

Electrochemical characterization of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$: An electrolyte or a negative electrode for solid state Li-ion batteries?



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ARTICLE INFO

Article history:

Received 16 November 2015

Received in revised form 27 August 2016

Accepted 30 August 2016

Available online xxxx

Keywords:

LGPS structure

Sulfide

Solid electrolyte

Electrochemical properties

Conversion reaction

ABSTRACT

$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, the tin analogue of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ superionic conductor is characterized. Rietveld refinement of capillary powder XRD confirms that the material provided by NEI Corp. is mainly composed of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ with LGPS structure, with some Li_2SnS_3 impurity. Very strong reactivity at low voltage and vs. Li metal is shown by impedance measurements using Au and Li electrodes, as well as 3-electrode cyclic voltammetry. Galvanostatic measurements in half-cells with liquid and solid electrolytes confirm that $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ reacts with respectively 16 and 8 lithium per mole of tin below 0.5 V vs. Li^+/Li , most probably following a conversion/allying reaction. Making use of this reactivity, we tested the concept of a $\text{LiCoO}_2/\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ cell, where the electrolyte also acts as negative electrode at the contact with the negative current collector. 0.5 Li can be deintercalated from such cells, with very poor reversibility as probably hampered by the conversion/allying reaction in the solid state, at least with a non-optimized electrode formulation. Although the voltage slowly but strongly relaxes when opening the circuit suggesting propagation of the reaction from the negative electrode to the electrolyte, it does not seem to reach the positive since no short-circuit was observed.

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1. Introduction

Among all electrical energy storage technologies, Li-ion batteries become more and more favored, since their high energy densities are of first interest for portable devices, electrical vehicles or smart grids development. However, safety issues remain, since organic liquid electrolyte currently used in such batteries can leak (with hydrofluoric acid emission), or ignite [1]. Development of Li-all-solid state batteries can be considered as a possible alternative, since they are based on non-flammable solid electrolytes, in place of organic liquid electrolytes.

The solid electrolyte should exhibit key properties: low electronic conductivity, chemical stability vs. the electrode materials, wide electrochemical stability window and high ionic conductivity. The latter was considered as the main issue for the development of all-solid state batteries, since the best solid electrolytes exhibited an ionic conductivity at room temperature of $10^{-3} \text{ S} \cdot \text{cm}^{-1}$, which is less than that of liquid electrolytes ($10^{-2} \text{ S} \cdot \text{cm}^{-1}$).

Kanno published recently a new solid electrolyte, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, exhibiting a room temperature ionic conductivity of $1.2 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$, comparable to or higher than ionic conductivities of organic electrolytes used in Li-ion batteries [2]. It crystallizes in a

tetragonal LGPS structure ($P4_2/nmc$ space group) with isolated (Ge/P) S_4 tetrahedra, where phosphorus occupies $2b$ sites (or $2a$ sites depending on the origin chosen for the space group) with 100% occupancy and share the $4d$ site with Ge with (nominally) 50% occupancy. This LGPS structure, later confirmed by single crystal XRD [3], is different from the one published a few years before for the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ composition: in the $\text{Li}_4 - x\text{Ge}_{1-x}\text{P}_x\text{S}_4$ solid solution with Li_4GeS_4 and Li_3PS_4 end members, Kanno had indeed presented materials which crystallize in an orthorhombic thio-LiSICON structure ($\gamma\text{-Li}_3\text{PO}_4$ -type) with different monoclinic superlattice modifications depending on x [4].

Computation results on $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ ($M = \text{Si, Ge, Sn}$) with LGPS structure predicted these solid electrolytes to decompose into Li_3PS_4 and Li_4MS_4 , and thus the “tetragonal” LGPS structure for $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ composition to be metastable, although weakly. However, an ordered structure was necessarily considered for the calculation and resulted in a $P1$ space group, which is different from the tetragonal LGPS obtained experimentally [5,6].

Very recently, Kanno reported an $\text{Li}_4 - x\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($0.5 \leq x \leq 0.65$) solid solution range for which materials have a pure LGPS structure, with different Ge/P ratios in the $4d$ site depending on the composition [7]. For other $\text{Li}_4 - x\text{M}_{1-x}\text{P}_x\text{S}_4$ ($M = \text{Si, Sn}$), similar solid solution ranges crystallizing in a pure LGPS structure were also reported, but for different compositions [8].

