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Synthesis, structure and electrochemical performance of the argyrodite Li_6PS_5Cl solid electrolyte for Li-ion solid state batteries

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ABSTRACT

The high lithium conductivity of argyrodite Li_6PS_5Cl makes it an attractive candidate as solid electrolyte in all solid-state Li batteries. Aiming at an optimal preparation strategy the structure and conductivity upon different mechanical milling times is investigated. Li_6PS_5Cl material with high ionic conductivity of $1.1 \cdot 10^{-3}$ S/cm was obtained by milling for 8 hours at 550 rpm followed by a heat-treatment at 550 °C. All solid-state Li-S batteries were assembled, combining the Li_6PS_5Cl solid electrolyte, with a carbon-sulfur mixture as positive electrode and Li, Li-Al and Li-In as negative electrode. An optimum charge/discharge voltage window between 0.4 and 3.0 V vs. Li-In was obtained by CV experiments and galvanostatic cycling displays a very large capacity around 1400 mAh/g during the first cycles, decreasing below 400 mAh/g after 20 cycles. Impedance spectroscopy suggests that the origin of the capacity fading is related to an increasing electrode-electrolyte interface resistance.

1. Introduction

The demand for safe electrical energy storage technologies with high energy density for electric vehicle applications is emerging [1]. Li-ion batteries with organic liquid electrolytes have safety issues due to potential electrolyte leakage and the inherent flammability [2]. Unlike liquid electrolytes, solid electrolytes are non-flammable mitigating most safety issues and in addition the reduced packaging demands potentially improves the gravimetric and volumetric energy density. However, one of the biggest obstacles for the commercial applicability of solid electrolytes in all solid state batteries is their low ionic conductivity compared to conventional organic liquid electrolytes [2].

Numerous efforts have been devoted to finding solid Li-ion conductors with high ionic conductivities, a wide electrochemical stability window and excellent chemical stability. For practical battery application the conductivity of the solid electrolyte needs to exceed 10^{-3} S/cm near room temperature. Intensive research has led to several families of electrolytes, including the sulphides (Li_2S-P_2S_5, Li_2S-SiS_2, Li_2S-GeS_2) [3,4], the oxides ($Li_7La_3Zr_2O_{12}$ and $Li_{3x}La_{2/3-3x}TiO_3$) [5,6] and the phosphates (LiPON, $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$) [7–9]. Among them, oxides and phosphates display relatively small low ionic conductivities, mainly attributed to the high grain boundary resistances [2]. More recently there has been a renewed interest in $Li_{10}GeP_2S_{12}$, having a very high ionic conductivity of 10^{-2} S/cm at room temperature [10]. However, the large costs of the GeS_2 starting material required for its synthesis limits its potential for large scale applications. Another important emerging family of solid electrolytes are the Li-argyrodites Li_6PS_5X (X = Cl, Br and I) with Li-ion conductivities in the range of 10^{-2}–10^{-3} S/cm at room temperature [11]. In addition to high Li-ion conductivities Li_6PS_5Cl is reported to have a wide electrochemical window up to 7.0 V vs. Li/Li$^+$ [12]. The conductivities of these materials are comparable to $Li_{10}GeP_2S_{12}$, however the much cheaper precursors gives this family of materials a large potential to be applied in all solid state batteries. Sylvain et al. [12,13] assembled solid state cells using Li_6PS_5Cl as the electrolyte, $LiCoO_2$ as the cathode, and spinel $Li_4Ti_5O_{12}$ as anode, exhibiting excellent electrochemical performance. The theoretical capacity of $LiCoO_2$ however is relatively small motivating research on high capacity electrode materials. Sulphur has attracted much attention in past years because of its high theoretical capacity of 1672mAh/g, giving a theoretical specific energy of 2500 Wh/kg, making it one of the most promising anode materials for next generation lithium batteries [14]. However, Li-ion batteries with sulphur in combination with a liquid electrolyte has many problems including short cycle life, low charging efficiency, poor safety, and a high self-discharge rate, all of which are related to the dissolution of lithium polysulfide, the series sulphur reduction intermediates in liquid electrolyte and resulting

