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Lithium secondary cells using LiX ($X = ClO_4, BF_4$) as electrolyte and poly(2,5-pyrrolylene) and poly(2,5-thienylene) as materials for positive electrodes

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Repeated charge–discharge cycles of lithium secondary cells using poly(2,5-pyrrolylene) and poly(2,5-thienylene) on carbon fibre plates as the materials for positive electrodes have been tested. When the Li | $LiBF_4$ | poly(2,5-pyrrolylene) secondary cell is charged and discharged at 0.1 mA cm^{-2}, it gives 91% current efficiency and 70% energy efficiency with an average discharging voltage of 2.75 V at the 9th charge–discharge cycle. This secondary cell has a theoretical energy density of 135 kW kg^{-1} based on the energy stored and the weights of poly(2,5-pyrrolylene) and the active materials. The Li | $LiClO_4$ | poly(2,5-thienylene) secondary cells show somewhat lower current efficiency and energy efficiency at the 9th charge–discharge cycle. The lithium cells using the polymers are rechargeable more than 50 times, but after about 50 cycles considerable lowering of the current efficiency and energy efficiency of the cells is observed, presumably due to degradation of the polymer.

1. Introduction

Lithium cells are now widely used as cells having a high energy density, and many efforts are currently being made to develop rechargeable systems. Recently, preparation of lithium secondary cells using π-conjugated polymers as materials for positive electrodes has been attempted [1–13]. For example, usability of poly(acetylene) [1–5], poly(2,5-pyrrolylene) [6, 7], poly(2,5-thienylene) [8, 9], poly(*p*-phenylene) [5, 10], dehydrochlorinated poly(vinyl chloride) [11] and poly(aniline) [12, 13] as materials for the positive electrodes of lithium secondary cells has been reported. As a part of a programme to develop polymer-based cells [14–19], we have tested the rechargeability of lithium secondary cells using poly(2,5-pyrrolylene) and poly(2,5-thienylene), which are electrochemically deposited on carbon fibre plates, in repeated charge–discharge cycles. The results are reported in this paper.

2. Experimental details

2.1. *Materials*

Thiophene was purified by distillation after drying over sodium wire, and pyrrole was purified by distillation. These monomers were stored under N_2. Samples of $[Bu_4N][ClO_4]$ (where Bu = butyl) and $[Bu_4N][BF_4]$ were purified by recrystallization from H_2O. The 1,2-dimethoxyethane was dried over sodium wire, distilled under N_2 and stored under N_2. Propylene carbonate was dried over molecular sieves, and distilled and stored under N_2. Poly(2,5-pyrrolylene) and poly(2,5-thienylene) were prepared electrochemically on carbon fibre plates (Kureha KGF-100, 1.0 × 1.0 cm). The electrochemical

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polymerization occurred at both sides of the plates. All polymerizations were carried out at 5° C by using platinum and the carbon fibre plate as cathode and anode, respectively, and the polymer film formed on the surface of the plate was used as the material for the positive electrode. The mass of the polymer formed on the surface of the anode was estimated from the weight increase of the anode after washing and drying (under vacuum) of the anode. The masses of samples A and C roughly agree with the reported masses of poly(2,5-pyrrolylene) (mass = $0.41\,\mathrm{mg\,C^{-1}}$ [20]) and poly(2,5-thienylene) (mass = $0.39\,\mathrm{mg\,C^{-1}}$ [21]) prepared by analogous electrochemical polymerization on platinum anodes. However, the mass of sample B is somewhat larger than the reported mass of poly(2,5-pyrrolylene). Difficulties in determining the relatively small mass from the mass increase of the anode should be taken into consideration. The preparation of each polymer is described below.

Samples A and B: poly(2,5-pyrrolylene) [20, 22–24]. An acetonitrile solution containing pyrrole ($0.25\,\mathrm{mol\,dm^{-3}}$) and $[\mathrm{Bu_4N}][\mathrm{BF_4}]$ ($0.1\,\mathrm{mol\,dm^{-3}}$) (for sample A) or $[\mathrm{Bu_4N}][\mathrm{ClO_4}]$ ($0.1\,\mathrm{mol\,dm^{-3}}$) (for sample B) was electrolysed for 2 h at 1 mA. The electric current for the preparation of the polymers was controlled by a Hokuto Denko HA 301 potentiostat–galvanostat. The mass of the polymer was about 3 mg (A) and 5 mg (B).

