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Comparative Study of TiS_2/Li-In All-Solid-State Lithium Batteries Using Glass-Ceramic Li_3PS_4 and $Li_{10}GeP_2S_{12}$ Solid Electrolytes

Bum Ryong Shin, Young Jin Nam, Dae Yang Oh, Dong Hyeon Kim, Jin Wook Kim, Yoon Seok Jung*

School of Energy and Chemical Engineering, Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Korea

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ABSTRACT

A systematic investigation on the electrochemical performances of all-solid-state TiS_2/Li-In cells with various configurations using glass-ceramic Li_3PS_4 (LPS) and $Li_{10}GeP_2S_{12}$ (LGPS) solid electrolytes is presented. In spite of the superior conductivity of LGPS to that of LPS, LGPS shows poor stability in the low voltage range below ~1 V (vs. Li/Li^+) as evidenced by cyclic voltammetry (CV) and *ex-situ* XRD experiments. The combined use of the LGPS cathode layer and an LGPS-LPS SE bilayer where LPS forms an interface with the Li-In anode ((TiS_2-LGPS)/(LGPS-LPS)/Li-In cell) results in the best overall performance at 30 °C, exhibiting a capacity of ~60 mA h g^{-1} (~25% of the theoretical capacity) at 20C, over a voltage range of 1.5–3.0 V (vs. Li/Li^+). Combined analyses by electrochemical impedance spectroscopy (EIS) and conductivity measurements of the cathode layers highlight the importance of having an SE of high conductivity and optimizing the structure of the composite electrode.

1. Introduction

Conventional lithium-ion batteries (LIBs) utilize organic liquid electrolytes in which lithium salts are dissolved in organic alkyl carbonate solvents [1]. Not only flammability but also possible leakage of the organic liquid electrolyte in LIBs causes serious safety concern [1–3]. Recently, all-solid-state lithium batteries (ASSLBs) using inorganic solid electrolytes (SEs) have been seriously considered for large-scale energy-storage applications in devices such as electric vehicles and smart grids, because of their inherent safety [1,4,5]. Although thin-film ASSLBs using LiPON ($Li_{3.3}PO_{3.9}N_{0.17}$) have been reported to show excellent cycle performance [6,7], their large-scale application is not feasible because of the expensive vacuum-deposition process required for fabrication [6,7]. Alternatively, sulfide SE materials provide promising advantages for commercialization of large-scale ASSLBs. Several sulfide SEs have been developed that display high ionic conductivity on the order of 10^{-3}–10^{-2} S cm^{-1}, which is similar to that of conventional organic liquid electrolytes [4,5,8–10]. Moreover, sulfide SE materials exhibit ductility, displaying Young's moduli between those of typical oxide ceramics and organic polymers [3,11]. The high ionic conductivity and ductility of sulfide SEs enable the realization of bulk-type (or composite-type) all-solid-state batteries in which the electrode layer is formed by simply cold pressing a mixture of the active powders, SE powders, and conductive carbon [3–5,11].

The choice of SE makes a significant impact on the performance of ASSLBs, with ionic conductivity being of prime importance. The Kanno group reported thio-LISICON ($Li_{3.25}Ge_{0.25}P_{0.75}S_4$) [8] SE displaying conductivities up to 2.2×10^{-3} S cm^{-1} and LGPS ($Li_{10}GeP_2S_{12}$) [4] SE displaying conductivities up to 1.2×10^{-2} S cm^{-1}. Conductivities over 10^{-3} S cm^{-1} have also been demonstrated using xLi_2S-(100-x)P_2S_5 glass-ceramic (GC) SEs by the Tatsumisago group [9], who recently reported that the conductivity of $70Li_2S$-$30P_2S_5$ GC SE can be further enhanced to 1.7×10^{-2} S cm^{-1} by minimizing the grain boundary interface resistance via hot-pressing [5]. Since ionic conductivity of 1×10^{-2} S cm^{-1} is equal to that of organic liquid electrolytes used in conventional lithium-ion batteries (LIBs) and the transference number of Li^+ ions in the SE is unity, the performance of ASSLBs should be competitive to that of conventional LIBs. However, ionic conduction pathways in ASSLBs are more complicated than those in conventional LIBs. While liquid electrolytes can wet almost all surfaces of the active materials, the contacts between SEs and the active materials are highly dependent on factors such as the particle size distribution and mixing conditions [12]. In some cases, desired electronic conduction pathways are overtaken by poor ionic conduction pathways [12]. Therefore, the ionic conductivity of SEs is not directly proportional to the performance of ASSLBs. In this regard, a systematic investigation on the

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* Corresponding author. Tel.: +82-52-217-2944; fax: +82-52-217-3009.
E-mail address: ysjung@unist.ac.kr (Y.S. Jung).

