Comparison of Cathode Utilization between Polymeric Organodisulfide and Titanium Disulfide in Solid Polymer Electrolyte Rechargeable Lithium Cells

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Cathode utilization of a polymeric organodisulfide prepared from 2,5-dimercapto-1,3,4-thiadiazole was compared with that of titanium disulfide in an all-solid-state, thin film, rechargeable cell based on a solid polymer electrolyte operated at 95°C. The cathode utilization of the polymeric organodisulfide was remarkably enhanced by the use of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ instead of LiCF_3SO_3 in a polyethylene oxide-based electrolyte and achieved up to 80 % (1.3 mAhcm^{-2}) at a 0.5 mAcm^{-2} discharge rate, where 30 wt % of the active material was loaded in the cathode. The cathode utilization of titanium disulfide was almost the same as the polymeric organodisulfide at equivalent loading levels on a volume basis.

1 INTRODUCTION

All-solid-state rechargeable lithium cells based on solid polymer electrolytes represented by a complex formed between a polyethylene oxide (PEO) and a lithium metal salt have proposed by Armand¹⁻⁴⁾.

Subsequently, several groups have shown interest in developing the practical batteries for consumer electronics, load-levelling and electric vehicle applications based on this concept⁵⁻⁸⁾.

The cathode materials tested in these advanced batteries can be classified into three categories. The first one includes inorganic intercalation compounds such as titanium disulfide^{6,7)}, molybdenum dioxide⁶⁾, vanadium oxides^{5,8-12)}, titanium dioxide^{12,13)} and manganese dioxide¹⁴⁾. The second one consists of electronically conducting polymers such as

polyacetylene^{15,16)}, polypyrrole^{17,18)} and polyaniline¹⁹⁾.

The last one is a group of polymeric organodisulfides, which has been named solid redox polymerization electrodes (SRPE) due to the reversible polymerization-depolymerization reaction that occurs on charge-discharge process²⁰⁻²⁵⁾.

Among polymeric organodisulfides, a polymer prepared from 2,5-dimercapto-1,3,4-thiadiazole (noted as X1) is a promising active material from the point of good reversibility, high open circuit voltage and high energy density based on the simple delocalized structure^{21,22)}.

In this paper, we will report initial results on how the loading level of an active material in a cathode composite influences the available capacity of a PEO-based thin film rechargeable lithium cell operated at 95°C. As an active material, the X1 polymer was evaluated in comparison with a reliable inorganic sulfide counterpart, TiS_2 .

Two kinds of supporting electrolyte salts, LiCF_3SO_3 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ²⁶⁾, were used in PEO electrolytes and their performance in the cell was also examined.

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2 EXPERIMENTAL

2.1 Preparation of polymer X1

The general preparative method is illustrated by the following reactions^{21,22}:

2,5-dimercapto-1,3,4-thiadiazole (Aceto Chemical) was recrystallized twice from acetone to give a white powder.

IR; 3400 (broad), 1500, 1450 cm^{-1} . Mp; 161 °C.

4.508 g (30 mmol) of the recrystallized monomer and 2.518 g (60 mmol) of $\text{LiOH} \cdot \text{H}_2\text{O}$ (Aldrich) were dissolved in 50 ml of water, respectively. When one equivalent of LiOH solution was added to the monomer solution, the color of the mixture turned slightly yellow and the addition of another equivalent of LiOH solution changed it to a colorless solution. The solution was evaporated to dryness and the resultant white powder was washed with hexane and dried *in vacuo* at 120°C for 24 hours. The yield was 6.62 g, which indicated the incorporation of about three water molecules per dithiolate salt.

IR; 3250 cm^{-1} (broad).

Calcd. for $\text{C}_2\text{N}_2\text{S}_3\text{Li}_2 \cdot 3\text{H}_2\text{O}$: C; 11.11, H; 2.80, N; 12.96.

Found: C; 12.13, H; 2.51, N; 13.53.

The polymer X1 was prepared without the isolation of the lithium salt. Into the solution of lithium dithiolate (30 mmol), 7.614 g (30 mmol) of iodine (J. T. Baker) was added and heated at 75°C for 2 hours to give a slightly yellow precipitate. The precipitate was washed with boiling water, hot acetone, methanol, hexane and ether successively and dried *in vacuo* at 120°C for 24 hours to give 3.74 g (84 % in yield) of the polymer, which was ground into a fine powder.

IR; 1500, 1475, 1450 cm^{-1} . Decomp. temp.; 188°C.