Sample C: poly(2,5-thienylene) [21, 25–27]. A nitrobenzene solution containing thiophene ($0.25\,\mathrm{mol\,dm^{-3}}$) and $[\mathrm{Bu_4N}][\mathrm{ClO_4}]$ ($0.1\,\mathrm{mol\,dm^{-3}}$) was electrolysed at 1 mA for 2 h. The mass of the polymer was about 3 mg.

A role of lithium film (thickness, 0.5 mm) was donated by the Mitsui Mining and Smelting Co. Ltd, and from this the lithium electrode was prepared.

2.2. *Charge and discharge*

A standard U-type glass cell was used. After replacement of air in the cell by dry N_2, a solution (1 : 4 mixture of propylene carbonate and 1,2-dimethoxyethane) containing electrolyte ($\mathrm{LiClO_4}$ or $\mathrm{LiBF_4}$ at a concentration of $1\,\mathrm{mol\,dm^{-3}}$) was added to the cell. $\mathrm{LiClO_4}$ was used as the electrolyte for the secondary cells using samples B and C, whereas $\mathrm{LiBF_4}$ was used as the electrolyte for that using sample A. The dimensions of the immersed parts of the lithium electrode and the positive electrode in the electrolyte solution were 1 × 1 cm, respectively. The secondary cell was placed in a thermostated chamber and charging and discharging were controlled by galvanostats and a computer. Voltages were measured against a lithium reference electrode.

3. Results and discussion

Fig. 1 shows a typical early (9th cycle) charge–discharge profile for the lithium secondary cell. In this case $\mathrm{LiBF_4}$ was used as electrolyte and poly(2,5-pyrrolylene) (sample A) as the positive electrode. The cell was charged for 60 min at a constant electric current of 0.2 mA, allowed to stand for 120 min (pause) and then discharged at a constant electric current of 0.2 A until the closed circuit voltage of the cell dropped to 1.0 V. Closed circuit voltages are shown for the regions of charging and discharging, whereas the open circuit voltage is shown in the region of pause.

The following features of the $\mathrm{Li|LiBF_4|}$poly(2,5-pyrrolylene) (sample A) secondary cell at the 9th charge–discharge cycle are seen from Fig. 1.

(i) The cell can be discharged for 55 min, corresponding to about 91% current efficiency. For a blank test a similar charge–discharge test was performed by using a $\mathrm{Li|LiX}$ ($\mathrm{X = ClO_4}$ or $\mathrm{BF_4}$)|carbon fibre plate cell. However, the cell did not work as a secondary cell, revealing the important role of poly(2,5-pyrrolylene) in the secondary cell. The current efficiency of the lithium secondary cell using poly(2,5-pyrrolylene) is much higher than that observed for similar lithium secondary cells using poly(acetylene) as the material for the positive electrode [1–5], indicating that the extent of self-discharge of the present lithium secondary cell is not large. When the pause time was decreased to 5 min, the current efficiency was almost 100%.

(ii) Averaged charging and discharging voltages are about 3.60 V and 2.75 V, respectively. Based on the current efficiency and averaged charging and discharging voltages, the energy efficiency of the secondary cell is calculated to be 70%.

