Preparation of Ultra-thin Solid-state Lithium Batteries utilizing a Plasma-polymerized Solid Polymer Electrolyte

Zempachi Ogumi,*[a] Yoshiharu Uchimoto,[a] Zen-ichiro Takehara,[a] and Yoshinori Kanamori[b]

[a] *Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan*
[b] *Japan Storage Battery Company, Limited, Nishinosho, Kisshoin, Minami-ku, Kyoto 601, Japan*

Ultra-thin solid-state lithium batteries were fabricated using a thin polymer electrolyte film prepared by hybridization of the plasma polymer formed from tris(2-methoxyethoxy)vinylsilane and $LiClO_4$, a thin TiS_2 film prepared by chemical vapour deposition as a cathode active material, and a vapour-deposited lithium thin film.

Recently, considerable attention has been focused on the preparation of solid-state lithium batteries utilizing solid polymer electrolytes.[1—3] Unmodified forms of these materials have low conductivities and one way of decreasing the electrolyte resistance is to use ultra-thin films as described previously.[4—7] In this communication we describe the fabrication of thin solid-state lithium batteries using consecutive vapour-phase deposition techniques.

The apparatus used for the plasma polymerization has been described elsewhere.[4] The glass reactor (9 cm diam. × 35 cm height) was equipped with two inner parallel electrodes (each 28.3 cm^2, with an electrode gap of 3.5 cm) connected to an RF supply (13.56 MHz). The remainder of the system consisted of a monomer inlet, a Pirani gauge, and a vacuum pump. A TiS_2 film was deposited onto a borosilicate glass surface from $TiCl_4$ and H_2S using a low-pressure thermal chemical vapour deposition (CVD) technique. This film was nearly stoicheiometric ($Ti_{1.03}S_2$) and had a predominant (110) orientation. The TiS_2 film was used as the substrate for an ultra-thin solid polymer electrolyte film, which was prepared as follows.[6] The substrate was placed between the electrodes and plasma assist gas [Ar, 10 cm^3 (STP)/min] and tris(2-methoxyethoxy)vinylsilane [1 cm^3 (STP)/min] were introduced. The pressure was maintained at 0.3 Torr. RF power of 5 W was then applied across the electrodes, and a polymer layer about 0.5—1.0 μm thickness was deposited. The treated substrate

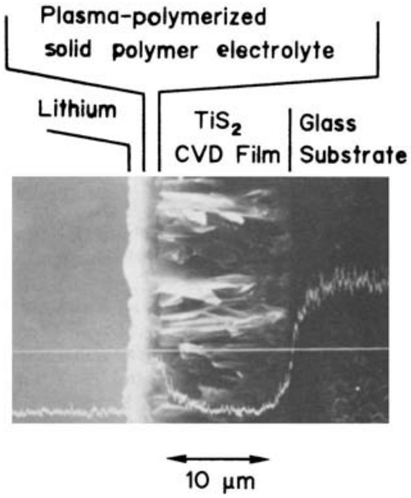

Figure 1. Scanning electron micrograph of the cross-section of the thin solid-state lithium battery (Si *X*-ray line).

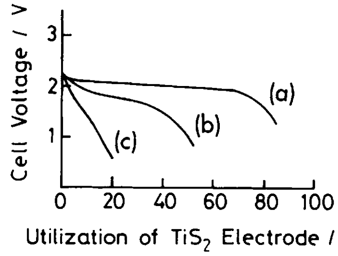

Figure 2. Utilization curves of thin solid-state lithium batteries at different discharge current densities at room temperature. (a): 10, (b): 20, (c): 40 μA/cm^2.

was removed from the reactor and sprayed with methanol containing 3% $LiClO_4$ at 60 °C under reduced pressure (10—300 Torr) in order to deposit a $LiClO_4$ layer. The substrate was then returned to the reactor and further deposited with a second plasma polymer layer (0.5—1.0 μm) in the same manner. The resulting three-layered composite was maintained at 80 °C for 24 h under 10^{-3} Torr in order for the $LiClO_4$ to be distributed uniformly throughout the plasma polymer. This treatment led to the formation of an ultra-thin solid polymer electrolyte layer (1—2 μm) deposited on the TiS_2 CVD film. This film exhibited a conductivity between 10^{-5} and 10^{-6} S cm^{-1} at room temperature. The resistance of the film was calculated to be about 10—100 Ω cm^2. Finally a lithium layer (various thicknesses) was thermally vapour-deposited onto the electrolyte film. The above process produced an all-solid-state lithium battery which consisted of the CVD TiS_2 film as cathode, the plasma-polymerized solid polymer film as electrolyte, and the thermally vapour-deposited lithium layer as anode.

Figure 1 shows the scanning electron micrograph of a cross-section of battery. The TiS_2 CVD film is about 12 μm thick, and is covered with the plasma-polymerized solid polymer electrolyte (~1.5 μm thick) and the lithium layer (~1.5 μm).

The discharge characteristics of these batteries were examined at different discharge current densities (effective surface area 0.5 cm^2) at room temperature. The results are shown in Figure 2. The discharge curves imply a fairly high internal resistance, possibly due to the formation of a resistive layer at the interface between the lithium and the electrolyte layer. At a low current density of 10 μA/cm^2, this battery showed high performance and applicability as a practical battery.

This type of battery is rechargeable and its rechargeable performance is now under investigation.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture in Japan (No. 63430015).

Received, 5th July 1989; Com. 9/02848J

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.*, 1985, **132**, 1333.
2 K. M. Abraham, M. Alamgir, and S. J. Perrotti, *J. Electrochem. Soc.*, 1988, **135**, 535.
3 Z. Ogumi, Y. Uchimoto, Z. Takehara, and Y. Kanamori, *J. Electrochem. Soc.*, 1988, **135**, 2649.
4 Z. Ogumi, Y. Uchimoto, and Z. Takehara, *J. Electrochem. Soc.*, 1989, **136**, 625.
5 Z. Ogumi, Y. Uchimoto, and Z. Takehara, *Chem. Lett.*, 1988, 1811.
6 Z. Ogumi, Y. Uchimoto, and Z. Takerhara, *J. Chem. Soc., Chem. Commun.*, 1989, 358.
7 Z. Ogumi, Y. Uchimoto, and Z. Takehara, *J. Electrochem. Soc.*, in the press.