Calcd. for $(\text{C}_2\text{N}_2\text{S}_3)_n$: C; 16.21, N; 18.90, S; 64.90.

Found: C; 16.13, N; 18.60, S; 65.00.

Impurities: Li; 57 ppm, Na; 27 ppm.

2.2 Preparation of cathode and electrolyte films

Cathode films were prepared from polymer X1 powder or TiS_2 powder (Cerac), Shawinigan acetylene black powder (Chevron Chemical), Brij 35 (Aldrich) as a dispersant and PEO (5×10^6 in average molecular weight, Aldrich). Electrolyte films were prepared from

LiCF_3SO_3 (3M) or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3M) and the same PEO. All materials were dried under vacuum at 50°C for several days and stored under helium atmosphere.

When the loading level of active materials was changed, the amount ratios of acetylene black and Brij 35 to the active material were kept constant as shown in Table 1. The ratio of Li^+ ion to an ethylene oxide monomer unit in the polymer electrolytes was adjusted to 1 : 8 as shown in Table 2.

A viscous slurry mixture was obtained in acetonitrile (HPLC grade, Aldrich) by vigorous stirring with a high-speed homogenizer. Appropriate amounts of the homogenized mixtures depending on the desired film thickness were cast into glass rings (41.8 mm in diameter) placed on a clean Teflon surface and the solvent was allowed to evaporate in air overnight.

The thin cathode film (30 - 120 μm in thickness) and the thin electrolyte film (35 - 45 μm in thickness) were peeled off and were cut into disks (16.0 and 25.0 mm in diameter, respectively) and dried under vacuum at 50°C for several days and stored under helium atmosphere. These films were subjected to vacuum drying prior to use.

Table 1. Formulation of cathode mixtures.

material	loading level	
	30 wt %	45 wt %
PEO (MW = 5×10^6)	600 mg	400 mg
Polymer X1 or TiS_2	300 mg	450 mg
Acetylene black	70 mg	105 mg
Brij 35	30 mg	45 mg
CH_3CN	22 ml	15 ml

Table 2. Formulation of electrolyte mixtures.

material	A	B
PEO (MW = 5×10^6)	693 mg	551 mg
LiCF_3SO_3	307 mg	-
$\text{LiN}(\text{CF}_3\text{SO}_2)_2$	-	449 mg
CH_3CN	40 ml	30 ml

2.3 Estimation of film thickness

Thickness (t) of the films was estimated using apparent densities (d) of the films, which were calculated based on physical mixing of each component. Densities of Li, PEO, polymer X1, TiS_2 , acetylene black, Brij 35, LiCF_3SO_3 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were 0.53, 1.21, 1.60, 3.22, 2.26, 0.95, 1.90 and 1.91, respectively. Estimated thickness of the films agreed with the measured values within 10 % in error.

2.4 Assembly and evaluation of test cells

Battery-grade lithium foil (25 μm in thickness, Lithco) was cut into disks (18.4 mm in diameter) and test cells were assembled using exterior cases of 2016 coin cells as shown in Fig. 1. A screw clamp was used to apply slight pressure on the assembled cell. The cell was maintained in a furnace thermostatted at $95 \pm 2^\circ\text{C}$.

All the above procedures were carried out inside a helium glove box equipped with a moisture removing apparatus (Vacuum Atmospheres).

Discharge-charge characteristics were examined with a galvanostat (Princeton Applied Research, model 371) controlled by a personal computer (IBM, PC/AT) equipped with a D/A board and developed software²⁷.

Test cells were discharged/charged at $0.5/0.1 \text{ mAcm}^{-2}$ between 3.1 and 2.0 V (1.5 V for TiS_2). Open circuit voltages of the cell were monitored periodically in order to know the polarization. Cell impedances were also measured before and after discharge by a pulse technique. Because large cell impedance ($> 70 \Omega\text{cm}^{-2}$) occasionally resulted from poor contact between cell components and these cells generally showed poor discharge behavior.

Fig. 1. A schematic view of a test cell.

3 RESULTS AND DISCUSSION

3.1 Discharge-charge profile

Representative discharge-charge curves both for Li/X1 and Li/ TiS_2 cells using a PEO- LiCF_3SO_3 electrolyte are shown in Fig. 2, where cell voltage (E) was plotted against capacity (Q). Since all cells were constructed cathode-limited, theoretical capacities were derived by weighing the cathode films.