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parasitic reactions [15–17]. By combining sulphur with solid electrolytes, such as Li_3PS_4 [18] and Li_2S-P_2S_5 [19], the high capacities of sulphur may be better utilised, making this a promising system for future applications. Chen et al. [20] combined S with Li_6PS_5Br to construct a solid-state cell, showing an initial discharge capacity of 1355mAh/g and reversible capacity of 1080 mAh/g after 50 cycles. They attributed the excellent electrochemical performance of the solid-state battery to the small particle size of the active materials.

Rao *et al.* [21] reported on the synthesis protocols for argyrodite Li_6PS_5X (X = Cl, Br, I) using high speed mechanical milling followed by an annealing treatment, resulting in crystalline materials with Li-ion conductivities on the order of 10^{-3} S/cm at room temperature. Using neutron powder diffraction during annealing Rao et al. [22] were able to establish a clear correlation between the annealing temperature and the ionic conductivity. It was concluded that an annealing temperature of at least 250 °C is required to obtain ionic conductivities reaching 10^{-3} S/cm. [22] With combined refinement of XRD and Neutron Diffraction patterns Rayavarapy et al. [23] showed that besides the disorder in the lithium distribution the disorder in the S^2/Cl^- or $S^2//Br^-$ distribution promotes the Li-ion mobility, also supported by recent bond-valence analysis calculations [24]. Various studies have been performed to obtain the ionic in Li_6PS_5X (X = Cl, Br, I) using impedance spectroscopy [11,12,21–23,25,26] resulting in conductivities varying between 10^{-7} and 10^{-2} S/cm and activation energies varying between 0.11 and 0.56 eV.

By considering the structure and conductivity depending as a function of the ball mill synthesis route the present work aims at an optimal synthesis route of Li_6PS_5Cl. Batteries combining Li_2S as positive electrode, Li_6PS_5Cl as electrolyte and In as negative electrode were assembled to determine the optimal dis(charge) window, resulting in high initial capacities approaching 1500 mAh/g degrading over 20 cycles towards 400 mAh/g.

2. Experimental

Reagent-grade Li_2S (99.98%, Sigma-Aldrich), P_2S_5 (99%, Sigma-Aldrich), and LiCl (99.0%, Sigma-Aldrich) crystalline powders were used as starting materials. The required amount of starting materials were ball milled in a WC coated (inner) stainless steel jar with 10 WC balls (8 g/ball) in an Argon filled glovebox (H_2O, $O_2 < 0.3$ ppm) because of the reactivity with oxygen and moisture. The total weight of the mixture was almost 2.0 grams, and the ball milling speed was fixed at 550 rpm. The milling duration was varied to find the optimal milling time. After subsequent mixing times a small amount of powder was collected to perform powder XRD. After the ball milling process, the mixture was sealed in a quartz tube and annealed at 550 °C for 5 hours to obtain the final Li_6PS_5Cl solid electrolyte.

Powder XRD patterns were collected over a 2θ range of 10-160° to identify the crystalline phases of the prepared materials using $Cu_{K\alpha}$ X-rays (1.5406 Å at 45 kV and 40 mA) on an X'Pert Pro X-ray diffractometer (PANalytical). To prevent reaction with moisture and oxygen the powders were sealed in an airtight XRD sample holder in an Argon filled glove box.

The neutron data were collected on the new neutron powder diffractometer PEARL of the TU Delft [27]. Data were collected at room temperature using the (533) reflection of the germanium monochromator (lambda = 1.665AA). The sample was loaded under Argon in a 6 mm diameter air-tight vanadium sample can. The sample was measured for 18 hours from 10.4–160 degrees 2θ. The sample can is under vacuum during the data collection. The data treatment consisted of a relative correction for detection efficiency of (each of) the 1408 detector pixels and a substraction of the background, caused by the instrument and the sample can. Rietveld refinement was performed using GSAS [28].

