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Lithium ionic conduction in composites of $Li(BH_4)_{0.75}I_{0.25}$ and amorphous $0.75Li_2S\cdot0.25P_2S_5$ for battery applications

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ABSTRACT

Solid state electrolytic properties of mixtures of $Li(BH_4)_{0.75}I_{0.25}$ and amorphous $0.75Li_2S\cdot0.25P_2S_5$ are reported in this study. The enhanced Li-ion conductivities for the $Li(BH_4)_{0.75}I_{0.25}$ phase after addition of $0.75Li_2S\cdot0.25P_2S_5$ were found to be within the range for practical solid-state electrochemical storage near room temperature. The highest ionic conductivities are found for the borohydride/sulfide system at 1:2 wt ratio with ~10^{-3} S cm^{-1} at room temperature and an activation energy of 0.30(2) eV. Combined experimental analyses with powder X-ray diffraction and infrared spectroscopy suggest that the synthesized material still include both $[PS_4^{3-}]$ and $[BH_4^-]$ entities. Density functional theory (DFT) calculations provide more insights about the origin of the observed ionic behavior according to the induced structural modifications in the BH_4—BH_4 interactions. Finally, the electrolyte functionality and its compatibility toward an active material are successfully demonstrated by means of cyclic voltammetry (Au *vs.* Li^+/Li) in a large voltage window (up to 5 V) and battery cycling tests with TiS_2 electrode, respectively.

1. Introduction

The emerging applications for Li-ion batteries are very demanding regarding high energy density, reasonable lifespan, stability under extreme conditions such as wide temperature range, mechanical stress and fast solicitations for high power devices [1–4]. Solid electrolytes (SEs) can be beneficial in all these aspects compared to current liquid, gel or polymer-based electrolytes, for improved safety and performance of Li-ion batteries [5–9].

The glass system Li_2S-P_2S_5 has been extensively studied as electrolyte for application in all-solid-state Li-ion batteries [10–14]. However, these electrolytes have been reported to create unstable interface with Li [11,15]. The addition of lithium halides to Li_2S-P_2S_5 has been shown to increase the ionic conductivities and improve the contacts at the electrode/electrolyte interface [10,16]. Recently, the $LiBH_4$-Li_2S-P_2S_5 system has attracted attention owing to its adjustable ionic conductivity as function of composition for solid state battery electrolytes [17,18].

The crystal structure and ionic properties of $LiBH_4$ has been the subject of many reports [19–24]. It undergoes a first-order polymorphous transition around 113 °C, from orthorhombic (LT, *Pnma*, 10^{-8} S cm^{-1} at 30 °C) to hexagonal (HT, $P6_3mc$, 10^{-3} S cm^{-1} at 120 °C) involving a reorientation of the tetrahedral $[BH_4^-]$ anions. High mobility of the complex anions $[BH_4^-]$ in the HT-phase, along with short Li-Li distances in a compact structure with transport channels gave fast Li-ionic conduction [24–26]. Thus, $LiBH_4$ is a good Li-ion conductor between the phase transition temperature and the melting point at 280 °C, i.e. an operating domain less than $\Delta T = 167$ °C [22,27]. Below the transition temperature, the HT-phase reverts back to the poorly conducting LT-$LiBH_4$. However, the Li-ion conducting hexagonal phase can be stabilized by partly substituting $[BH_4^-]$ with halides, e.g. $Li(BH_4)_{0.75}I_{0.25}$, thus suppressing the phase transition and preserving high ionic conductivity down to room temperature (*RT*), with a value close to 10^{-4} S cm^{-1} [28–31]. This phase has been reported to form a stable electrode/electrolyte interface in a lithium battery-cell [26,32].

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The present work explores the effect of mixing crystalline hexagonal Li-ion conducting $Li(BH_4)_{0.75}I_{0.25}$ (LI) with amorphous $0.75Li_2S\cdot0.25P_2S_5$ (LPS) for solid-state electrolyte applications. The prepared electrolytes were investigated with respect to their structural and ionic properties and application for all-solid-state batteries. The experimental analytical investigations are supported by DFT calculations to gain better understanding of the nature of the interaction between LI and LPS.

2. Experimental

2.1. Materials synthesis and characterization

$LiBH_4$ (95%), LiI (99.9%), Li_2S (99.98%) and P_2S_5 (99%) were purchased from Sigma-Aldrich and stored in an Ar-filled glove box (<1 ppm O_2, H_2O). The halide-stabilized hexagonal phase $Li(BH_4)_{0.75}I_{0.25}$ was synthesized according to the procedures described elsewhere [33]. The amorphous $0.75Li_2S\cdot0.25P_2S_5$ was prepared by ball-milling for 20 h using a Fritsch Pulverisette 6 (P6) planetary ball-mill with stainless steel vials and balls (ball-to-powder ratio 40:1, 300 or 370 rpm) [15,28,34]. The final electrolytes were obtained by mixing the two precursors LI/LPS at different wt. ratios using P6 planetary milling for 5 h at 370 rpm.

