



Characterization of thin-film electrolytes for all solid-state batteries



Inseok Seo ^{a,*}, Youngsik Kim ^b, Steve W. Martin ^{c,**}

^a Research Institute of Industrial Science and Technology, POSCO Global R&D Center, 180-1 Songdo-Dong, Yeonsu-Gu, Incheon, 406-840, Republic of Korea

^b School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology, UNIST-gil 50, Ulsan, 689-798, Republic of Korea

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

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ABSTRACT

In this study, amorphous lithium thio-germanate thin-films were prepared as electrolytes for solid-state lithium rechargeable batteries by using RF sputtering deposition in an Ar atmospheres. High quality lithium germanium sulfide, $n\text{Li}_2\text{S} + \text{GeS}_2$ ($n = 1, 2, \text{ and } 3$) thin-films have been successfully made by RF sputtering and synthesized as solid-state electrolytes. Although these materials are unstable in air the thin-films were thoroughly characterized by X-ray diffraction (XRD), Scanning electron spectroscopy (SEM), Raman spectroscopy, Infrared spectroscopy (IR), and impedance spectroscopy using special setups to prevent contamination. The ionic conductivities of the thin-films are ~ 3 order magnitude higher than reported values for oxide thin-films. In this way, this work may provide a new way for developing new thin-film electrolytes for solid-state lithium ion batteries.

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1. Introduction

Renewable energy harvesting, conversion, storage, and distribution are of great interest due to demand created by portable electronics, transportation, and ESS (energy storage system) [1–3]. 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 metal [4]. Further, lithium is very lightweight and has a high electrochemical equivalency and these properties make lithium an attractive battery anode. Therefore, rechargeable lithium batteries using lithium metal as an anode are attractive for numerous reasons: high voltages, high energy densities, wide operating temperature ranges, 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 a lithium metal is attractive as an anode, electrolytes with high ionic conductivity that are stable in contact with metallic lithium are still lacking. Around 10 years ago, lithium batteries using a lithium metal as an anode with liquid electrolytes failed because of serious safety issues

[5]. Lithium metal anodes tend to form dendrites during charging and discharging due to plating-out reactions between lithium metal and liquid electrolytes [6]. For these reasons, many researchers have been studied solid electrolytes instead of liquid electrolytes. Solid electrolytes do not have the aforementioned safety issues and show a smaller temperature dependence on the ionic conductivity compared to some liquid 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, and do not have grain boundaries. Because of their open disordered structure, amorphous materials typically have higher ionic conductivities than the corresponding crystalline materials [7–9]. 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.

Recently, as the increasing tendency of many advanced technologies is aiming at smaller dimensions with higher power densities. The development of technologies and miniaturization in the microelectronic industry has reduced the power and current requirements of electronic devices. Therefore, thin-film batteries are of interest in small power electronics such as smart cards and other CMOS-based integrated circuit applications [10,11]. In addition, thin-film batteries have lower temperature dependencies and are able to resolve many of the safety issues of lithium batteries using liquid electrolytes [4]. Although thin-film batteries have many

* Corresponding author. Tel.: +82 32 200 2314; fax: +82 32 200 2339.

** Corresponding author. Tel.: +1 515 294 0745; fax: +1 515 294 5444.

E-mail addresses: isseo@rist.re.kr (I. Seo), swmartin@iastate.edu (S.W. Martin).

advantages over competitive batteries, solid electrolytes must have improved ionic conductivity for them to succeed in being applied commercially.

Thin-film batteries have been studied for many years and thin-film solid state batteries using LiPON (lithium phosphorus oxynitride) solid electrolytes have become commercial products [12,13]. LiPON thin-films have been shown to have good stability in contact with lithium and have high cyclability [14]. However, this easily prepared material has a relatively low Li-ion conductivity of $\sim 10^{-6}$ (S/cm) at 25 °C as compared to other solid electrolytes such as sulfides whose Li-ion conductivities are in the range of 10^{-3} (S/cm) at 25 °C [15–17]. Recently, sulfide materials have been investigated such as SiS_2 [18], GeS_2 [19], P_2S_5 [20] and B_2S_3 [21]. 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 $n\text{Li}_2\text{S} + \text{GeS}_2$ ($n = 1, 2,$ and 3) thin-film electrolytes for Li-ion thin-film batteries were grown by RF magnetron sputtering techniques in an Ar atmospheres.

In this research, in order to fabricate solid state electrolytes of high ionic conductivity, sulfide-based $n\text{Li}_2\text{S} + \text{GeS}_2$ ($n = 1, 2,$ and 3) thin-film electrolytes were grown by RF magnetron sputtering in Ar atmospheres. Structural properties, compositional properties, and the ionic conductivity were characterized by XRD, Raman spectroscopy, IR, FE-SEM, and impedance spectroscopy.