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effects of the configuration of all-solid-state cells on their performance is needed. Electrochemical stability of SEs is another critical factor that restricts the choice of possible electrode materials and affects the cycle performance and kinetic properties of all-solid-state cells [13–17], as observed in conventional LIBs [18,19]. For example, Li_xMO_2 (M = Co, Ni, Mn, etc., $0 \leq x \leq 1$) cathode materials used in conventional LIBs show poor performance originating from the low oxidation onset potential of sulfide SEs (~3 V vs. Li/Li$^+$) [15–17] and incompatibility with the sulfide SE [14]. Stable metal oxide coatings, such as $Li_4Ti_5O_{12}$ [14], $LiNbO_3$ [4,20], Li-Si-O [15], Al_2O_3 [21], and $BaTiO_3$ [22], are necessary to reduce large charge transfer resistances at the interface between the sulfide SE and oxide cathode. The underlying mechanism can be explained in terms of blocking of interatomic diffusion [23] or suppression of the formation of a space charge layer in the sulfide SE [14,22]. Use of sulfide-based cathode materials can avoid the instability problem of sulfide SEs because of low operating voltages (<~3 V vs. Li/Li$^+$). In previous reports, TiS_2 was demonstrated to exhibit capacity close to the theoretical one ($TiS_2 + Li^+ + e^- \rightarrow LiTiS_2$, 239 mA h g^{-1}) with excellent durability [12]. Recently, our group also reported that $LiTi_2(PS_4)_3$ formed a favorable interface with $75Li_2S$-$25P_2S_5$ GC SEs, leading to stable cycle performance [17].

In this study, the performances of all-solid-state TiS_2/Li-In cells with various configurations were systematically investigated using two different SEs: GC Li_3PS_4 (LPS) and LGPS. Cyclic voltammetry (CV) and *ex-situ* X-ray diffraction (XRD) results confirmed that the higher conductivity of LGPS compared to that of LPS is negated by poor stability in the negative voltage range. The use of an LGPS-LPS SE bilayer in which LPS forms an interface with the Li-In anode is demonstrated to optimize battery performances in terms of stability and rate capability. Additionally, the effects of composition and loading of the cathode layer are compared by measuring Li$^+$ ion- and electronic conductivities.

2. Experimental

Preparation of LPS and LGPS SE powders – LPS (or $75Li_2S$-$25P_2S_5$) GC SE powders were prepared by mechanical milling and subsequent heat-treatment [17]. 2 g of batches of Li_2S (99.9%, Alfa Aesar) and P_2S_5 (99%, Sigma Aldrich) mixture were mechanically milled at 500 rpm for 10 h at room temperature using a planetary ball mill (Pulverisette 7PL; Fritsch GmbH) with a ZrO_2 vial (80 mL) and 115 g of ZrO_2 balls (5 mm in diameter). The obtained glass powders were put into a glass ampoule and sealed under vacuum (≤40 Pa). The sealed ampoule was subjected to heat treatment at 243 °C for 1 h. For the preparation of LGPS powders, stoichiometric amounts of Li_2S, P_2S_5, and GeS_2 (99.9%, American Elements) powders were thoroughly mixed using a Thinky Mixer (AR-100, THINKY Inc.) with a plastic vial (12 mL) and eight ZrO_2 balls (5 mm in diameter) at 2000 rpm (33 s^{-1}) for 30 min. The mixed powders pelletized under 360 MPa were put into a quartz tube and sealed under vacuum (≤40 Pa). The sealed quartz tube was subjected to heat treatment at 550 °C for 10 h with ±1 °C min^{-1}.

Materials characterization – For the XRD analyses, a specially designed cell was used, in which the air-sensitive SE powders or disassembled pelletized cells were placed on a beryllium window and hermetically sealed inside the Ar-filled dry box. Then, the prepared XRD cell was mounted on a D8-Bruker Advance diffractometer equipped with Cu K$_\alpha$ radiation (1.54056 Å). All the XRD patterns were recorded at 40 kV and 40 mA using a continuous scanning mode at 1.5° min^{-1}. Field emission scanning electron microscopy (FESEM) images were obtained using S-4800 (Hitachi).