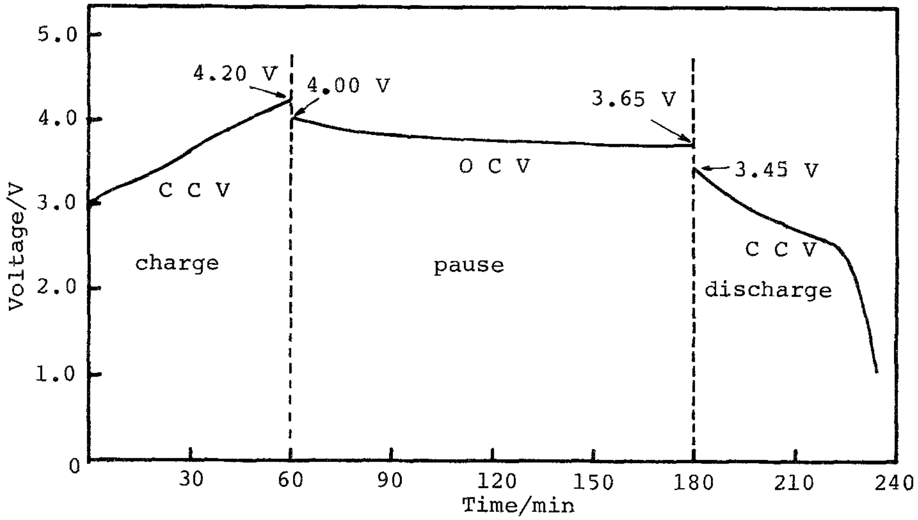

Fig. 1. A charge–discharge profile of the Li|LiBF$_4$|poly(2,5-pyrrolylene) (sample A) secondary cell at the 9th charge–discharge cycle, at 25° C and 0.2 mA. CCV, closed circuit voltage, OCV, open circuit voltage.

(iii) From the difference between the closed circuit and open circuit voltages ($4.20 - 4.00\,\mathrm{V} = 3.65 - 3.45\,\mathrm{V} = 0.20\,\mathrm{V}$) and the charging and discharging current (0.2 mA), the internal resistance of the cell is calculated to be 1000 Ω. On the other hand, the electric resistance between the positive and negative electrodes is roughly calculated as 400 Ω from the electric conductivity of the solution of LiBF$_4$ ($8.9 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$) and the geometry of the electrolyte solution between the two electrodes (area, $\sim 1.0\,\mathrm{cm^2}$; length, 3.4 cm). The difference seems to be ascribable to overpotential and the electrical resistance of the positive electrode itself. At the relatively early charge–discharge cycle, the difference between the internal resistance and the electric resistance due to the electrolyte solution is not large. However, it increases considerably as the cycle number becomes larger than about 50 (*vide infra*).

(iv) The energy stored in the cell is calculated as 0.50 mW h from the discharging electric current (0.2 mA), the average discharging voltage (cf. Fig. 1), and the discharging time (55 min); i.e. $0.2 \times 2.75 \times (55/60) = 0.50$. The theoretical energy density calculated on the basis of the energy stored and the weights of poly(2,5-pyrrolylene) (3 mg) and active materials (lithium + BF$_4$: $93.8 \times 0.2 \times 3600 \times (1/96\,500) = 0.7\,\mathrm{mg}$) is about $135\,\mathrm{W\,h\,kg^{-1}}$. The following electrode reaction is assumed [1–11]:

$$(2,5\text{-pyrrolylene})_n + ny\mathrm{BF}_4^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} (2,5\text{-pyrrolylene}^{+y}\cdot y\mathrm{BF}_4^-)_n + ny\,e \qquad (1)$$

It is reported that 0.45 mol of 2,5-pyrrolylene unit in poly(2,5-pyrrolylene) is formed per Faraday in the electrochemical polymerization of pyrrole in a solution containing 0.1 M [Et$_4$N][BF$_4$] [20]. If one assumes the same faradaic yield of poly(2,5-pyrrolylene) for sample A, then 3.4×10^{-5} mol ($0.45 \times 0.001 \times 7200 \times (1/96\,500) = 3.4 \times 10^{-5}$) of 2,5-pyrrolylene unit is formed during electrochemical polymerization for 2 h at 1 mA (see Experimental section). On the other hand, charging of the cell (Equation 1) at 0.2 mA for 60 min corresponds to 7.5×10^{-6} Faraday ($0.0002 \times 3600 \times 1/96\,500) = 7.5 \times 10^{-6}$). Division of 7.5×10^{-6} by 3.4×10^{-5} gives the value of 0.22 for the y value in Equation 1.