2. Experimental procedures

2.1. GeS_2 preparation as a starting material

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. Surface moisture on the inside of the tube was then removed under roughing pump vacuum by passing the tube over a natural gas/oxygen flame. The tube was sealed using a high-temperature the natural gas/oxygen torch under vacuum. The sealed tube was then placed into a furnace held at an angle of $\sim 5^\circ$ where it was heated at a rate of 1 °C/min from room temperature to 900 °C. After the tube was held at 900 °C for 16 h, it was quenched in air to room temperature. The final product from this process was a homogeneous, transparent, and yellow glass.

2.2. Preparation of target materials

To make the Li_2GeS_3 , Li_4GeS_4 and Li_6GeS_5 ($n = 1, 2,$ and 3) target materials for the sputtering, stoichiometric amounts of Li_2S (Alfa, 99.9%) and GeS_2 (as prepared above) powders were used. Batches of 3–4 g were melted in a covered vitreous carbon crucible at 950 °C for 15 min inside a mullite tube lined muffle furnace attached hermetically to the side of a glovebox. The melted charge was poured out of the crucible onto a brass plate and allowed to cool to room temperature. Fifteen grams of the powder was prepared in this way and weighed out and poured into a hardened 2" diameter steel die set. The top press was placed into the die set and allowed to settle on top of the powder. This assembly was sealed inside a plastic bag to prevent contamination (oxidation) during the consolidation process and taken outside the glovebox to be uniaxially pressed. The target was then adhered to a 2" diameter and 0.125" thick copper backing plate using silver paste so that it could be water-cooled during the RF deposition process to prevent overheating.

2.3. Preparation of Ni/Si substrates for Raman spectroscopy characterization

The cleaned silicon substrates with sizes of 1 cm \times 1 cm \times 360 μm were loaded into a d.c. sputtering chamber in the glovebox and a Ni adhesion layer of ~ 120 nm thickness was grown in ~ 40 min at ~ 3 nm/min on the surface of the silicon substrates. The Ni/Si substrates then were loaded into the RF magnetron sputtering chamber on which the thin-films were grown.

2.4. Deposition of the thin-films

After pumping down the chamber to ~ 10 – 11 Pa and baking the chamber with heating tapes to drive off moisture, the chamber was filled high purity Ar gas (99.9999%) to ~ 100 mtorr (~ 13 Pa) and the plasma was lit by turning on the RF power to the target. Pre-sputtering was performed to remove moisture contamination on the surface and the deposition of the thin films continued. All thin films were produced with a power of 50 W and a 25 mtorr (~ 3.3 Pa) dynamic pressure of the Argon sputtering gas.

2.5. X-ray diffraction

X-ray diffraction powder patterns were collected on finely ground samples at room temperature using a Scintag XDS 2000 diffractometer using CuK_α radiation ($\lambda = 1.5406$ Å). It was operated at 40 kV and 30 mA in the 2θ range of 30° – 80° in continuous scan mode with step size 0.03° and scan rate 2.0 deg/min.

2.6. Raman spectroscopy

The Raman spectra were collected at room temperature with a Renishaw inVia spectrometer using the 488 nm line of an Ar^+ laser at 50 mW power. The instrument was calibrated using an internal silicon reference and the band positions were accurate to within ± 1 cm^{-1} . The samples were placed into a small cup-like plastic sample holder and then covered with clear amorphous tape to

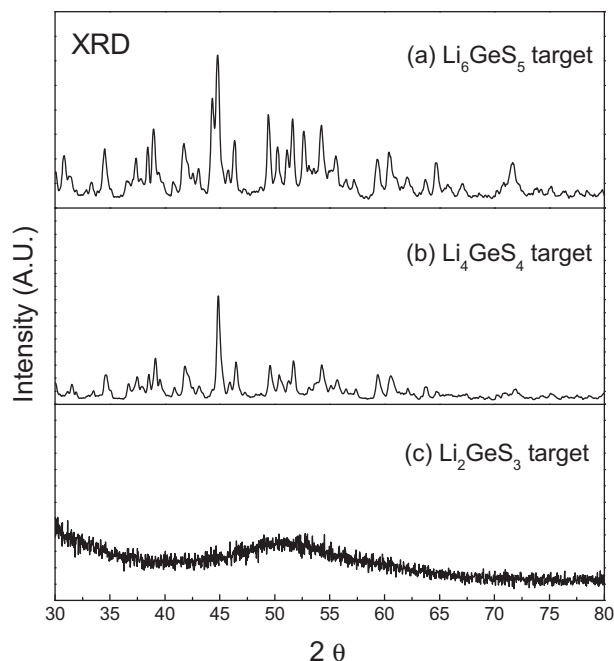


Fig. 1. X-ray diffraction data of (a) Li_2GeS_3 , (b) Li_2GeS_3 and (c) Li_2GeS_3 bulk materials.

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