Cyclic voltammetry of selected Ge, Si and Sn LGPS-type materials using a pellet with a gold sputtered working electrode facing a lithium

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counter and reference electrode was reported [2,8]. These materials were thus presented to be stable up to 5 V vs. Li^+/Li (no decomposition peaks being observed), making these solid electrolytes suitable for high energy density batteries application. Nevertheless, the calculation results predicted all $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ with LGPS structure to be unstable at 0 V and 5 V vs. Li^+/Li [6].

$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ has been made available commercially by NEI Corp., even before the first preparation report of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ by Bron et al. [9]. In the latter report, X-ray diffraction confirms single crystals with this composition crystallizing in the LGPS structure, and the ionic bulk conductivity of $7 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at room temperature is in agreement with previous calculations [6].

In the present study, we describe a characterization of the commercial $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ material. Rietveld refinement of X-ray diffractograms confirms the tetragonal LGPS structure with some Li_2SnS_3 impurity; impedance measurements show an unexpected effect of the measurements itself; three-electrode cyclic voltammetry reveals the narrow electrochemical stability window of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ and especially at low potential. We finally propose the concept of a solid state battery using this material both as solid electrolyte and as negative electrode material. We note that the concept of using an LGPS-type material as electrolyte and as active electrode was actually very recently proposed by Han et al. while we were investigating it independently [10]. These authors even propose that $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ also act as positive electrode; however, they did not address the behavior upon long relaxation.

2. Experimental

$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ was purchased from NEI Corporation and is referred to as $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ (nominally >95% purity).

Based on previous studies [11], Li_2SnS_3 was prepared as follows: the precursors Li_2S (Sigma Aldrich, 99.9% of purity), Sn (Sigma Aldrich, 99.8% of purity) and sulfur are mixed and ground in a mortar in stoichiometric proportions. The powder mixture is placed in a vitreous carbon crucible, which is then placed in a silica tube. All these operations are carried out in a glove box under Ar atmosphere. The tube is sealed under vacuum and heat treated at 750 °C during 24 h.

X-ray diffraction patterns were obtained using a Panalytical Empyrean diffractometer operating with $\text{Cu K}\alpha_1\alpha_2$ radiation ($\lambda_1 = 1.5406 \text{ \AA}$ and $\lambda_2 = 1.5443 \text{ \AA}$) in capillary configuration (transmission) with 0.2 mm diameter capillaries. Le Bail and Rietveld refinements of the XRD pattern were performed using the Fullprof suite [12].

Impedance measurements were carried out using a Solartron 1260 analyzer on pellets ($\varnothing 13 \text{ mm}$ - 5 tons/370 MPa). Depending on the experiment, a heat treatment (500 °C during 12 h in an evacuated glass ampoule) was applied or not on the pellet, as indicated in each case. Gold blocking electrodes were sputtered on each face of the pellets using a device directly opening into the dry box. Measurements were carried out between 10 MHz and 1 Hz or between 10 MHz and 10 kHz, with an amplitude of 20 mV. For the temperature dependence study, impedance diagrams were measured every 5 °C once the oven temperature was stable (variation lower than 0.5 °C during 10 min) between 25 °C and 110 °C. For the Arrhenius plots, the temperature used is the one measured by a sensor in the measuring cell very close to the sample.

Impedance measurements were also carried out on cold-pressed pellets ($\varnothing 13 \text{ mm}$ - 5 tons/370 MPa), with Li foils as electrodes. The measurements were carried out at different times between $t = t_0$ and $t = t_0 + 94 \text{ h}$ and for frequencies between 10 MHz and 1 Hz with an amplitude of 50 mV.