Synchrotron radiation powder X-ray diffraction (SR-PXD) patterns were obtained at the Swiss-Norwegian Beamlines (SNBL, BM01), ESRF, Grenoble with a Pilatus2M 2-dimensional detector and a wavelength of 0.7454 Å. The samples were contained in 0.5 mm boronglass capillaries that were rotated 90° during the 30 s exposure. The sample-detector distance was 345.97 mm 1D data were obtained by integration of the 2D diffraction patterns with the program Bubble [35]. Lab-PXD data were obtained with a Bruker AXS D8 Advance diffractometer equipped with a Göbbel mirror and a LynxEye 1D strip detector. In this case, patterns were obtained in a Debye–Scherrer geometry using Cu Kα radiation (1.5418 Å) and rotating glass capillaries, filled and sealed under Ar atmosphere. The PXD data were analyzed using DIFFRAC.SUITE EVA software.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were collected with a Bruker Alpha-Platinum spectrometer with a diamond crystal. The spectra were obtained in the range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}. The samples were measured without any dilution inside an Ar-filled glove box. IR spectra were ATR-corrected and normalized using the OPUS software. Further characterizations of the vibrational states were performed by Raman spectroscopy (Nicolet Almega-HD, Thermo Scientific) using a dedicated cell without any air exposure.

2.2. Electrochemical analysis and battery tests

Ionic conductivities were determined by electrochemical impedance spectroscopy (EIS). The powder samples were pressed into 8 mm diameter pellet of <2 mm thickness by a uniaxial press at around 240 MPa without sintering. The pellets were sandwiched by lithium foils as non-blocking electrodes and sealed in a homemade cell [36] for measurements outside the glovebox. The cells were placed in the heating jacket and the EIS were carried out over a frequency range from 1 MHz to 4 Hz using a HIOKI 3532-80 from *RT* to 150 °C in heating and cooling runs. Measured impedance spectra were analyzed by equivalent circuits using ZView2 software (Scribner Associates Inc.). Additional EIS measurements and cyclic voltammetry were performed using Bio-Logic® VSP multi-channel potentiostat, either in coin cells or a home-made cell described elsewhere [37].

For battery tests, TiS_2 (99.9%, Sigma-Aldrich) and Li foil were used as working and counter/reference electrode, respectively. The TiS_2 and the prepared SE powders in 2:3 mass ratio were hand mixed in an agate mortar. The obtained mixture was used as the electrode composite. Around 6 mg of this composite and 30 mg of the SE were introduced in a 10 mm die set and uniaxially pressed together at 240 MPa. A Li foil was placed on the opposite side of the electrode composite before the pellet was inserted in a coin cell. The assembled cells were moved out of glovebox and annealed at 60 °C for 5 h before testing at the cycling station (Bio-Logic instrument) in a temperature-controlled cabinet at 50 °C.

3. Computational details

Total energies were calculated by the projected-augmented plane-wave (PAW) implementation of the Vienna *ab initio* simulation package (VASP) [38,39]. These calculations were made with the Perdew, Burke, and Ernzerhof (PBE) exchange correlation functional [40]. Ground-state geometries were determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3} eV Å^{-1}. Brillouin zone integration was performed with a Gaussian broadening of 0.1 eV during all relaxations. From various sets of calculations it was found that 512 **k** points in the whole Brillouin zone for the structure with a 600 eV plane-wave cut-off are sufficient to ensure optimum accuracy in the computed results. The **k**-points were generated using the Monkhorst-Pack method with a grid size of $8\times8\times8$ for structural optimization. A similar density of **k**-points and energy cut-off were used to estimate total energy as a function of volume for all the structures considered in the present study. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 1 meV/cell. For the *ortho*-$LiBH_4$ (*Pnma*) and *hexa*-$LiBH_4$ ($P6_3mc$) phases the calculated lattice parameters (see SI. Table ST 1 and 2) are found to be in good agreement with experimental data. The lithium diffusion barrier height of the studied phase was investigated with the cNEB method using supercell approach [41,42]. Large supercells ($2\times2\times1$ for both *orthorhomic* and *hexagonal* phases) were used to ensure that the atoms were separated from their periodic image, providing a more accurate output values for the activation barrier in the diluted limit. To determine the minimum energy path (MEP) through the climbing Nudged Elastic Band (cNEB) method, six replicas of the system were created, in each the diffusing Li atom was moved by equidistant steps to positions between the initial and final states for the path obtained by linear interpolation.

4. Results and discussion

Fig. 1a presents lab-PXD patterns of $0.75Li_2S\cdot0.25P_2S_5$ samples before and after mechanical milling. The hand mixed sample shows Bragg peaks from Li_2S and P_2S_5 without any noticeable peaks from any reaction products. After ball-milling, an amorphous phase with no Bragg peaks is formed in agreement with previous studies [15]. Ionic conductivity measurements were performed on 2 different LPS batches prepared at different ball-milling conditions, i.e. rotation speed 300 and 370 rpm. The high energy (370 rpm) ball-milled LPS batch shows the highest conductivity and was retained for this study. We believe that the energy of ball-milling has a direct effect on the crystallite size and amorphization process, which may influence the resistance contributions of bulk and grain boundaries.

The SR-PXD of the synthesized LI hexagonal phase (space group $P6_3mc$, refined lattice parameters $a = 4.3646(2)$ Å, $c = 7.0562(5)$ Å) is shown in Fig. 1b. The Rietveld refinement shows that LI is the only crystalline phase in the material. This LI phase was then added to the amorphous LPS at three weight fractions $\alpha = 0.67$, 0.5 and 0.33 in αLI-(1-α)LPS. Fig. 2a shows the composition-dependent