometer. [c] Initial closed circuit voltage when discharged at 500 kΩ. [d] Initial closed circuit voltage when discharged at 10 kΩ. [e] Time elapsed until C.C.V. drops to 2.3 V at 500 kΩ discharge.

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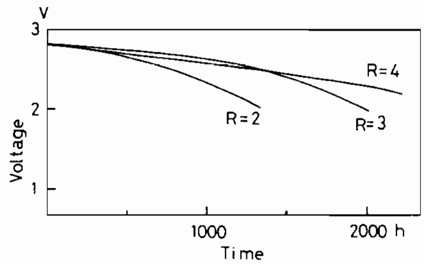

Fig. 2. Discharge curves of the Li galvanic cells listed in Table I (25 °C, 500 kΩ). As for the R-value, see Table I.

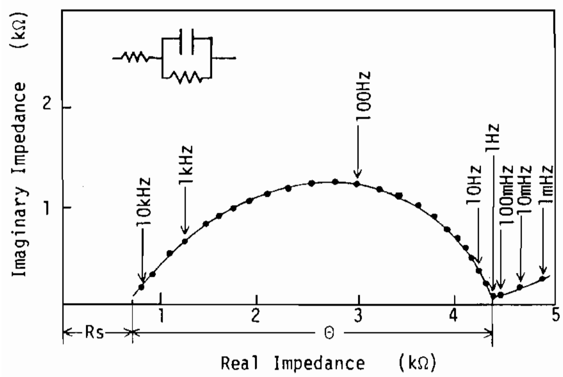

Fig. 3. Dependence of internal complex impedance of the Li galvanic cell on the frequency of the alternative current (Cole–Cole plot). Li galvanic cell = No 4 in Table I.

the frequency of an alternative current applied to the Li galvanic cell (Cole–Cole plot) [5]. The internal resistance of the Li galvanic cell estimated from the Cole–Cole plot (internal resistance = Rs + θ in Fig. 3) increases as I_2 in the adduct is consumed according to the discharge (Fig. 4). As stated above, the electric conductivity of the I_2–nylon-6 decreases steeply with decrease in the proportion of I_2 in the adduct, and the increase in the internal resistance due to the decrease in the I_2–cotent is apparently responsible for the decrease of C.C.V. during the discharge as shown in Fig. 2.

As described above, the iodine adduct with the popular polymer (nylon-6) is usable as a good cathode of the Li galvanic cell, and this finding may

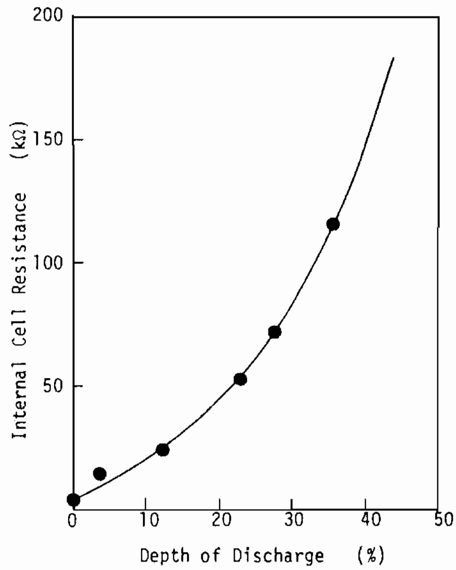

Fig. 4. Change of the internal cell resistance during discharge of the cell. Depth of discharge = (I_2 consumed according to the discharge)/(I_2 added).

provide a route to design a new low-priced commercial Li galvanic cell.

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