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Thin All-Solid-State Lithium Batteries Utilizing Solid Polymer Electrolyte Prepared by Plasma Polymerization

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Solid polymer electrolytes prepared by mixing of poly(ethylene oxide)(PEO) as well as poly(propylene oxide)(PPO) with alkali metal salts have attracted considerable attention due to their potential application to all-solid-state lithium batteries.[1-3] Ionic conductivity of reported solid polymer electrolytes is typically 10^{-6}-10^{-8} S/cm at room temperature, and these values are lower than those of liquid electrolytes.[4] Because of their low ionic conductivity, lithium batteries using solid polymer electrolytes generally does not exhibit good properties in both utilization and charge/discharge characteristics until around 100 °C. Therefore, solid polymer electrolyte films for practical lithium batteries are required to decrease actual resistance. Preparation of the thinner film will meet this requirement. Plasma polymerization is a useful method to provide an ultra-thin uniform polymer layer deposited on various substrates.[5] We have prepared ultra-thin solid polymer electrolyte films by hybridization of plasma polymerized octamethylcyclotetrasiloxane (OMCTS) with PPO and $LiClO_4$.[6] This paper describes a preparation of thin all-solid-state rechargeable lithium batteries using this hybrid film.

The apparatus used for the plasma polymerization consists of a glass reactor (9 cm diameter and 35 cm height) equipped with capacitively coupled inner electrodes (6 cm diameter) connected with an RF power supply (13.56 MHz). A TiS_2 film deposited on borosilicate glass was utilized as a substrate, which was placed between the electrodes. Argon gas [10 cm^3 (STP)/min] and OMCTS [2 cm^3 (STP)/min] were introduced into the glass reactor. The pressure was maintained at 0.5 Torr by controlling a throttle valve connecting to a vacuum pump. At this point, the RF power at 5 W was turned on. The plasma polymer films deposited on the substrate were soaked in butanol-PPO [M.W. 4,000]-$LiClO_4$ solution for 1 hour and then dried at 80 °C under vacuum (10^{-3} Torr) for 24 hours to remove butanol and water. The concentration of lithium ion in a plasma polymer-PPO mixture was determined by atomic absorption spectrophotometry. The ionic conductivity of the hybrid polymer electrolyte (plasma polymer-PPO-$LiClO_4$) was estimated by an AC impedance measurement with a vector impedance analyzer over the frequency range 2×10^{2}-2×10^{4} Hz.

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Thin film of TiS_2 for the cathode active material was deposited by a low pressure chemical vapor deposition (CVD) technique from a mixture of $TiCl_4$ and H_2S diluted with argon as the source gas. A film prepared by this method was nearly stoichiometric TiS_2 films which had predominant (110) orientation.[7] All-solid-state lithium batteries were constructed with the hybrid polymer electrolyte (2-3 μm) deposited on TiS_2 CVD cathode (10-15 μm) and a Li foil anode.

IR spectrum of plasma polymer formed from OMCTS suggested that the basic structure of the plasma polymer was similar to that of poly(dimethylsiloxane). SEM observation indicated that the plasma polymer was uniform and pinhole-free.

Figure 1 shows the temperature dependence of the ionic conductivity of the hybrid polymer electrolyte [plasma polymer/PPO/ $LiClO_4$= 78/20/2wt%]. An actual electrical resistance of the hybrid films(1 μm thick) per unit area is also shown in Fig.1 at right ordinate. The temperature dependence of ionic conductivity exhibit the WLF-type[8,9] dependence rather than the Arrhenius-type one. Conductivity of hybrid

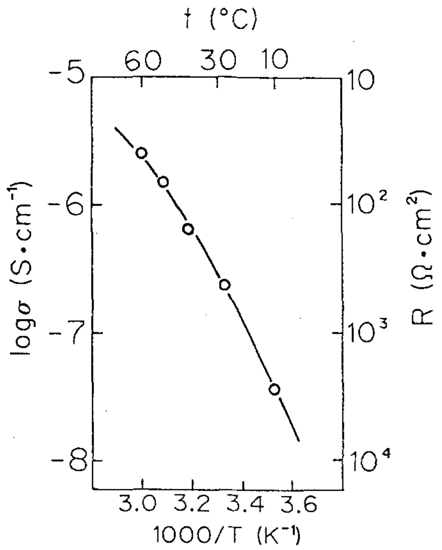

Fig. 1. Ionic conductivity dependence of the hybrid film on temperature, which contains PPO(20wt%) and $LiClO_4$(2wt%).

polymer electrolyte reached 2.6×10^{-6} S/cm (40 ohm per 1 cm^2) at 60 °C. The hybrid polymer electrolyte is considered to have a micro-heterogeneous structure [plasma polymerized OMCTS segment-PPO segment] and PPO segment mainly contributes to the ionic dissociation of $LiClO_4$.[10]

Figure 2 illustrates SEM figure of the cross-section of hybrid polymer electrolyte deposited on a TiS_2 CVD film. The figure shows that TiS_2 CVD film is about 15 μm and a hybrid polymer electrolyte layer is about 2 μm. The hybrid polymer electrolyte is pin-hole free, and covers TiS_2 film completely.

