Advanced amorphous thin film electrolytes for the solid state batteries

In-Seok Seo[2]*, and Steve. W. Martin[1]

[1]Department of Materials Science and Engineering Iowa State University, Ames, Iowa 50010, USA
[2]Secondary Battery Research Team, Research Institute of Industrial Science and Technology, San 32 Hyoja dong, Nam-gu, Pohang, North Gyeongsang Province
* Corresponding author, Phone : +82-54-279-6938
E-mail : isseo@rist.re.kr

Recent developments in electronic devices such as smart cards, mobile phones, laptop computers and microchemical systems require new small energy sources with high power capacity. A thin film lithium ion battery is one of the powerful candidates for satisfying these demands and has a good stability at elevated temperature conditions. In order to meet the requirements of recent electronic devices using high quality Li-ion rechargeable batteries, improved electrolytes are required.

In this study, lithium thio-germanate thin amorphous films were prepared as electrolytes for lithium rechargeable batteries by RF sputtering deposition in Ar atmosphere. The targets for RF sputtering were prepared by milling the appropriate amounts of the starting materials in the $nLi_2S + GeS_2$(n = 1, 2 and 3), Li_2GeS_3, Li_4GeS_4 and Li_6GeS_5, binary system. The ~1 μm thin film electrolytes were grown onto a variety of substrates using 50 Watt power and 30 mtorr gas pressure. The sputtering conditions were optimized and the samples were handled with care at every processing step to minimize contamination by moisture and air. X-ray diffraction (XRD) was used to determine if the starting and target materials were of high purity and their degree of crystallinity.

Raman and IR spectroscopies were used to characterize the chemical bonding in the films. From the Raman spectroscopy, the thin films are amorphous. By using FE-SEM, the surface morphology and sputtering rates were determined and smooth surfaces were found to deposite at ~1 nm/min. The compositions of and chemical speciation in lithium thio-germanate thin films were determined by means of x-ray photoelectron spectroscopy (XPS). The Li_2GeS_3 (n=1) thin film was found as expected to exhibit a 2 : 1 (NBS : BS) ratio. As the Li_2S content increased, the Li_4GeS_4 and Li_6GeS_5 thin films exhibited also as expected, 100 % NBS. For the S2p core peaks, the binding energy of S in GeS_2 is the highest due to the nearly covalent bonding in the BS structure, ≡Ge-S-Ge≡. As the Li_2S content increased, the binding energy of S in the thin films progressively decreased due to the progressive increase in the fraction (and number) of NBS (more ionic), $\equiv Ge\text{-}S^-Li^+$, in the films.

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 to 1 MHz. The d.c. ionic conductivities, determined from complex plane plots of the impedance of the Li_2GeS_3, Li_4GeS_4, and Li_6GeS_5 amorphous thin-films at 25 °C, were found to be 1.1×10^{-4} S/cm, 7.5×10^{-4} S/cm, and 1.7×10^{-3} S/cm, respectively. The ionic conductivities of the thin-films at 25 °C are the highest reported for Li^+ ions in a glassy material and are at least two orders of magnitude higher than those of commercial LiPON thin-film electrolytes.

This means that the thin-films materials are stable over wide temperature ranges, so that it can be assumed that the lithium ion batteries based on these sulfides materials are very stable over wide temperature ranges and are very promising to apply to commercial products.