Fig. 2 shows a comparison of the charge–discharge profiles (at the 9th cycle) of the secondary cells using the polymers as materials for the positive electrodes. It is seen from Fig. 2 that the secondary cell using poly(2,5-pyrrolylene) (sample A) and LiBF$_4$ (Li|LiBF$_4$|sample A secondary cell) shows the best charge–discharge performance. The Li|LiClO$_4$|poly(2,5-pyrroly-

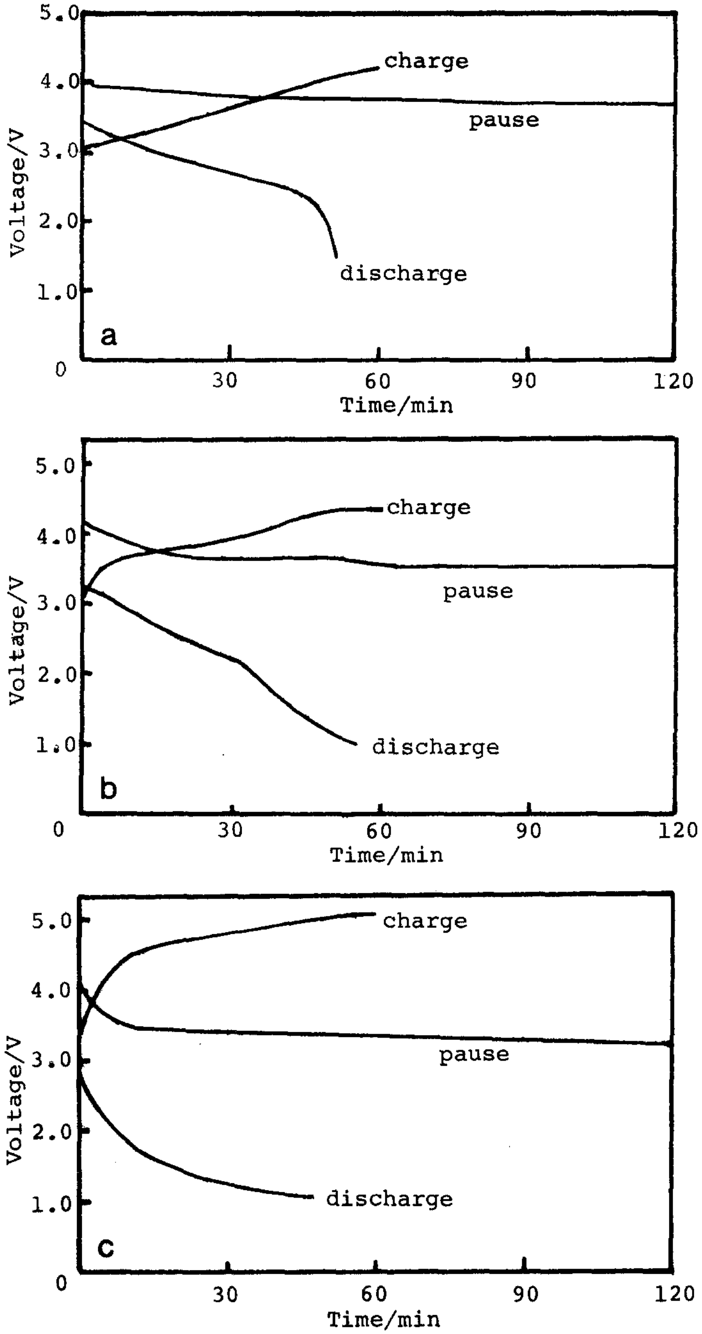

Fig. 2. Comparison of charge–discharge profiles of the lithium secondary cells at 25°C and 0.2 mA (a) Li|LiBF$_4$|poly(2,5-pyrrolylene) (sample A), corresponding to Fig. 1; (b) Li|LiClO$_4$|poly(2,5-pyrrolylene) (sample B); (c) Li|LiClO$_4$|poly(2,5-thienylene) (sample C). Closed circuit voltage is shown for 'charge' and 'discharge', whereas open circuit voltage is shown for 'pause'.

