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Fast lithium ion conducting solid state thin-film electrolytes based on lithium thio-germanate materials

Inseok Seo, Steve W. Martin [*]

Department of Materials Science and Engineering, Iowa State University, 2220 Hoover Hall, Ames, IA 50011, USA

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Abstract

In this study, lithium thio-germanate thin-film electrolytes for lithium rechargeable batteries have been successfully prepared by radio-frequency (RF) magnetron sputtering deposition in Ar gas atmospheres. The targets for RF sputtering were prepared by melting, milling and pressing the appropriate amounts of the starting materials in the $n\mathrm{Li_2S} + \mathrm{GeS_2}$, $n = 1$–4, binary system. 2 mm wide × 18 mm long Au electrodes with a parallel configuration of 2 mm spacing were sputtered to ~100 nm thick at a sputtering rate at ~5 nm min^{-1} on Al_2O_3 single crystal substrates. Thin-film electrolytes were grown on this electrode assembly at 50 W power and 25 mtorr in Ar gas pressure. The ionic conductivities of the thin-film electrolytes were measured from −25 °C to 100 °C with 25 °C increments over the frequency range 0.1 Hz–1 MHz. The d.c. ionic conductivities determined from complex plane plots of the impedance of the Li_2GeS_3, Li_4GeS_4, Li_6GeS_5, and Li_8GeS_6 amorphous thin films at 25 °C were found to be 1.1×10^{-4} S cm^{-1}, 7.5×10^{-4} S cm^{-1}, 1.7×10^{-3} S cm^{-1}, and 7.0×10^{-5} S cm^{-1}, respectively. As the Li_2S content in the thin film increases, the ionic conductivities of the thin films increase from $n = 1$ to $n = 3$. However, for the $n = 4$ Li_8GeS_6 thin film, the ionic conductivity decreased and the activation energy increased. The maximum in the conductivity for the $n = 3$ film is among the highest ever reported for an amorphous solid state Li^+ ion conductor.
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Keywords: Thin-film electrolyte; RF sputtering; Solid state battery; Ionic conductivity; Thio-germanate

1. Introduction

The enormous growth in portable consumer electronic devices such as mobile phones, laptop computers, digital cameras, and personal digital assistants over the past decade has generated a large interest in compact, high-energy-density and lightweight batteries. As power requirements become more demanding, batteries are also expected to provide higher energy densities. Lithium-based batteries have begun to fill this need due to the high theoretical capacity of Li [1]. Further, lithium is very lightweight and has a high electrochemical equivalency and these properties make lithium an attractive battery anode. Therefore, rechargeable lithium batteries are attractive for numerous reasons: high voltages, high energy densities, wide operating temperature ranges, good power density, flat discharge characteristics, and excellent shelf life. Due to these many advantages of lithium metal, much effort has been expanded to develop rechargeable lithium batteries for use in a wide variety of applications.

Although the implementation of lithium metal as the anode material in lithium batteries is attractive, electrolytes with high ionic conductivity that are stable in contact with metallic lithium are still lacking. Around 10 years ago, lithium batteries with lithium metal anodes using liquid electrolytes, which show the highest ionic conductivities, failed because of serious safety issues [2]. Lithium metal anodes tend to form dendrites during charging and discharging due to plating-out reactions between lithium metal and liquid electrolytes [3]. For these reasons, lithium-based solid state electrolytes instead of liquid

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[*] Corresponding author. Tel.: +1 515 294 0745; fax: +1 515 294 5444.
E-mail address: swmartin@iastate.edu (S.W. Martin).

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electrolytes are attractive and many researchers have been interested in incorporating them in solid state batteries because solid electrolytes do not have the aforementioned safety issues and show a smaller temperature dependence on the ionic conductivity compared to some liquid electrolytes. In addition, with the recent surge in interest of various kinds of portable electronic devices and electric and hybrid-electric vehicles, the importance of portable energy sources like secondary batteries has increased. It is widely recognized that all-solid-state energy devices show promise towards improving the safety and reliability of lithium batteries.

Although solid state thin-film batteries have many advantages over competitive batteries, solid electrolytes must have improved ionic conductivity for them to succeed in being applied commercially. Solid electrolytes are a key material of all-solid-state energy devices and have been extensively studied in the fields of materials science [4], polymer science [5], and electrochemistry [6]. Much research has been devoted to the preparation of solid electrolytes made of various materials including ceramics [7], glasses [8,9] and organic polymers [10].