In Fig.3, the charge-discharge curve of the battery is shown. The cell was cycled at 16 μA/cm^2. The fairly good rechargeability of the battery is confirmed by Fig.3, while internal resistance of this batteries is fairly large. It was inferred that solid polymer electrolyte did not closely contact with lithium electrode. The first discharge performance of cells at various current density at room temperature are given in Fig.4. At a low current density of 8 μA/cm^2, the discharge curve plateau extend to 85% of utilization of TiS_2 (to $LiTiS_2$). The utilization was highly enough for practical batteries at low discharge current densities.

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References

1. M. Gauthier, D. Fauteux, G. Vassort, A. Belanger, M. Duval, P. Ricoux, J. M. Chabagno, D. Muller, P. Rigaud, M. B. Armand and D. Deroo, J.Electrochem.Soc., 132, 1333(1985).
2. K. M. Abraham, M. Alamgir and S. J. Perrotti, J.Electrochem.Soc., 135, 535(1988).
3. A. Hooper and J. M. North, Solid State Ionics, 9&10, 1161(1983).
4. Y. Matsuda, J.Power Sources, 20, 19(1987).
5. H.Yasuda, J.Polym.Sci.,Macromol.Rev., 16, 199(1981).
6. Z. Ogumi, Y. Uchimoto and Z. Takehara, submitted for publication.
7. Y.Kanamori, Z. Ogumi and Z. Takehara, GS News, 46, 21(1987).
8. M. L. Williams, R. F. Randel and J. D. Ferry, J.Amer.Chem.Soc., 77, 3701(1955).
9. M. Cohen and D. Turnbull, J.Chem.Phys., 31, 1164(1959).
10. M. Watanabe, S. Nagano, K. Sanui and N. Ogata, J.Power Sources., 20, 327(1987).

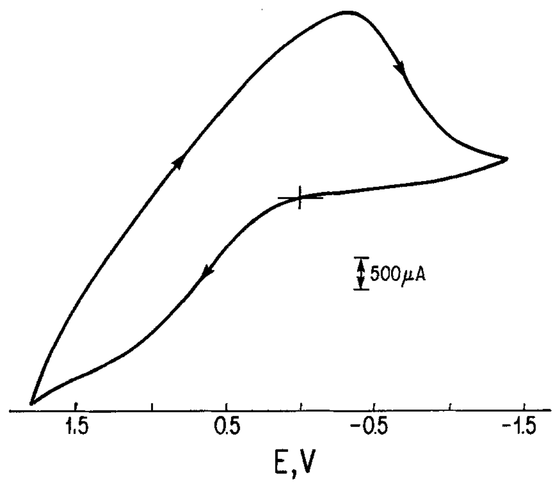

Fig. 2. SEM figure of the cross-section of hybrid polymer electrolyte deposited on TiS_2 CVD film.

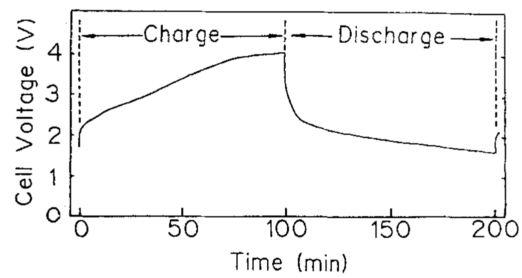

Fig. 3. Charge/discharge cycle for all-solid-state lithium battery at room temperature.
Discharge current: 16 μA/cm^2
Charge current : 16 μA/cm^2

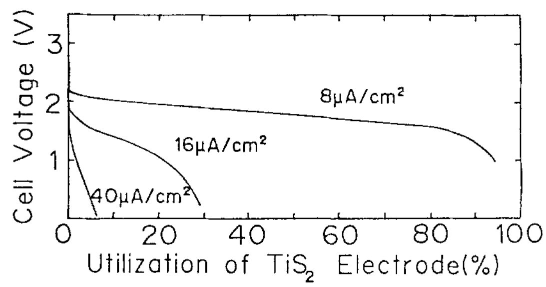

Fig. 4. Utilization of all-solid-state lithium batteries vs. discharge current densities at room temperature.