A Novel Thin Film of a Solid Polymer Electrolyte composed of Plasma-polymerized Tris(2-methoxyethoxy)vinylsilane–$LiClO_4$ Hybrid

Zempachi Ogumi,* Yoshiharu Uchimoto, and Zen-ichiro Takehara

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

A novel ultra-thin film of a solid polymer electrolyte with high ionic conductivity has been synthesized by hybridization of plasma-polymerized tris(2-methoxyethoxy)vinylsilane and $LiClO_4$; the resulting hybrid film exhibits a conductivity of higher than 10^{-6} S cm^{-1} at room temperature.

Solid polymer electrolytes prepared by the treatment of polyethers with alkali metal salts have received considerable attention[1,2] owing to their wide application in electrochemistry. Among these polymers, polyethers containing siloxane units are attractive[3—7] because it is known that the introduction of siloxane units into the polymer leads to a low glass transition temperature, which favours the enhancement of the ionic conductivity of the solid polymer electrolyte.[8] Ionic conductivities of these solid polymer electrolytes are typically 10^{-6}—10^{-8} S cm^{-1} at room temperature. Since these values are lower than those of typical liquid electrolytes,[9] in order to use solid polymer electrolyte films for practical electrochemical devices it will be necessary to decrease their practical operating resistance. Thin films of solid polymer electrolytes should meet this requirement. Plasma polymerization is a useful method to deposit a uniform, ultra-thin polymer film on various substrates. This communication reports on the production of ultra-thin (~1 µm) solid polymer electrolyte films prepared by the hybridization of plasma-polymerized tris(2-methoxyethoxy)vinylsilane and $LiClO_4$; the resulting solid polymer electrolyte films exhibit conductivities of greater than 10^{-6} S cm^{-1} at room temperature.

The system for plasma-deposition of polymers consists of a glass reactor equipped with capacitively coupled inner electrodes connected to an RF supply (13.56 MHz), a monomer inlet, a Pirani gauge, and a vacuum pump.[10] Substrates are placed between the electrodes. Figure 1 shows a diagram of the process for the synthesis of a solid polymer electrolyte film.

Glass plates deposited with gold were utilized as the substrate. Argon gas [10 cm^3 (STP)/min] and tris(2-methoxyethoxy)vinylsilane vapour [1 cm^3 (STP)/min] were introduced into the glass reactor. The pressure in the reactor was maintained at 0.3 Torr by controlling a valve connected to the vacuum pump. Under these conditions, RF power of 5 W was turned on. The resulting plasma polymer layer was about 0.5 µm thick. Then the substrate was removed from the reactor and sprayed with methanol containing 3% $LiClO_4$ at 60 °C in order to deposit a $LiClO_4$ layer. The substrate was then again placed between the electrodes and further deposited with plasma polymer (~0.5 µm) (Figure 1a). The resulting three-layer composite (plasma polymer–$LiClO_4$–plasma polymer) was maintained at 80 °C for 24 h under 10^{-3} Torr in order to distribute the $LiClO_4$ uniformly in the plasma polymer (Figure 1b). This treatment led to an ultra-thin (~1 µm) film of solid polymer electrolyte [plasma-polymerized tris(2-methoxyethoxy)vinylsilane–$LiClO_4$ hybrid] (Figure 1c).

The $LiClO_4$ content of the film was determined by atomic absorption spectrophotometry. The ionic conductivity of the solid polymer electrolyte was estimated by an AC impedance measurement over the frequency range of 2×10^2—2×10^4 Hz using a vector impedance meter. Prior to the measurement, gold was deposited on the surface of the solid polymer electrolyte.

The i.r. spectrum of the plasma polymer was similar to that of tris(2-methoxyethoxy)vinylsilane, except for the complete absence of the characteristic peak for the alkene group. Therefore it was concluded that the plasma polymer was quite similar to poly[tris(2-methoxyethoxy)vinylsilane]. Electron probe microanalysis (EPMA) measurements showed that the distributiton of Cl (ClO_4^-) was almost uniform across the cross-section of the solid polymer electrolyte; *i.e.*, lithium ions were distributed uniformly in the polymer film to satisfy the requirement for electroneutrality. A cross-sectional scanning electron micrograph showed that the solid polymer electrolyte film was about 1 µm thick and pinhole-free within the scale of the observations.

Figure 2 shows the temperature dependence of the ionic conductivity as well as the apparent electrical resistance of the solid polymer electrolyte film (~1 µm thick) containing 7 wt% $LiClO_4$. The temperature dependence of the ionic conductivity exhibits a Williams–Landel–Ferry (WLF)-type[11,12] dependence rather than an Arrhenius-type one. The conductivity of the solid polymer electrolyte film reached a maximum value of

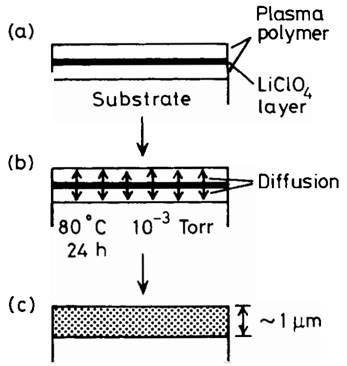

Figure 1. Schematic diagram of the process for synthesis of thin films of solid polymer electrolyte by polymerization.

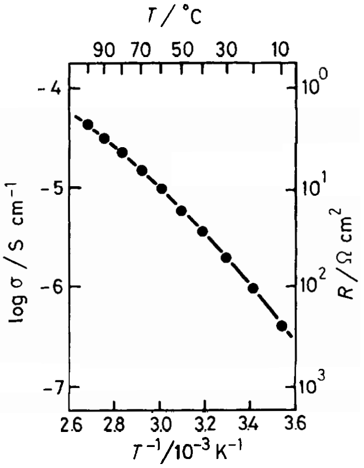

Figure 2. Temperature dependence of ionic conductivity of solid polymer electrolyte containing 7 wt% $LiClO_4$.

4.4×10^{-5} S cm^{-1} (2.3Ω per 1 cm^2) at 100 °C. This solid polymer electrolyte was pinhole-free and was of uniform film thickness. Therefore it is promising for a wide range of electrochemical applications.

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