Electrochemical and interfacial behavior of all solid state batteries using $Li_{10}SnP_2S_{12}$ solid electrolyte

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HIGHLIGHTS

- Successfully utilizing $Li_{10}SnP_2S_{12}$ solid electrolyte in all-solid-state batteries.
- Atomic inter-diffusion between LCO and LSPS causes a poor cycling stability.
- Li_3NbO_4 coating improves the performance of the LCO/LSPS solid state batteries.

ARTICLE INFO

ABSTRACT

Thio-Lithium Superionic Conductor (Thio-LISICON) $Li_{10}GeP_2S_{12}$ equivalent $Li_{10}SnP_2S_{12}$ (LSPS) is comparable in ionic conductivity yet with a lower cost as an electrolyte for all solid-state batteries (ASSBs). ASSBs with LSPS solid electrolyte (SE), lithium-indium alloy anode, and $LiCoO_2$ (LCO) cathode were successfully fabricated and their electrochemical performance at 60 °C was examined. Atomic layer deposition of Li_3NbO_4 on LCO was conducted to improve the interfacial stability. The Li_3NbO_4 coating effectively improves the cycle stability of the ASSB. Electrochemical impedance spectroscopy tests indicate a rapid growth of charge transfer resistance upon cycling for the cell with the uncoated LCO, primarily due to the surface instability and build-up of a space charge layer. However, the ASSBs with Li_3NbO_4 coated LCO show a more stable interface with a negligible impedance increase upon cycling, attributable to the buffering and passivating roles of the Li_3NbO_4 coating. The interfacial microstructure was analyzed to elucidate at the underlying reasons for the impedance increase and the pivotal role of the Li_3NbO_4 coating.

1. Introduction

Lithium ion batteries (LIBs) are widely commercialized to power portable devices. Due to their high energy density, it is the most attractive option for hybrid electric vehicles, electric vehicles, and other portable applications [1]. Given the sensitive and widespread nature of these applications, high energy LIBs with superior reliability and safety are desirable. Most commercially available LIBs use flammable liquid electrolytes, which risks fire or explosions in the event of a failure [2]. From a safety point of view, replacing the flammable liquid electrolyte with a solid one would be desirable. An eligible solid electrolyte (SE) should have an ionic conductivity comparable to that of current liquid electrolytes, *e.g.*, 10^{-3}-10^{-2} S cm^{-1} [2]. Other benefits of SEs include larger electrochemical windows and excellent thermal stability, as well

as the possibility of high power and energy density, such as when paired with a lithium metal anode [3]. The recent finding of $Li_{10}GeP_2S_{12}$ (LGPS), with an outstanding ionic conductivity of 12 mS cm^{-1}, comparable to liquid electrolytes, has made the use of sulfide-based SEs an appealing option for all solid-state batteries (ASSBs) [4,5]. The high cost of Ge, however, largely limits the practical use of LGPS. Creating isostructural analogues by substituting Ge with Si, Al, or Sn, has been suggested [6–8]. The Sn analogue $Li_{10}SnP_2S_{12}$ (LSPS) is the most promising of the group [8].

The main hurdle for developing successful ASSBs, however, is in minimizing the interfacial impedances between the SE and the electrodes, especially for the cathode/SE interfaces. The interfacial impedances primarily dominate the rate capability and cycling stability of the ASSBs [1,4,9]. First, SEs must be chemically and electrochemically

stable against the electrode materials and able to form a stable and conductive interface (solid electrolyte interphase-like interface layer) [9–13]. Based on the theoretical calculations, sulfide-based SEs show narrow electrochemical windows, such as ~1.8–2.3 V vs. Li$^+$/Li for LGPS [14]. The narrow electrochemical windows of sulfides have been experimentally verified, although these had been largely overestimated by the conventional experimental method of using a Li/electrolyte/ inert metal semi-blocking electrode with limited contact areas [15]. In addition, due to the difference in Li$^+$ chemical potential and resultant asymmetric Li$^+$ migration, the depletion of Li$^+$ on the sulfide side and the formation of a space charge layer largely increase the interfacial resistance [16].

To facilitate successful ASSBs, interfacial modifications on either electrodes or SE are necessary to mitigate the chemical diffusion and space charge layer, thus reducing the interfacial impedance and extending the electrochemical window beyond 4.2 V (vs. Li$^+$/Li) [9–13,17–20]. To mitigate the interfacial resistance, the coating material should be a good ionic conductor, while thin and uniform. Typically, wet chemical methods such as sol-gel or spray coating, are used for creating surface coatings; these methods, however, leave non-uniform and thick coatings [21]. Alternatively, atomic layer deposition (ALD) boasts excellent conformity, atomic scale thickness control, and uniformity over large areas, emerging as a promising process for battery electrode coating [9,22]. The sequential and self-limiting nature of ALD allows for ultra-thin and pinhole free coatings to be applied. These subnanometer coating layers have the added benefits of lessened mechanical stresses due to the crystal mismatch and reduced thickness constraints as far as the electron and lithium ion conductivities of the coating material are concerned [21].

To evaluate the potential of LSPS as an SE and study its interfacial behavior with typical cathode materials, ASSBs with LSPS SE, Li/In anode, pristine and ALD Li$_3$NbO$_4$-coated LiCoO$_2$ cathodes were fabricated. Li$_3$NbO$_4$ was chosen because of its reasonable ionic conductivity and excellent chemical stability against both layered oxide cathodes and LSPS, thus effectively protecting the cathode from undesirable side reactions with the electrolytes [23–26]. The electrochemical performance and interfacial characteristics of the ASSBs using pristine and coated LiCoO$_2$ were systematically explored by galvanostatic cycling, AC electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDS), etc. The study shows that the ALD coating largely improves the electrochemical performance of ASSBs with the LSPS SE, in large part due to the improved interfacial compatibility and decreased charge transfer impedance.