lene) (sample B) secondary cell shows the second best charge–discharge performance with 88% current efficiency and 54% energy efficiency at the 9th charge–discharge cycle. The Li|LiClO$_4$|poly(2,5-thienylene) (sample C) secondary cell shows 76% current efficiency and 27% energy efficiency. These two secondary cells have larger internal resistances (about 2 kΩ) than that observed for the Li|LiBF$_4$|poly(2,5-pyrrolylene) (sample A) secondary cell. Since the electrical conductivity of the solution of LiClO$_4$ (1.5×10^{-2} S cm^{-1}) used for the cell is higher than that of the solution of LiBF$_4$ (8.9×10^{-3} S cm^{-1}), the higher internal resistances of the Li|LiClO$_4$|

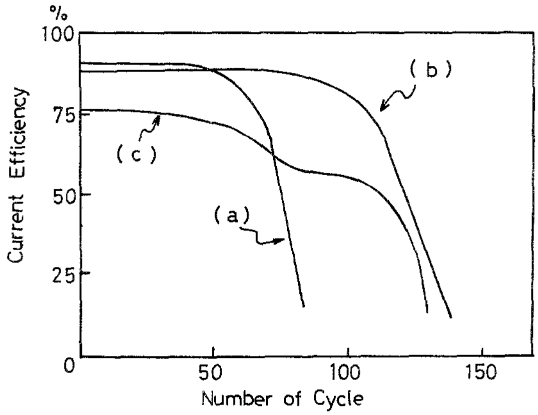

Fig. 3. Change of current efficiency with charge–discharge cycle number. Curves (a–c) correspond to Fig. 2a, 2b and 2c, respectively.

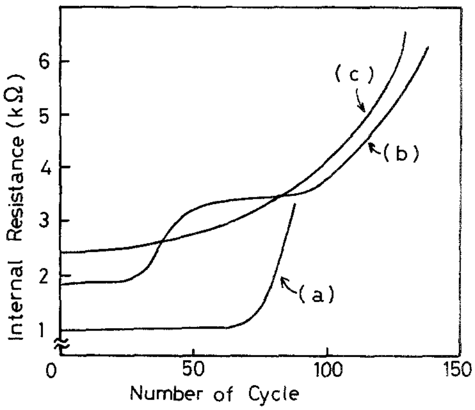

Fig. 4. Change of internal resistance with charge–discharge cycle number. Curves (a–c) correspond to Fig. 2a, 2b and 2c, respectively.

sample B and Li|$LiClO_4$|sample C secondary cells than that of the Li|$LiBF_4$|sample A secondary cell are attributed to larger overpotential or larger electrical resistance of the positive electrodes in these cells.

Fig. 3 shows the change of current efficiency with charge–discharge cycle number. Although the Li|$LiBF_4$|poly(2,5-pyrrolylene) (sample A) secondary cell showed good charge–discharge performance at relatively early charge–discharge cycles, the current efficiency of the secondary cell decreased rapidly after about 50 charge–discharge cycles. The current efficiency of the Li|$LiClO_4$|poly(2,5-pyrrolylene) (sample B) secondary cell remained above 80% even at the 100th charge–discharge cycle; however, it decreased to about 50% at about the 125th cycle. The current efficiency of the Li|$LiClO_4$|poly(2,5-thienylene) (sample C) secondary cell also decreased to about 50% at about the 110th cycle. Degradation of the polymers during the charge–discharge cycles accounts for the decreases in the current efficiency. The initially colourless electrolytic solution gradually became reddish purple or brown as the number of the charge–discharge cycle increased. This suggests degradation of the polymer during the cycle and dissolution of degradation products in the solution. The IR spectra of samples taken from surface portions of the positive electrodes showed that the electrodes lost most of the π-conjugation polymers after the charge–discharge cycle was stopped. Without the charge–discharge the polymers were stable and colouration of the electrolytic solution was not observed.

The decreases in the current efficiency accompanied increases in the internal resistances of the cells (Fig. 4). Attempts to prepare 'all-plastic secondary cells' using poly(2,5-pyrrolylene) or poly(2,5-thienylene) as the material for both the positive and negative electrodes of lithium secondary cells (electrolyte = LiX) were not successful due to the very rapid self-discharge of the secondary cells tested.

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