Ionic conductivities of the ball-milled powders and the final Li_6PS_5Cl solid electrolyte were measured by preparing pallets of the powder with a diameter of 10 mm. Stainless-steel disks were attached on both faces of the pellets. AC impedance measurements were performed on an Autolab (Autolab PGSTAT302N) in the frequency range of 0.1 Hz to 1 MHz with an applied voltage of 0.05 V.

Laboratory-scale solid-state Li-S batteries were fabricated in the following manner: The S-C composite was obtained firstly by mixing S at 450 rpm for 6 h, Active carbon (Super P, TIMCAL) was added with a weight ratio of 1:1, and the composite was mixed at 500 rpm for 3 h. After that, the ball-milled S-C mixture was sealed in a quartz tube and annealed at 155 °C for 12 h [29]. Finally, the obtained S-C composite was mixed with Li_6PS_5Cl and super P with a weight ratio of 4:4:2 and a rotation speed of 450 rpm for 1 h. Then, a two-layer pellet (d = 10 mm), consisting of 12 mg of the described cathode mixture and 88 mg Li_6PS_5Cl solid electrolyte was pressed together using 6 tons of pressure. After that, a piece of Li-In alloy foil (or Li metal, Li-Al alloy) was attached on the other side, this triple-pellet was pressed with 2 tons of pressure for 30 s. The Li-In and Li-Al electrodes were obtained by pressing a piece of Li metal ($\phi = 8$ mm) and a piece of In or Al foil ($\phi = 6$ mm) together. The assembled cell was charged and discharged under a current density of 0.064 mA/cm^2 between 0.4 and 3.0 V to evaluate the electrochemical performance. The test cell was cathode-limited, which means that there was a lithium excess in the Li-In alloy anode. The obtained capacity was normalized by the weight of S in the cathode electrode. The CV measurements of the solid-state battery were performed at different voltage windows with a sweep speed of 0.5 mV/s. The EIS measurements were conducted with an Autolab (Autolab PGSTAT302N) before and after the charge/discharge process in the frequency range of 0.1 Hz and 1 MHz with an applied voltage of 0.05 V.

3. Results and discussions

Fig. 1 shows XRD patterns for the mixture prepared by mechanically milling Li_2S, P_2S_5 and LiCl powders between 1 to 16 h. The raw materials were mixed and ball milled at 110 rpm for 1 h to get a homogenous mixture. The reflections of the mixture

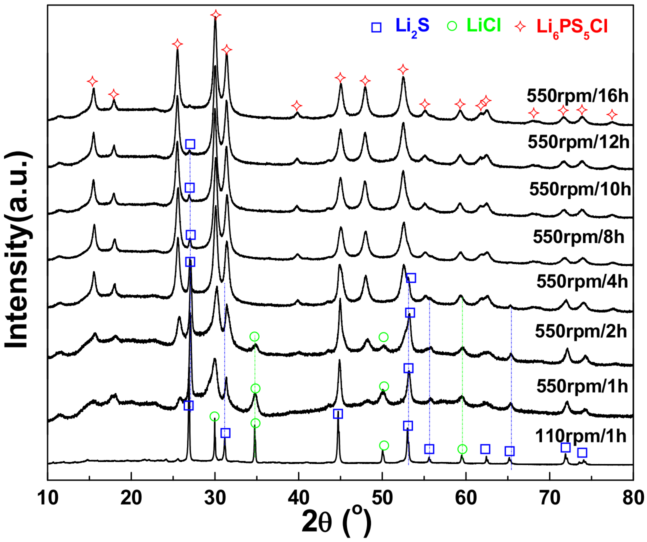

Fig. 1. XRD patterns of the mixture of Li_2S, P_2S_5 and LiCl powders ball milled with different milling times.