Among these materials for electrolytes, amorphous or glassy materials often have superior ionic conductivities over corresponding crystalline materials because they can form over a wide range of compositions, have isotropic properties, do not have grain boundaries, and can form thin films easily. Because of their open disordered structure, amorphous materials typically have higher ionic conductivities than the corresponding crystalline material [11–13]. In addition, single ion conduction can be realized because glassy materials belong to decoupled systems in which the mode of ion conduction relaxation is decoupled from the mode of structural relaxation [14].

Amorphous or glassy materials are thus among the more promising candidates of solid electrolytes because of their properties of single ion conduction and high ionic conductivities.

Oxide-based electrolytes are currently widely studied because of their stability in air, easy preparation, and their long shelf life. However, they show a critical disadvantage, which is low ionic conductivity. “LiPON” films formed from sputtering Li_3PO_4 in N_2 atmospheres are currently one of the primary solid state thin-film electrolytes in use because of these above-mentioned advantages [15–18]. However, this easily prepared material has a relatively low Li^+ ion conductivity of $\sim 10^{-6}$ S cm^{-1} at 25 °C as compared to sulfide-based materials whose Li^+ conductivities are in the range of 10^{-3} S cm^{-1} at 25 °C [19–21].

Because lithium-containing thio-materials show higher ionic conductivity than corresponding oxide materials, much research has been conducted on using the thio-materials as solid electrolytes [22]. Recently, sulfide materials, such as SiS_2 [23], GeS_2 [24–25], P_2S_5 [26], and B_2S_3 [27], have been investigated. Among these sulfide materials, this study uses GeS_2 as a base material because it is less hygroscopic, more oxidatively stable and enables a more electrochemically stable matrix for lithium ion conduction to be prepared.

Since the GeS_2-based materials are more stable in air than other sulfide materials, GeS_2-based $n\mathrm{Li_2S} + \mathrm{GeS_2}$, $n = 1$–4, thin-film electrolytes for Li-ion thin-film batteries were grown by RF magnetron sputtering techniques in Ar atmospheres. In order to determine if a maximum conductivity in the $n\mathrm{Li_2S} + \mathrm{GeS_2}$ system exists, the Li_2S content ranged from $n = 1$ to $n = 4$, 50% Li_2S to 80% Li_2S. Ionic conductivities of the thin films were characterized by impedance spectroscopy. The ionic conductivities were measured over the temperature range from −25 °C to 100 °C in 25 °C increments and over the frequency range from 0.1 Hz to 1 MHz.

2. Experimental methods

2.1. GeS_2 starting material preparation

Glassy GeS_2 was prepared by reacting stoichiometric amounts of germanium metal powder (Alfa, 99.999%) and sulfur (Alfa, 99.999%) in an evacuated silica tube at 900 °C. First, a bare silica tube was cleaned with a 2% aqueous ammonium bifluoride, NH_4HF_2, solution and rinsed with deionized water. The tube was then fitted with a valve assembly and evacuated to 30 mtorr (~4 Pa) through a liquid nitrogen trap using a roughing pump. Surface moisture on the inside of the tube was then removed by passing the tube over a natural gas–oxygen flame. Once this moisture was removed, the valve was closed and the tube was transferred to the glove box where a mixture of appropriate amounts of Ge and S were placed into the tube. The tube was then reconnected to the valve assembly, the valve was closed, and the tube was removed from the glove box and evacuated with the roughing pump again to a pressure of ~30 mtorr (~4 Pa). Following evacuation, the tube was sealed using a natural gas–oxygen torch.

The sealed tube was then placed into a furnace held at an angle of ~5° where it was heated at a rate of 1 °C min^{-1} from room temperature to 900 °C. The tube was rotated at ~7 rpm to promote mixing and reaction of the components. After the tube was held at 900 °C for 16 h, it was air quenched to room temperature. The air quenched GeS_2 material inside the silica tube was put into the glove box and the silica tube was broken to remove the GeS_2 glass product. The final product from this process was a homogeneous transparent yellow colored glass.

2.2. Target materials preparation

To make the Li_2GeS_3, Li_4GeS_4, Li_6GeS_5, and Li_8GeS_6, $n = 1$–4 in $n\mathrm{Li_2S} + \mathrm{GeS_2}$, target materials, stoichiometric amounts of Li_2S (Alfa, 99.9%) and GeS_2 were used. These powders were vibratory Spex milled for 15 min in a steel container with one steel grinding ball inside the glove box to ensure good mixing and to start the reaction process. Batches of 3–4 g were melted in a covered vitreous carbon