PREPARATION AND CHARACTERIZATION OF A THIN FILM OF POLYMER ELECTROLYTE BY PLASMA CVD
PART IV. ALL-SOLID-STATE LITHIUM BATTERIES

ZEMPACHI OGUMI*, YOSHIHARU UCHIMOTO and ZEN-ICHIRO TAKEHARA

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida-hommachi, Sakyo-ku, Kyoto 606 (Japan)

Summary

Octamethylcyclotetrasiloxane was polymerized by RF-plasma polymerization to provide a host polymer film which was hybridized with poly-(propylene oxide) and lithium perchlorate. Rechargeable, all-solid-state lithium batteries were fabricated using a thin film of TiS_2 (10 - 15 μm) prepared by chemical vapor deposition (CVD) as a cathode active material, and an ultra-thin film of solid polymer electrolyte (2 - 3 μm) as an electrolyte. The batteries were examined in respect of their charge/discharge properties at room temperature at current densities of 8 - 40 μA cm^{-2}. The first discharge and charge reached the 90% level.

Introduction

Recently, a relatively high ionic conductivity has been reported in polymer complexes of polyethers such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) with alkali metal salts [1 - 3]. The ionic conductivity of solid polymer electrolyte is typically 10^{-6} - 10^{-8} S cm^{-1} at room temperature. This is lower than that of liquid electrolyte. These solid polymer electrolytes are expected to be used in lithium batteries [4 - 7].

Thin films of solid polymer electrolyte are required to satisfy two demands: (i) to decrease the bulk resistance of the solid polymer electrolyte; (ii) to decrease its thickness. However, it is difficult to prepare ultra-thin films of solid polymer electrolyte by conventional techniques because of the generation of pin-holes.

Plasma polymerization is an attractive method of providing an ultra-thin, uniform polymer layer strongly adhering to various substrates. In this article, octamethylcyclotetrasiloxane (OMCTS) was selected as a monomer. An ultra-thin polymeric layer of plasma polymerized OMCTS (plasma polymer) was synthesized as a host polymer. This ultra-thin plasma polymer

---

*Author to whom correspondence should be addressed.

was hybridized with PPO and $LiClO_4$ to form an ultra-thin film of solid polymer electrolyte.

. All-solid-state, rechargeable lithium batteries were prepared using this hybrid film (2 - 3 μm). A thin film of CVD TiS_2 (10 - 15 μm) was selected as the cathode active material.

Experimental

The apparatus used for depositing polymer films by plasma polymerization is described elsewhere [8]. The system consists of a glass reactor (9 cm dia. and 35 cm high) equipped with capacitively-coupled inner electrodes connected to an RF power supply (13.56 MHz), a monomer inlet, a Pirani gauge, and a vacuum pump. A TiS_2 film on borosilicate glass was employed as the substrate which was placed between the electrodes. OMCTS [2 cm^3 (STP) min^{-1}] and argon gas [10 cm^3 min^{-1}] were introduced into the glass reactor and RF power of 5 W was applied. The pressure was controlled at 0.5 Torr by regulation of a needle valve.

The plasma polymerized OMCTS (plasma polymer) was selected as host polymer because of its low glass transition temperature (T_g). The plasma polymer was soaked in butanol–PPO[M.W. 4000]–$LiClO_4$ solution for more than 1 h to attain equilibrium, and then dried under vacuum (10^{-3} Torr) for 24 h at 80 °C. The concentration of lithium ion in the plasma polymer–PPO mixture was determined by atomic absorption spectrophotometric measurement. The ionic conductivity of the hybrid polymer electrolyte (plasma polymer–PPO–$LiClO_4$) was estimated over the frequency range 2×10^2 - 2×10^4 Hz, by an a.c. impedance measurement, using a vector impedance meter.

A thin film of TiS_2 for the positive active mass of the solid-state lithium batteries was grown 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. TiS_2 films deposited by this method are nearly stoichiometric with predominant (110) orientation [9].

The all-solid-state lithium battery, of a simple disk sandwich structure, is shown in Fig. 1. All experiments were carried out under argon atmosphere.
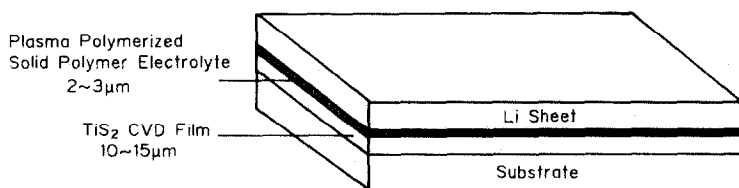

Fig. 1. A schematic diagram of an all-solid-state Li/TiS_2 battery with plasma polymerized solid polymer electrolyte.

Results and discussion

The characterization of the plasma polymer is not easy. Its FT–IR spectra were very similar to that of poly(dimethylsiloxane), and there are many common absorption bands. These observations suggest that the general structure of the plasma polymer is similar to that of poly(dimethylsiloxane).

The complex impedance plot of Au/hybrid-polymer-electrolyte/Au, gave two arcs. The first, in the high frequency range, could be attributed to bulk electrolyte impedance. The arc was extrapolated to the real axis to obtain bulk electrolyte resistance.

