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High capacity all-solid-state Cu–Li_2S/Li_6PS_5Br/In batteries

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ABSTRACT

Inorganic lithium ion fast conductor Li_6PS_5Br has high ionic conductivity and consequently is promising as solid electrolyte in all-solid-state lithium secondary batteries. Here we fabricated Li_6PS_5Br by ball milling and subsequent heat treatment. The argyrodite phase already formed at 300 °C and is electrochemically stable between 0 and 4 V. Preparing Cu–Li_2S–argyrodite composite cathode mixtures by ball milling increases the initial charge and discharge capacity of all-solid-state Cu–Li_2S/Li_6PS_5Br/In batteries compared to mortar-ground composite cathode mixtures. A charge capacity of 500 mAh/g and discharge capacity of 445 mAh/g were achieved using composite cathode powder ball milled for 30 min. However, batteries using composite cathode prepared by either method show similar reversible discharge capacity for a range of C rates as the capacity is mainly limited by volume change of cathode material and the mixed mobile ion effect. Rietveld refinements after 20 cycles show an incomplete conversion stage with partial Cu^+ for Li^+ insertion both in the active material and the solid electrolyte.

1. Introduction

New applications particularly in electromobility place a strong demand on the next generation of batteries with high safety, reliability and energy density. An effective way to enhance operational safety is to substitute inorganic solid electrolyte for liquid electrolyte. Among the promising class of thiophosphate-based fast ion conductors for such all-solid-state lithium secondary batteries, we focus on lithium argyrodites Li_6PS_5X (X = Br, Cl) [1–4] that reach room temperature conductivity of 7×10^{-4} S/cm and are electrochemically stable. So far there are only a few studies on Li_6PS_5X solid electrolyte (SE) in all-solid-state lithium secondary batteries, e.g. LTO:C:SE/SE/Li [3,5] or $LiCoO_2$:C:SE/SE/In [6].

To prepare all-solid-state batteries with superior energy density, it appears natural to combine the sulfide-based electrolytes with transition metal sulfide conversion-type cathode materials, such as Cu–Li_2S (theoretical specific capacity of 490 mAh/g). By introducing finely dispersed metallic copper, Cu–Li_2S overcomes the electronically insulating nature of the discharge product Li_2S. In addition, Cu–Li_2S can be combined with negative electrodes that do not contain lithium sources, e.g. carbon, indium. Hayashi et al. [7] reported all-solid-state lithium secondary battery with Cu–Li_2S as cathode and Li_2S–P_2S_5 glass ceramic as electrolyte, achieving an initial capacity of 490 mAh/g.

Here we report the combination of lithium argyrodite Li_6PS_5Br solid electrolytes with Cu–Li_2S. The all-solid-state Cu–Li_2S/Li_6PS_5Br/In batteries showed a maximum initial specific charge capacity of 500 mAh/g and discharge capacity of 445 mAh/g. Studies on CuS as initial cathode materials for the all-solid-state batteries are in progress and will be reported separately.

2. Experimental

Lithium argyrodite Li_6PS_5Br electrolyte was fabricated by ball milling and subsequent heat treatment [2,3]. Stoichiometric mixtures of reagent-grade Li_2S, P_2S_5 and LiBr were milled using a high-energy planetary ball mill (Fritsch Pulverisette 7) under a rotating speed of 500 rpm for 20 h. The resulting precursor mixture was pelletized, annealed at 300 °C for 5 h under argon atmosphere and ground again for further application.

The electrochemical stability of Li_6PS_5Br was evaluated by cyclic voltammetry. The Li_6PS_5Br powder was pelletized and sandwiched between a stainless steel disk working electrode and a lithium foil counter electrode. Potential sweeps were then applied between −0.5 V and 4 V at a scanning rate of 2 mV/s using a potentiostat/galvanostat (Arbin BT2000). The morphology of Li_6PS_5Br after pelletization under a pressure of 6000 kg/cm^2 was investigated by scanning electron microscopy (SEM).