Electrochemical characterization – Measurements of Li$^+$ ion conductivity and electronic conductivity of the SEs were carried out by AC method and DC method using a Li$^+$ ion blocking cell (Ti/SE/Ti) at 30 °C, respectively. For the CV experiments, Ti/SE/$Li_{0.5}$In cells were constructed. Li$^+$ ion conductivity and CV data obtained by using 30 μm thick Au film (Au/SE/Au for AC method and Au/SE/$Li_{0.5}$In for the CV experiments) matched perfectly with the data using Ti electrodes, confirming that Ti acts as an inert electrode. After 150 mg of SE powders were pelletized under 370 MPa for 5 min, 100 mg of a partially lithiated indium ($Li_{0.5}$In, nominal composition) powders prepared by mechanically milling the mixture of In (Aldrich, 99.99%, containing Mg) and Li (FMC Lithium corp.) powders were put on one side of the as-formed SE pellet and pressed under 370 MPa for 3 min. The scan rate was 0.2 mV s^{-1}. For fabrication TiS_2/$Li_{0.5}$In all-solid-state cells, composite electrodes were prepared by manually mixing the TiS_2 (99.9%, Aldrich, 200 mesh) and SE powders. Note that no conductive additive is required because TiS_2 is metallic [12,24]. The weight ratio of the TiS_2/SE was 0.5. SE pellets were formed by pressing 150 mg of the SE powders at 74 MPa. TiS_2 composite electrode materials (10 mg) were then carefully spread on the top of the SE layer and the cell was pelletized by pressing at 370 MPa for 3 min. Finally, 50 mg of the prepared $Li_{0.5}$In powders were attached to the back SE face at 370 MPa for 3 min. All pressings were carried out in a polyaryletheretherketone (PEEK) mold (diameter = 13 mm) with Ti metal rods as current collectors for both the working and counter/reference electrodes. All the processes for preparing the SEs and fabricating the all-solid-state cells were performed in an Ar-filled dry box. The galvanostatic discharge–charge cycling of the all-solid-state cells was performed between 1.5 and 3.0 V (*vs.* Li/Li$^+$) at 30 °C. The capacity is based on the weight of TiS_2. The electrochemical impedance spectroscopy (EIS) study was performed using an Iviumstat (IVIUM Technologies Corp.). The AC impedance measurements were recorded using a signal with an amplitude of 10 mV and a frequency range from 500 kHz to 5 mHz. The cells were discharged to 2.1 V (*vs.* Li/Li$^+$) at 50 mA g^{-1} and a constant voltage of 2.1 V was applied with a limiting current of 12.5 mA g^{-1}. Then, the cell was allowed to rest for approximately 3 h before the EIS measurements. In order to measure Li$^+$ ion conductivity of the TiS_2/SE electrode, specially designed electron-blocking symmetric cell of Li/SE/electrode/SE/Li by DC and AC methods [25].

3. Results and discussion

Fig. 1a and b shows FESEM images of the as-prepared LPS (Li_3PS_4 or $75Li_2S$-$25P_2S_5$ GC) and LGPS SE powders. Both of the SE powders are a few to tens of μm size with irregular morphology. Fig. 1c shows XRD patterns of the LPS and LGPS SE pellets. The peaks of LPS match well with previous reports [26]. The as-prepared LGPS exhibits characteristic peaks (denoted '◊') corresponding to the tetragonal $Li_{10}GeP_2S_{12}$ with a space group of $P4_2/nmc$ [27] along with minor impurity peaks (denoted '?'). XRD data of LGPS that was obtained from rotating XRD cells (15 rpm) exactly matches with the one without rotation, confirming that any preferred crystal orientation does not occur during the cold pressing process for fabricating the SE pellets. Fig. 1d displays the Nyquist plots of Ti/SE/Ti cells measured by the AC method. The intercept at the x-axis equals the SE resistance, which can be converted to electrical conductivity. As electronic conductivities of LPS and LGPS measured by the DC method are on the order of 1×10^{-8} S cm^{-1}, electrical conductivities obtained by the AC method are directly assigned as Li$^+$ ionic conductivities. At 30 °C, the LPS and LGPS exhibit conductivities of 1.0×10^{-3} S cm^{-1} and 6.3×10^{-3} S cm^{-1}, respectively. The LGPS conductivity (6.3×10^{-3} S cm^{-1}) is approximately half of the previously reported value (1.2×10^{-2} S cm^{-1}) [4], which is a result of using a cold pressed pellet in this work as grain boundary resistances that originate from voids in the pellet work to lower the overall conductivity [5]. The presence of minor impurities, seen in the XRD pattern, may also contribute the decrease in conductivity.