The polymer X1 cathode always shows two plateaus, which come from the different electrode potentials of the reactions, polymer to dimer and dimer to monomer:

This observation was also confirmed in the solution containing the monomer by cyclic voltammetry.^{28,29}

Although the TiS_2 cathode initially shows a high open circuit voltage around 3.0 V, the potential falls rapidly upon discharge. It decreases constantly with time, because the electrode potential of the cathode decreases as the following reaction proceeds:

The discharge-charge curve fairly agrees with the curves reported for Li / $\text{p}(\text{EO})_8\text{LiClO}_4$ / TiS_2 ⁶, although it was reported that LiCF_3SO_3 was inferior to LiClO_4 in Li / PEO-LiX / TiS_2 cells^{6,21}.

Fig. 2. Typical discharge-charge curves for Li / $\text{p}(\text{EO})_8\text{LiCF}_3\text{SO}_3$ / X1 and Li / $\text{p}(\text{EO})_8\text{LiCF}_3\text{SO}_3$ / TiS_2 cells at 95°C . theoretical capacity: 0.75 mAhcm^{-2} (30 wt % loading), discharge rate: 0.5 Acm^{-2} , charge rate: 0.1 Acm^{-2} .

3.2 Cathode utilization

The capacity of the test cell was varied from 0.6 to 2.3 mAhcm⁻² by changing the amount of an active material in the cathode in two ways, by changing thickness of the cathode film and changing a mixing ratio of an active material in the cathode composites (loading level).

The first discharge curves of the test cells using a p(EO)₈LiCF₃SO₃ or a p(EO)₈LiN(CF₃SO₂)₂ electrolyte were shown in Fig. 3, 4, 5 and 6 for Li/X1 and Fig. 7, 8, 9 and 10 for Li/TiS₂ cells, respectively.

Horizontal axes of all figures are represented by the cathode utilization (U), which indicates the ratio of available capacity (Q) to theoretical capacity (Q_t).

Theoretical capacity of each cell is given in the figures

and the corresponding film thickness to the theoretical capacity can be estimated from the conversion coefficients (t/Q_t) given in Table 3.

Table 3. Estimated density and thickness of the cathode composites.

cathode composite	d / gcm ⁻³	t/Q_t / μm/mAhcm ⁻²
30 wt % polymer X1	1.34	68.8
45 wt % polymer X1	1.42	43.3
30 wt % TiS ₂	1.53	91.1
45 wt % TiS ₂	1.77	52.4

Fig. 3. Discharge curves at 0.5 mAhcm⁻² for Li / p(EO)₈LiCF₃SO₃ / X1 (30 wt %) at 95°C.

Fig. 5. Discharge curves at 0.5 mAhcm⁻² for Li / p(EO)₈LiN(CF₃SO₂)₂ / X1 (30 wt %) at 95°C.

Fig. 4. Discharge curves at 0.5 mAhcm⁻² for Li / p(EO)₈LiCF₃SO₃ / X1 (45 wt %) at 95°C.

Fig. 6. Discharge curves at 0.5 mAhcm⁻² for Li / p(EO)₈LiN(CF₃SO₂)₂ / X1 (45 wt %) at 95°C.

The following three factors on the cathode utilization can be discussed from these results both for Li/X1 and Li/TiS₂ cells.

- i. Thickness of a cathode film
- ii. Loading level of an active material in a cathode film
- iii. Kind of a supporting salt (LiX) in a PEO-based electrolyte

The values of cathode utilization obtained in each cell were plotted against the thickness of the cathode films in Fig. 12 for Li/X1 and Fig. 13 for Li/TiS₂.

(a) Li/X1 cell

The cathode utilization generally became lower as the thickness of the cathode film and the loading level of

X1 in the cathode increased as shown in Fig. 3 vs. 4 and Fig. 5 vs. 6. It is believed that this is because of the inadequate transport of Li⁺ in the cathode composite.

However, the utilization of LiN(CF₃SO₂)₂ as a supporting salt in the polymer electrolyte markedly enhanced the cathode utilization as shown in Fig. 3 vs. 5 and Fig. 4 vs. 6. Particularly, Li / p(EO)₈LiN(CF₃SO₂)₂ / X1 (30 wt %) cell showed no decline of the cathode utilization as shown in Fig. 12.

It is known that the conductivity of p(EO)₈LiClO₄ at 95°C (10⁻³ S cm⁻¹) is about ten times higher than that of p(EO)₈LiCF₃SO₃, because p(EO)₈LiClO₄ has a lower glass temperature than p(EO)₈LiCF₃SO₃³⁾. The conductivity of p(EO)₈LiN(CF₃SO₂)₂ at 95°C is almost

Fig. 7. Discharge curves at 0.5 mAcm⁻² for Li / p(EO)₈LiCF₃SO₃ / TiS₂ (30 wt %) at 95°C.

