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Sodium-ion conduction in $Na_2Zn_2TeO_6$ solid electrolytes

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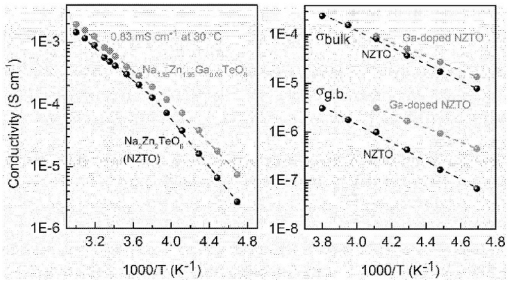
HIGHLIGHTS

- Solid $Na_2Zn_2TeO_6$ electrolytes were sintered at temperatures of 800 ~ 850 °C.
- Sodium-ion conduction in the grain bulk and at grain boundaries was investigated.
- The sodium-ion conductivity was enhanced to 0.83 mS cm^{-1} by Ga-doping.
- Ga-doping enhanced the ionic conductivities of the grain bulk and grain boundaries.
- The mechanisms for the enhancement of the ionic conductivity were analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

The ionic conduction in a novel solid sodium-ion conductor of $Na_2Zn_2TeO_6$ (NZTO) is investigated from the point of view of defect chemistry. NZTO shows an ionic conductivity of 0.57 mS cm^{-1} at room temperature, and the grain bulk conductivity and the grain-boundary conductivity are individually measured using the AC impedance spectroscopy at temperatures down to −30 °C. The grain-boundary conductivities are about two orders of magnitude lower than those of the grain bulk; such a phenomenon can be ascribed to the Schottky barrier at the grain boundaries of the NZTO electrolyte. The concentration and mobility of the charge carriers in the grain bulk are calculated from the grain bulk conductivity. The concentration and mobility of the charge carriers and the Schottky barrier height can be tuned by doping; the ionic conductivity of NZTO is enhanced to 0.83 mS cm^{-1} by the doping of 2.5 mol% Ga at the Zn sites, because the Ga-doping increases the concentration and mobility of the charge carriers, and lowers the Schottky barrier height.

1. Introduction

Sodium batteries are promising alternatives to lithium batteries because of the abundance and low cost of the raw materials, especially for the large-scale energy storage systems [1,2]. However, conventional batteries face the serious safety concerns due to the easy leakage and flammability of organic liquid electrolytes. Therefore, all-solid-state sodium batteries (ASS-SB) attract growing attentions. This kind of batteries use solid electrolytes, which are of excellent safety, and they are capable of achieving high energy densities with metallic anode and high potential cathodes [1–3]. However, ASS-SBs are impeded from practical applications by several hurdles, among which the low ionic conductivity of solid electrolytes is essential. To improve the ionic conductivity, the ionic conduction in the solid electrolyte must firstly be understood.

Several research groups reported some solid sodium-ion electrolytes

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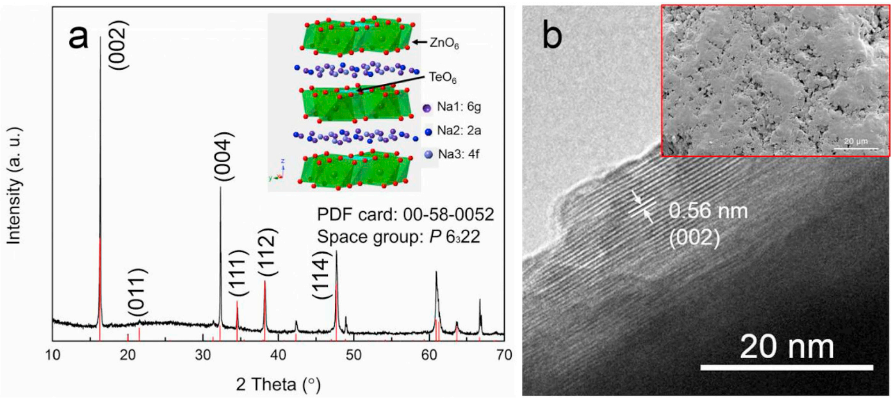

Fig. 1. (a) XRD pattern and (b) TEM image of NZTO electrolyte. The insets are the crystal structure of NZTO and the SEM image of the NZTO electrolyte, respectively.

for ASS-SBs, which can be roughly classified into three categories: inorganic [4–7], polymer [8,9] and composite [10,11] solid electrolytes. The sodium-ion conductivities of inorganic solid electrolytes are orders of magnitude higher than those of the other two kinds. Among the inorganic materials, the conductivities of sulfides are the highest, reaching 10 mS cm^{-1} [5], but sulfides are sensitive to humidity, and can produce poisonous H_2S. Fortunately, oxides exhibit high sodium-ion conductivities, for example, the conductivity of NASICON-type $Na_3Zr_2Si_2PO_{12}$ is 3.4 mS cm^{-1} at 25 °C [4], and shows good stability in air.

