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$LiBH_4$-NaX (X=Cl, I) composites with enhanced lithium ionic conductivity

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ABSTRACT

In the present study, ball-milled $LiBH_4$-NaX (X = Cl, I) composites were investigated as fast ionic conductors, in which both halide solid solution $LiBH_{4-x}Cl_x$ and eutectic composite $LiBH_4$-$NaBH_4$ coexist and facilitate the ionic transportation jointly within the system. Measurements by differential scanning calorimetry (DSC) observed that both transition enthalpies and transition temperatures were all reduced, implying that the high temperature phase of $LiBH_4$ was stabilized. $LiBH_4$-NaX (X = Cl, I) composites deliver a conductivity value of 10^{-2} S cm^{-1} when temperature is higher than 373 K. At the same time, these values are almost 100 times higher than that of pristine $LiBH_4$ at a temperature below 373 K. A window voltage of 3 V was identified by means of the cyclic voltammetry (CV) measurements on $LiBH_4$-NaX (X = Cl, I) composites for 4 cycles. Furthermore, the structural stability of $LiBH_4$-NaX (X = Cl, I) composites during the ramping process from room temperature to 393 K were demonstrated by *in-situ* X-ray diffraction (XRD) as well as Fourier Transform infrared spectroscopy (FTIR). It can be concluded that additional NaX (X = Cl or I) plays important roles in the enhancement of ionic conductivity of $LiBH_4$ due to stabilizing the high-temperature phase of $LiBH_4$.

1. Introduction

Researches on superior conductors would allow the improvement of solid-state Li-ion batteries, eliminating the hazard raised by liquid electrolytes and improving the electrochemical stability. However, still several issues are necessary to be solved. One is solid electrolytes which possess low ionic conductivity far from that of liquid electrolytes [1,2]. The other is interface between the electrolyte and electrode materials [3]. In this work, we mainly focused on the conductivity of solid electrolytes, especially at room temperature.

Many solid conductors for lithium ion have been developed so far [4–10]. LiI based solid state battery is one of few commercially distributed solid state batteries. Although the conductivity of LiI is in the order of 10^{-7} S cm^{-1} at room temperature, it still exhibits high stability [7]. The incorporation of aluminum oxide to LiI substantially increased the conductivity [8].

$LiBH_4$ possesses novel ionic conductivity at high temperature and has attracted much attention over ten years [11,12]. It usually undergoes a structural transition from orthorhombic to hexagonal (hereinafter called LT phase and HT phase, respectively) at about 383 K [13]. The conductivity of the HT phase approached to 10^{-3} S cm^{-1} at 383 K. Therefore, stabilization of the HT phase at low temperature is highly desired. The HT phase of $LiBH_4$ can be stabilized by a series of lithium halides (LiI, LiBr and LiCl) [14,15]. On the other hand, the ionic conductivity of $LiBH_4$-$NaBH_4$ eutectic system has been greatly improved from that of pristine $LiBH_4$ in our previous study [16]. Both chemical and electrochemical stabilities were enhanced as well. Therefore, it is expectable to synthesize a kind of $LiBH_4$-NaX (X = Cl, I) composites in which halides and the

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produced $NaBH_4$ might synergistically enhance the ionic conductivity of samples.

In this paper, both $NaBH_4$ and Li halides synergistically improve ionic conductivities of $NaBH_4$-LiX (X = Cl, I) composites from that of pristine $LiBH_4$. Their phase structures were investigated by means of *ex-situ* and *in-situ* X-ray diffraction (XRD) measurements, Fourier transform infrared spectra (FTIR) measurements and Raman spectra measurements. Their thermal stability was studied by diffraction scanning calorimetry (DSC). We examined the electrochemical stability of $LiBH_4$-NaX (X = Cl, I) composites by means of cyclic voltammetry (CV).

2. Experimental section

2.1. Preparation of the $LiBH_4$-NaX composites

The purchased $LiBH_4$ (95%, Alfa Aesar) and NaCl/NaI (95%, Alfa Aesar) powders are used directly without further treatment. They were mixed at a specific molar ratio, loaded in a QM-1SP planetary ball mill pot, and pulverized at 450 rpm. The weight ratio of powder to ball in each stainless steel grinding tank (100 mL) was 1: 40. All measurement procedures were performed in a glove box full of Ar (purity 99.9999%, pressure 0.1 MPa) to avoid oxygen and humidity.