Electrochemical stability was characterized by cyclic voltammetry using a 3-electrode set-up: on one side of the solid electrolyte pellet, a gold working electrode is sputtered on half the surface. On the other side of the pellet, a gold counter electrode is sputtered on the entire

surface. A thin piece of a pressed mixture of Ag_3SI (prepared as reported by Takahashi and Yamamoto [13] and Ag (Sigma Aldrich, 99.9% of purity)) is used as reference electrode and is kept in contact on the non-sputtered part of the pellet, next to the working electrode. The measured potential of the reference electrode was 2.11 V vs. Li^+/Li in agreement with earlier work [14]. Using a VMP galvanostat-potentiostat (Biologic), cyclic voltammograms were performed at $20 \text{ mV} \cdot \text{s}^{-1}$ between -2 V and 5 V vs. $\text{Ag}_3\text{SI}/\text{Ag}$, starting with anodic or cathodic sweep.

Liquid electrolyte coin cells (14 mm diameter) were built using 1 M LiTFSI in TEGDME/1,4-dioxane (Sigma-Aldrich) as electrolyte soaked in a Celgard plus Viledon separator, a Li metal foil as negative, and the positive was a mixture of the $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ or Li_2SnS_3 active material (80 mass%), Super P carbon (15 wt%) as conducting additive, and PTFE (Sigma Aldrich - 5 wt%) as binder. All solid state cells with $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ (or Li_2SnS_3) used as active positive electrode material were built as follows: composite electrodes were prepared by mixing in a mortar 40 mg of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ (or Li_2SnS_3), 5 mg of Vapor Grown Carbon Fiber (VGCF - Shoma Denko) and 60 mg of $\text{Li}_6\text{PS}_5\text{Cl}$ prepared as reported by Boulineau et al. [15]. The batteries were assembled by cold pressing ($\varnothing 10 \text{ mm}$, 5 tons/370 MPa) 10 mg of composite as positive electrode (15 mg for Li_2SnS_3), 80 mg of $\text{Li}_6\text{PS}_5\text{Cl}$ as solid electrolyte, and a Li foil as negative electrode. Using a VMP galvanostat-potentiostat (Biologic), galvanostatic measurements were carried out at $64 \mu\text{A} \cdot \text{cm}^{-2}$ (starting with discharge) with potential limits at 0.1 V and 5 V vs. Li^+/Li . The measurements were performed in argon atmosphere using the device described in Fig. 1, which maintains a pressure on the all-solid state cell while cycling.

For all-solid state cells with $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ as negative electrode and electrolyte, composite electrodes are prepared by mixing in a mortar 40 mg of LiCoO_2 , 60 mg of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ and 5 mg of VGCF for the positive electrode composite and 100 mg of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ and 5 mg of VGCF for the negative electrode composite. 10 mg of positive electrode composite, 80 mg of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}\text{-NEI}$ and 10 mg of negative electrode composite are cold pressed ($\varnothing 10 \text{ mm}$, 5 tons 375 MPa) to form an all solid state battery, in the same device as described above. Galvanostatic measurements were carried out at $64 \mu\text{A} \cdot \text{cm}^{-2}$ (starting with charge) with voltage limits at 3.7 V and 2 V.

3. Results and discussions

3.1. Structural characterization

Fig. 2 shows the XRD pattern of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$. The sloping baseline is due to the capillary Debye-Scherrer setup used. The crystal structure published by Bron et al. was used as starting point for Rietveld refinement of this powder pattern [9]. Global although not perfect agreement was achieved by considering the presence of a second minority phase,

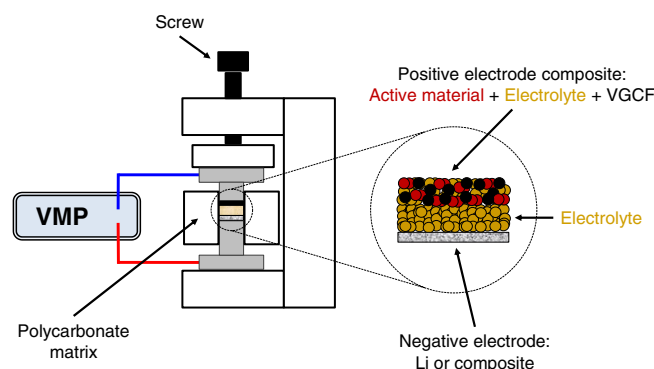


Fig. 1. Device for all-solid state cells.

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