For the preparation of the active cathode material, a mixture of reagent grade Cu (Merck) and Li_2S (Alfa Aesar, 99.9%) in a molar ratio of 1: 1 was ball milled at 500 rpm for 5 h. Composite cathode powders were then prepared by mixing Cu–Li_2S as prepared above, Li_6PS_5Br and carbon in a weight ratio of 40: 56: 4 by mortar grinding or ball

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milling at a rotating speed of 500 rpm for 30 min. The morphology of the composite powder was investigated by SEM.

For the assembly of all-solid-state Cu–Li_2S/Li_6PS_5Br/In batteries (in the discharged state), the respective composite cathode powder and Li_6PS_5Br solid electrolyte were pelletized in a 13 mm die under a pressure of 6000 kg/cm^2. An indium foil as negative electrode was then attached to the electrolyte side and the stack was sealed in a 13 mm Swagelok cell. Cyclic performance of the batteries was investigated using the potentiostat/galvanostat at a current density of 50 mA/g (based on the weight of active material Cu–Li_2S) between 0.05 V and 2.5 V at room temperature. Rate performance of the batteries was studied at various charging/discharging C rates, 0.5C – 0.02C, changing the C rate every 5 cycles.

X-ray powder diffraction (XRD) measurements were conducted on the ball-milled composite cathode before cycling and after 20 cycles (discharged state) between 0.05 V and 2.5 V at 0.1C. A Mylar film was used to protect the sample from air during measurement. Rietveld refinement of the resulting XRD patterns was performed using the generalized structure analysis system (GSAS) [8].

3. Results and discussion

Rietveld refinement of the initial composite cathode (see Fig. 1 (a)) shows no formation of any new phase besides Cu, Li_2S, Li_6PS_5Br and minor LiBr, suggesting there was no chemical reaction occurred during ball milling. The molar ratio of Cu:Li_2S in ball-milled Cu–Li_2S was confirmed by a separate Rietveld refinement to be 48: 52 in line with the 1: 1 mixture before ball milling, implying no significant preferential amorphization of either phase. The analysis of the XRD pattern also confirms the successful fabrication of argyrodite-type "Li_6PS_5Br" by ball milling and subsequent heat treatment. It should be noted that the annealing temperature applied was only 300 °C instead of 550 °C as reported earlier [1,4]. The halide content of argyrodite is slightly substoichiometric $Li_{6+x}PS_{5+x}Br_{1-x}$ ($x \approx 0.05$), in line with previous findings [1]. While argyrodite can be formed at even lower temperature or just mechanochemically [3,6], our recent study [3] clarified that halide content, distribution and ordering and thereby room temperature ionic conductivity depend on the annealing temperature.

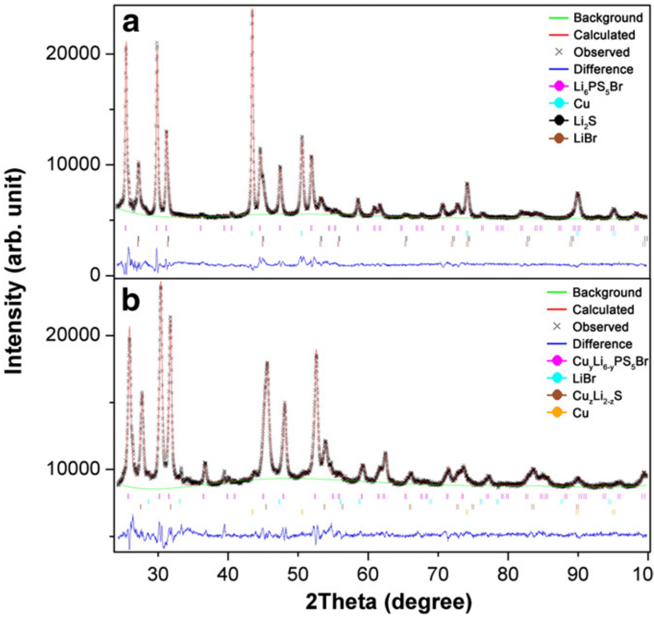

Fig. 1. Rietveld refinements of the composite cathode (a) before cycling and (b) after 20 cycles (discharged state) between 0.05 V and 2.5 V at 0.1C.