2.2. Structural characterization

To confirm the phase structure of the samples, XRD measurements were performed using a Rigaku SmartLabTM 3 kW Cu-Kα diffractometer, and each sample cell was covered with an amorphous polymer film (Scotch 810 #Magic Tape) to prevent moisture. FTIR measurements were performed on Thermo Nicolet 5700 in transmission mode. The weight ratio of the sample powder to the KBr powder in the mixture is about 1:200. The laser wavelength was 532 nm and the wave number ranged from 3500 cm^{-1} to 500 cm^{-1}. In order to observe real-time variation of the phase in the sample with increasing temperature, *in-situ* XRD (Rigaku) measurements were performed under a pressure of around 3×10^{-3}MPa. The test temperature was increased from room temperature to 393 K and the interval was 10 K.

2.3. Ionic conductivity

A sample pellet for conductivity measurement was prepared at a pressure of 20 MPa with a diameter of 10 mm and a thickness of approximately 1 mm. Before impedance measurement, lithium foil was covered on both sides of the pellet. Lithium ionic conductivity of each composition was measured by alternative current impedance method using CHI660e (Shanghai Chenhua Co. Ltd) through the frequency range from 1 Hz to 1 MHz. The temperature increased from 303 K to 393 K with a step of 5 K. Prior to impedance measurement, each interval would last for 20 min at a constant temperature.

2.4. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) measurements on $LiBH_4$-NaX were examined on the same electrochemical workstation as impedance measurements. Those manufactured pellets are not as sandwiched as AC impedance measurements. A lithium foil covered the pellets as previous work [16,17]. Their structure can be described as $LiBH_4$-NaX|Li, The lithium foil is reference electrode. The scan rate was at 10 mV s^{-1} ranging from −1 V to 3 V.

2.5. Differential scanning calorimetry (DSC)

In order to determine the phase transition temperature of $LiBH_4$-NaX system, DSC measurements were performed on ~ 2 mg of samples on a TA Q2000 instrument at a heating rate of 2 K min^{-1}. Samples were heated to 413 K from room temperature, and purged with high purity Ar (99.9999%, 0.1 MPa) at a flowing rate of 20 mL min^{-1}.

3. Results

3.1. Structural characterizations

Fig. 1 shows the XRD patterns of x$LiBH_4$-NaCl composites after being milled (x = 2, 3, 4 respectively). These patterns indicate that $LiBH_4$ did react with NaCl during ball milling because $NaBH_4$ and LiCl could be identified in XRD patterns. Ionic exchange took place between parent phases. It means that the product after ball milling should be a composite of $LiBH_4$-$NaBH_4$-LiCl. Diffraction peaks belonging to o-$LiBH_4$ phase are hardly found in these patterns because of its low diffraction intensity or forming amorphous phase after ball milling. Such phenomenon has been observed in previous work on $LiBH_4$-relevant composites [19]. In XRD patterns of y$LiBH_4$-NaI composites after ball milling (y = 1, 2, 4, 8 respectively) shown in Fig. 2, only NaI appears.

The crystallites sizes of both $NaBH_4$ and LiCl phases were calculated by Scherrer's equation [17,18]. Average sizes of NaI crystallites in different composites were calculated by equation (1) as well.

$$D = K\gamma / B\cos\theta \qquad (1)$$

D is the average crystallite size (nm), K is the Scherrer constant, γ reflects the X-ray wavelength and is a constant of 0.154056 nm. B represents the full width at half maximum of the diffraction peak of the sample. θ is the Bragg angle.

To further reveal the phase structure during ball milling, we conducted measurements of Raman spectra as Supplementary Fig. 2 and FTIR spectra as Supplementary Fig. 3. They demonstrate the presence of B-H bands belonging to $LiBH_4$ in ball milled $LiBH_4$-NaCl composites. In addition, the stretching vibration (γ_1) of

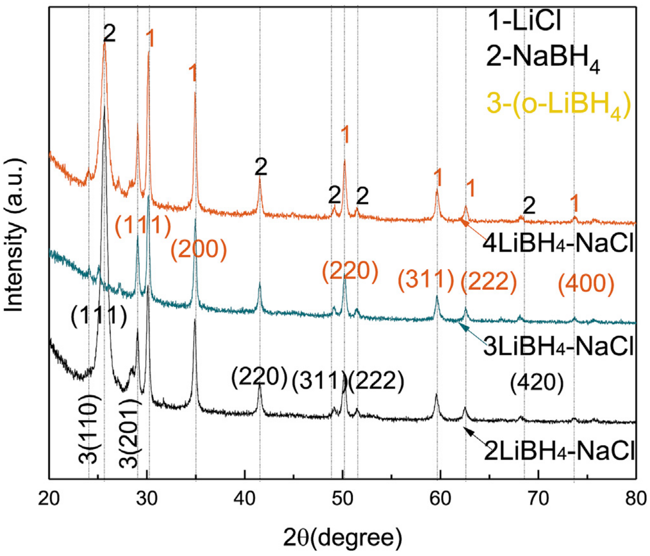

Fig. 1. XRD patterns of different $LiBH_4$-NaCl composites after ball milling.