Figure 2 shows the temperature dependence of the ionic conductivity of the hybrid polymer electrolyte [plasma polymer/PPO/LiClO$_4$ = 78/20/ 2 wt.%]. The conductivities were estimated from the complex impedance measurements, and correspond to film resistances in the range of 30 Ω - 3 kΩ. The temperature dependence of the ionic conductivity showed a WLF-type [10, 11] profile rather than that of the Arrhenius type. The conductivity of the hybrid polymer electrolyte reached 2.6 $\times$ 10^{-6} S cm^{-1} (40 Ω cm^{-2}) at 60 °C. The ionic conductivity of this hybrid polymer electrolyte is comparable with the ionic conductivity of PEO or PPO with lithium salts [1 - 3]. It is considered that the hybrid polymer electrolyte has a microheterogeneous structure (plasma polymerized OMCTS segment–PPO segment), and that the PPO segment contributes mainly to the ionic dissociation of LiClO$_4$ [12].

Figure 3 shows an SEM photograph of the cross-section of a solid state battery without a lithium layer. The Figure shows that the TiS$_2$ CVD film is about 15 μm thick; the hybrid polymer electrolyte layer is about 2 μm thick, uniform, pin-hole free, and completely covering the TiS$_2$ film.
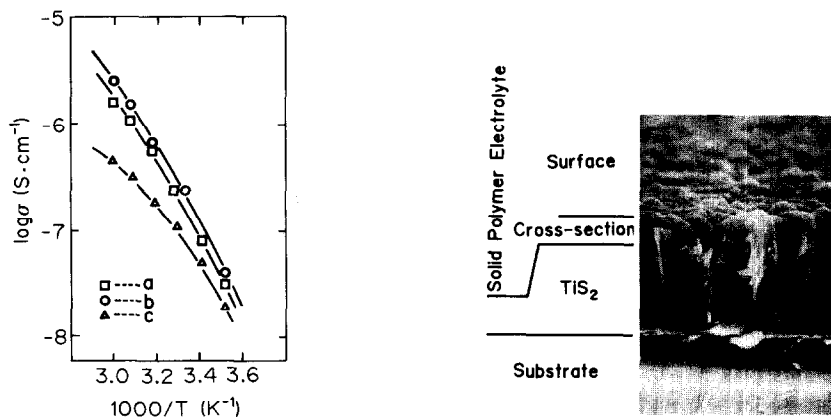

Fig. 2. Ionic conductivity dependence of plasma polymerized solid polymer electrolyte containing PPO (20 wt.%) and LiClO$_4$ (a: 4 wt.%, b: 2 wt.%, c: 1 wt.%) on temperature.

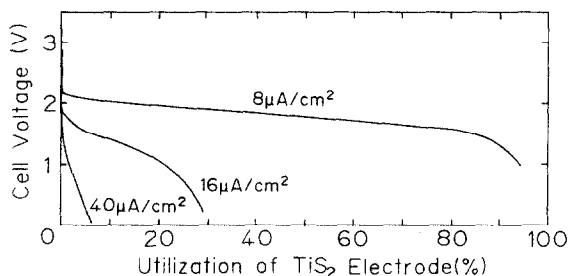Fig. 3. SEM photographs of the cross-section of all-solid-state battery other than for a lithium layer.

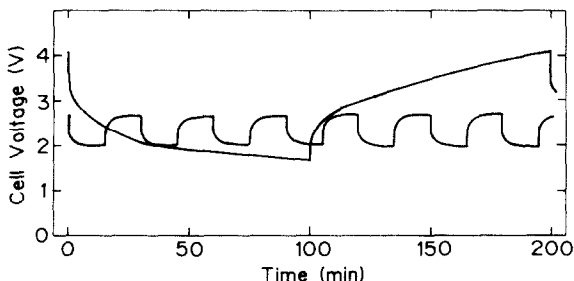Fig. 4. Utilization of all-solid-state lithium batteries *vs.* discharge current densities at room temperature.

Fig. 5. Charge/discharge cycle for all-solid-state lithium battery at room temperature. Discharge current: 16 μA cm^{-2}; charge current: 16 μA cm^{-2}.

The first discharge performances of cells at room temperature and at various current densities are given in Fig. 4. At a low current density of 8 μA cm^{-2}, the discharge curve plateau extends to 85% of TiS$_2$ utilization (to LiTiS$_2$). However, the internal resistance of this battery is fairly large. It is considered that the solid polymer electrolyte is not in close contact with the lithium electrode. In Fig. 5, the charge–discharge curves are shown. The cells were cycled at 16 μA cm^{-2}. The fairly good rechargeability of the battery is confirmed by Fig. 5.

References

1 D. E. Fenton, J. M. Parker and P. V. Wright, *Polymer, 14* (1973) 589.
2 P. V. Wright, *Br. Polym. J.,* 7 (1975) 319.
3 M. B. Armand, J. M. Chabagno and M. J. Duclot, in P. Vashista, J. M. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids,* Elsevier, New York, 1979, p. 131.
4 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* (1985) 1333.
5 H. Ohno, H. Matsuda, K. Mizoguchi and E. Tuchida, *Polym. Bull.,* 7 (1982) 271.
6 A. Hooper and J. M. North, *Solid State Ionics, 9&10* (1983) 1161.
7 K. M. Abraham, M. Alamgir and S. J. Perrotti, *J. Electrochem. Soc., 135* (1988) 535.
8 Y. Uchimoto, Z. Ogumi and Z. Takehara, *J. Electrochem. Soc., 136* (1989) 625.
9 Y. Kanamori, Z. Ogumi and Z. Takehara, *GS News, 46* (1987) 21.
10 M. L. Williams, R. F. Randel and J. D. Ferry, *J. Am. Chem. Soc.,* 77 (1955) 3701.
11 M. Cohen and D. Turnbull, *J. Phys. Chem., 31* (1959) 1164.
12 M. Watanabe, S. Nagano, K. Sanui and N. Ogata, *J. Power Sources, 20* (1987) 327.