Fig. 9. Discharge curves at 0.5 mAcm⁻² for Li / p(EO)₈LiN(CF₃SO₂)₂ / TiS₂ (30 wt %) at 95°C.

Fig. 8. Discharge curves at 0.5 mAcm⁻² for Li / p(EO)₈LiCF₃SO₃ / TiS₂ (45 wt %) at 95°C.

Fig. 10. Discharge curves at 0.5 mAcm⁻² for Li / p(EO)₈LiN(CF₃SO₂)₂ / TiS₂ (45 wt %) at 95°C.

the same as that of $\text{p}(\text{EO})_8\text{LiClO}_4^{30)}$ and the $\text{p}(\text{EO})_8\text{LiN}(\text{CF}_3\text{SO}_2)_2$ film has a similar elastic character (softness and stickiness) with the $\text{p}(\text{EO})_8\text{LiClO}_4$ film.

The enhancement in the cathode utilization caused by $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is explained by this conductivity enhancement of the polymer electrolyte, itself.

However, the improvement of the contact between the electrolyte and the cathode by the elastic character of the $\text{p}(\text{EO})_8\text{LiN}(\text{CF}_3\text{SO}_2)_2$ film should be considered, because the addition of a small amount of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in the cathode increased the cathode utilization of a $\text{Li} / \text{p}(\text{EO})_8\text{LiCF}_3\text{SO}_3 / \text{X1}$ cell as shown in Fig. 11.

(b) Li/TiS_2 cell

Similar tendencies have observed for Li/TiS_2 cell as far as the cathode utilization is concerned. However, only $\text{Li} / \text{p}(\text{EO})_8\text{LiCF}_3\text{SO}_3 / \text{TiS}_2$ (45 wt %) cell showed a decline of the cathode utilization as shown in Fig. 13.

Since the density of TiS_2 is twice that of X1, smaller volume occupied by TiS_2 in the cathode film resulted in the better cathode utilization than X1 at the same loading levels based on weight. However, the cathode utilization of Li/TiS_2 cells became almost the same as $\text{Li}/\text{X1}$ cell, if loading level on a volume basis was taken into account.

Fig. 11. Addition effect of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ($\text{Li}/\text{EO}=1/16$) in the cathode of $\text{Li} / \text{p}(\text{EO})_8\text{LiX} / \text{X1}$ (30 wt %) cells. theoretical capacity: 0.85 mAhcm^{-2} , discharge rate: 0.5 mAcm^{-2} at 95°C , bold lines: $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ added.

Loading levels of 30 wt % X1 and 45 wt % TiS_2 are equivalent to 25 vol % for both X1 and TiS_2 .

Furthermore, the cathode utilization of 60 wt % (35 vol %) loading of TiS_2 declined as shown in Fig. 10 and it coincided with that of 45 wt % (40 vol %) loading of X1. This observation indicates Li^+ transport in the cathode composite may be impeded by the existing volume of active materials.

Fig. 12. Available capacity of $\text{Li} / \text{p}(\text{EO})_8\text{LiX} / \text{X1}$ cells as a function of cathode film thickness.

Fig. 13. Available capacity of $\text{Li} / \text{p}(\text{EO})_8\text{LiX} / \text{TiS}_2$ cells as a function of cathode film thickness.

3.3 Calculation of energy density and power density

On the basis of the experimental results, energy densities (W) and sustained power densities (P) of Li/X1 and Li/TiS₂ cells were calculated volumetrically (V) and gravimetrically (g) as shown in Fig. 14. The cell capacity was fixed to 1 mAh cm⁻² at 0.5 mA cm⁻² discharge rate, which is comparable with reported values (0.4⁵⁾, 0.97⁶⁾, 1.45⁷⁾, 1.5⁸⁾ mAh cm⁻²).

Current collectors were neglected and cathode utilization was assumed to be 75 %. An average cell voltage (E_m) was used instead of an initial value (E_0).

In spite of a lower loading level on a weight basis, the Li/X1 cell affords higher energy and power density than the Li/TiS₂ cell, because of a higher cell voltage and a lower equivalent weight (74 for X1 and 112 for TiS₂).

Fig. 14. Estimation of energy density and sustained power density for thin film rechargeable lithium cells.

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