Electrochemical stability of Li_6PS_5Br was evaluated by cyclic voltammetry. The only two distinct peaks in Fig. 2, correspond to the cathodic deposition of lithium metal (−0.2 V to −0.5 V) and its anodic dissolution (0 V to 0.7 V), indicating that Li_6PS_5Br is essentially stable over the entire voltage range from −0.5 V to 4 V. However, there is a very small broad peak around 2 V, probably caused by the oxidation of free S^{2-} ions, as the oxidation potential of the free S^{2-} ions is calculated to be 2.2 V vs. Li/Li$^+$.[9] The small feature around 4 V might correspond to the oxidation of free Br^- ions. Accordingly, a wide electrochemical window for Li_6PS_5Cl is reported in ref. [6]. On the other hand DFT studies by Holzwarth et al. [10] suggest that Li_6PS_5Cl is only metastable with respect to decomposition into Li_3PS_4, Li_2S, and LiCl.

The morphologies of Li_6PS_5Br solid electrolyte and of composite cathode powders prepared by mortar grinding or ball milling were studied using SEM. Fig. 3 (a) shows the SEM image of a Li_6PS_5Br pellet. The annealed Li_6PS_5Br pellet was mortar ground and pelletized at a pressure of 6000 kg/cm^2 before the SEM analysis. Mortar-ground µm-sized Li_6PS_5Br particles were aggregated after pelletization, leaving as the contrast the individual crystallites with a size up to 100 nm. No distinct holes or gaps appeared on the pellet. Therefore, the pellet should be sufficiently compact to effectively separate the electrodes and prevent short-circuiting of the battery. The SEM image of composite cathode powder prepared by mortar grinding (Fig. 3b) shows argyrodite and copper particles with a diameter larger than 5 µm surrounded by smaller particles (Li_2S, C) of around 1 µm. Ball milling could effectively reduce the particle size of argyrodite, leaving copper particles of up to 5 µm as the largest particles (Fig. 3c). EDX analysis revealed that the mortar-ground sample still contained large carbon particles, while the carbon distribution in ball-milled composites was much more uniform, probably due to the exfoliation of carbon during ball milling.

Room temperature cyclic performances of all-solid-state Cu–Li_2S/Li_6PS_5Br/In batteries with composite cathode materials prepared by mortar grinding and ball milling were determined between 0.05 V and 2.5 V at a current density of 50 mA/g based on the weight of Cu–Li_2S (0.1C, corresponding to ca. 442 µA/cm^2). Charging and discharging curves of the resulting batteries during the first cycle are shown in Fig. 4 (a). The battery using the mortar-ground composite cathode had a practical initial charge capacity of 380 mAh/g and discharge capacity of 310 mAh/g, whereas ball-milling of the cathode composite greatly increases the practically achievable specific charge and

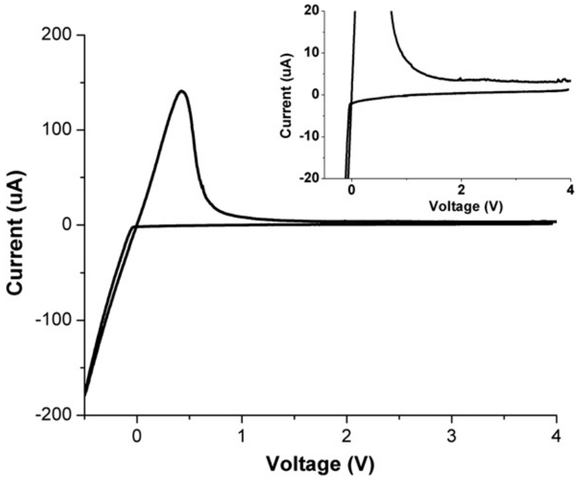

Fig. 2. Cyclic voltammogram of Li/Li_6PS_5Br/stainless steel cell at a scanning rate of 2 mV/s between −0.5 V and 4 V. Inset: enlarged voltammogram in the current range of −20 µA to 20 µA.

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