$Na_3Zr_2Si_2PO_{12}$ ceramics require high-temperature sintering at around 1200 °C. It is difficult to obtain all-ceramic solid sodium batteries, because of the inevitable interfacial reactions between the electrode and electrolyte at high temperatures. Evstigneeva et al. [12] synthesized a new family of fast sodium-ion conductors: $Na_2M_2TeO_6$ (M = Ni, Co, Zn, Mg) at 800–820 °C; among them $Na_2Zn_2TeO_6$ (NZTO) is quite promising, because no transition metals are involved. The ionic conductivity of NZTO is 0.09 mS cm^{-1} at room temperature [12], lower than that of $Na_3Zr_2Si_2PO_{12}$; therefore, to enhance the ionic conductivity is the prerequisite for their applications in all-ceramic solid sodium batteries.

NZTO is a honeycomb-structured compound with a space group of $P6_322$, and in the layers, every TeO_6 octahedron is surrounded by six ZnO_6 octahedra through edge-sharing, while sodium ions are located between the layers at three different sites, all of which are partially occupied, thus Na^+ ions can migrate among them and the sodium-ion conduction arises [12]. In this work, NZTO ceramics were synthesized and the sodium-ion conduction was analyzed from the view points of the grain bulk conduction and the grain boundary conduction for the first time. More significantly, a doping strategy was applied to increase the sodium-ion conductivity to ~0.83 mS cm^{-1} at room temperature. Not limited to the particular material system of NZTO, this work could also be beneficial to the enhancement of the ionic conductivity of other solid ionic conductors.

2. Experimental

NZTO and gallium-doped NZTO ceramic samples were prepared via solid state reaction from Na_2CO_3, ZnO, Ga_2O_3 and TeO_2, with 3 mol.% Na_2CO_3 in excess to compensate for the Na volatilization at high temperatures. The powder was firstly ball-milled for 12 h, and then fired in air at 800–900 °C for 15 h to ensure the oxidization of Te^{4+} to Te^{6+} and the initial chemical reactions, which was followed by another ball-milling for 12 h. Afterwards, the powder was cold isostatic pressed into pellets at 250 MPa, and sintered at 850–900 °C for 12 h in air. During sintering, the pellet was covered with the mother powder to minimize the sodium-loss. Finally, the obtained pellets were polished to a diameter of ~0.95 cm and a thickness of ~0.175 cm for the following tests.

The phase structure of the prepared sample was checked by X-ray diffraction (XRD) using X'pert PRO PANalytical X-ray diffractometer. The relative densities of the samples were measured by the Archimedes method using water. Sirion 200 Field-Emission Scanning Electron Microscope (FE-SEM) (FEI Corporation, Holland) was used to investigate the sample microstructure. Transmission Electron Microscope (TEM) investigations were performed on a Talos f200× Field-Emission TEM.

Ag pastes were coated on the parallel surfaces of the circular samples and then dried at 100 °C for 60 min to get ion-blocking Ag electrodes. AC impedance measurements were undertaken at temperatures from −60 to 60 °C on Ag/NZTO/Ag cells by means of a Solartron 1260 impedance analyzer in the frequency range of 1–5 × 10^6 Hz and at an amplitude of 50 mV. The sample was heated at desired temperatures for an hour before each measurement.

In addition, the sample resistances were corrected for porosity according to the Bruggeman symmetric model for the 3-3 connectivity of spherical grains and pores (assuming the latter to have zero conductivity) [13,14],

$$\sigma_t = \frac{\sigma_c}{1 - \frac{3f}{2}} \tag{1}$$

where σ_c is the conductivity of the porous ceramic body, f is the volume fraction of pores, and σ_t is the true conductivity of the sample.

3. Results and discussion

3.1. Crystalline phase and microstructure

The crystalline phase and the microstructure of the NZTO ceramic were investigated and the results are shown in Fig. 1. As shown in Fig. 1a, all the peaks in the XRD pattern can be indexed to NZTO with a space group of $P6_322$, and there is not any impurity phase in the sample. The NZTO is a layer-structured material, with ZnO_6 and TeO_6 octahedra constructing the framework through edge-sharing, and sodium ions are located at the interlaminar sites. As shown in the inset in Fig. 1a, there are three different sites for sodium ions: 6 g, 2*a* and 4*f*, and it is easy for sodium ions to transport between 6 g and 2*a* sites, while the sodium ions at 4*f* site are relatively refined [12,15]. Fig. 1b shows the TEM and SEM (inset) images of the NZTO ceramic. The interplanar spacing in the TEM image is about 0.56 nm, which can be indexed to the (002) plane. From the SEM image, it can be seen that there are pores in the NZTO ceramic, and its poriosty is ~15%.

3.2. Sodium ion conductivity

Fig. 2a exhibits a typical AC impedance spectrum of the NZTO electrolyte at room temperature. There is a distorted semicircle in the