2. Experimental

ALD of ultrathin lithium niobium oxide coatings were deposited using a Savannah 100 Atomic Layer Deposition system (Cambridge Nanotech Inc., USA), with lithium tert-butoxide (LiOtBu, (CH$_3$)$_3$COLi, Sigma Aldrich, USA) and niobium ethoxide [C$_{10}$H$_{25}$NbO$_5$, Sigma Aldrich] as the precursors. The distilled water was used as the oxidant and Argon (99.99%) as the carrier gas. The pulse, exposure, and purge times for all precursors are 0.1 s, 10 s, and 20 s, respectively, in each sub-cycle. The heating temperature was 160 °C for both Li and Nb precursors, and 80 °C for water. The deposition temperature was around 200 °C for the LiCoO$_2$ powder samples (LCO, 99.8%, Sigma Aldrich, USA).

The electrochemical properties LCO/LSPS/Li-In ASSBs were investigated using a homemade all-solid-state cells shown in Fig. S1 (Supporting Information, SI). Electrode mixtures consisted of pristine LCO or Li$_3$NbO$_4$ coated LCO (c-LCO) powders, and LSPS powders (Nanomyte SSE-10, NEI Corporation, USA) in a weight ratio of 70:30. They were prepared by hand grinding in a mortar for 30 min. Two-electrode all solid state cells (ASSCs) were fabricated using ~12.7 mg of electrode mixture as the cathode, 80 mg LSPS as the separator, and

Li-In foil as the anode. The working electrode and LSPS were placed in a stainless steel die with a diameter of 10 mm and pressed together under 500 MPa for 20 min. The cathode/LSPS pellet was then dissembled from the die and placed into an ASSC. 60 mg of In foil (0.62 V vs Li$^+$/Li [27], 99.99%, CMR-Direct, USA) and 10 mg of Li foil (99.9%, MTI Corporation, USA) were placed on the top of the SE and a pressure of 20 MPa was then applied. All cell preparation processes were carried in a glovebox (Lab Star, Mbraun, Germany, H$_2$O < 0.5 ppm, O$_2$ < 0.5 ppm). The ASSCs under a 20 MPa pressure were then galvanostatically charged/discharged using a Neware cycler in the voltage range of 2.0–3.7 V vs. Li-In at 60 °C.

AC EIS measurements were performed in a potentiostat (Versastat4, Ametek Scientific Instruments, USA). EIS data of a cold-pressed SE pellet were collected at room temperature in a symmetrical cell using carbon foil as the electrodes in the frequency range of 1–10^6 Hz and with an amplitude of 5 mV. Similarly, EIS tests of the ASSCs in the frequency range of 0.01–10^6 Hz and an amplitude of 10 mV were performed at various cycling stages. Cyclic voltammetry (CV) was carried out on LSPS pellets sandwiched between a stainless steel (SS) plate and Li or In foil as electrodes at a scanning rate of 10 mV s^{-1} from 0 to 5 V.

The crystal structure of the materials was investigated by powder X-ray diffraction (XRD, Bruker D8 Discover with IμS 2D detector, Germany). The LSPS powders were first placed in a capillary tube and sealed with wax before exiting the glovebox. A field emission SEM (FESEM, FEI Sirion XL30, USA) equipped with an Oxford EDS was used to image the particle morphology and obtain elemental analysis and mapping. The microstructures and compositions of the cycled electrodes were analyzed by a scanning TEM equipped with a high-angle annular dark-field (HAADF) detector and an EDS at the Pacific Northwest National Laboratory (STEM/HAADF/EDS, FEI Titan 80–300 kV, USA). In order to reduce air- or moisture-exposure and avoid the unintended contaminations, the cycled cells were disassembled, the cathodes were scraped, and the cathode powders were placed on a TEM mesh in an Ar filled glovebox. The TEM holder was sealed and rapidly transferred into the TEM chamber with a minimal exposure.

3. Results and discussion

3.1. Characterization of the solid electrolyte and cathode materials

Fig. 1a shows the crystal structure of LSPS, taken from the online database *Materials Project* [28]. LSPS crystalizes in a tetragonal structure with a space group P4$_2$/mc. The lattice parameters are a = 8.854 Å and c = 12.851 Å. The three-dimensional percolating structure ensures high Li$^+$ conductivity. To verify the crystal structure of the as-received LSPS, powder XRD was carried out, as shown in Fig. 1b. Based on the above crystal structure, the standard XRD pattern of LSPS was also simulated using the Materials Studio's software, also shown in Fig. 1b. Our simulated XRD matches well with the result presented in *Materials Project* and those given by Bron, Kuhn, and Tarhouchi et al. [7,29,30]. As shown, the experimental XRD can be well indexed to the simulated XRD, indicating good phase purity of the LSPS powders. In addition, the sharp and well-defined diffraction peaks indicate good crystallinity of the SE.

Fig. 1c shows the Nyquist plot for an LSPS pellet cold pressed at 500 MPa. Similar to the previous work done by Bron et al. [7], we observed grain resistance and relatively small grain boundary contribution, even without heat treatment. The Nyquist plot can be well fitted by the equivalent circuit shown in the inset of Fig. 1b. R_b, corresponding to the high-frequency intercept with the real axis, is the bulk resistance; the inductance segment L is mainly due to the cabling and leads of the set up [31]; the $R_{gb}|CPE_{gb}$ combination, showing as the semicircle in the mid-low frequency range, corresponds to the ionic resistance and capacitance of the grain boundaries in the LSPS pellet [8]. Based on the bulk resistance and geometry of the pellet, a total