Electrochimica Acta 282 (2018) 409–415

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Conductivity and stability of $Li_{3/8}Sr_{7/16-3x/2}La_xZr_{1/4}Ta_{3/4}O_3$ superionic solid electrolytes

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ARTICLE INFO

Article history:
Received 16 March 2018
Received in revised form
16 May 2018
Accepted 12 June 2018
Available online 12 June 2018

Keywords:
Oxide solid electrolyte
Solid-state reaction method
Impedance spectroscopy
Lithium ion conductivity

ABSTRACT

Oxide solid electrolytes $Li_{3/8}Sr_{7/16-3x/2}La_xZr_{1/4}Ta_{3/4}O_3$ (LSLZT, $x = 0$, 0.025, 0.05) with different A-site vacancy were synthesized using conventional solid-state reaction procedure at 1300 °C. Approximately single-phase perovskite-type was obtained which was analyzed by X-ray diffraction. Moreover, scanning electron microscope, AC impedance spectroscopy and potentiostatic polarization measurement methods were adopted to study the microstructure, Li^+ conductivities and electronic conductivities of the samples, respectively. Among these samples, the optimal composition of $Li_{3/8}Sr_{7/16-3x/2}La_xZr_{1/4}Ta_{3/4}O_3$ ($x = 0.025$) was selected with bulk conductivity of 1.26×10^{-3} S cm^{-1}, total conductivity of 3.30×10^{-4} S cm^{-1}, electronic conductivity of 6.60×10^{-9} S cm^{-1} at 30 °C and activation energy of 0.28 eV. Furthermore, the cyclic voltammogram analysis indicated the stability of this solid electrolyte at voltages higher than 1.3 V against metallic lithium. The solid electrolyte as a separator in $LiFePO_4$/Li half-cell showed good cycle performance that comprises 98.7% of original values at 0.2 C charge-discharge rates after 50 cycles.

1. Introduction

The Li-ion batteries (LIBs) have gained a wide interest of researchers in the synthesis of advanced energy-storage devices because of its remarkable properties such as good mechanical strength, efficient energy storage capacity and easy miniaturization [1]. The Li-ion batteries find their potential use in microcomputers, smartphones, plug-in hybrids (PHEVs) and all-electric vehicles (EVs) [2] though suffer some security issues. However, all solid-state batteries can provide a fundamental solution to safety concerns by replacing flammable organic liquid electrolyte. Additionally, it provides an increased life to the batteries as there are no species except Li-ion diffusing in the electrode and no side occur in the solid-solid interface [3,4]. Other advantages include high Li-ion conductivity and wide electrochemical window [4]. Up to now, the Li-ion conductivity of the solid electrolytes that have been studied was in the range of 10^{-5}~10^{-3} S cm^{-1} at room temperature. Recently, different solid electrolytes for all solid-state batteries have been extensively investigated, such as oxide electrolytes [5] and sulfide electrolytes [6]. However, the sulfide electrolytes suffer from various disadvantages such as high cost and chemical instability in air [6].

During a decade, different solid oxide electrolytes including Garnet-type [7–17], NASICON-type [15,16], LISICON-type [17,18], Perovskite-type [19–28] are getting a wide attention for their used in all solid-state batteries. The garnet-type Li-ion solid electrolytes $Li_7La_3Zr_2O_{12}$ (LLZO) was first reported by Murugan [7]. Subsequently, Kotobuki et al. reported the related compound, $Li_5La_3Ta_2O_{12}$ [8–10]. Later, it was noticed that the solid electrolytes such as $Li_7La_3Zr_2O_{12}$, $Li_5La_3Ta_2O_{12}$ and related materials possess great stability against molten lithium. Hence, there has been an upsurge of interest for these solid electrolytes in the recent years due to their high Li-ion conductivity of 10^{-4} S cm^{-1}. Several studies revealed that trivalent doping as Al^{3+} occupies the lithium positions [11] or zirconia sub-lattice [12–15] and tetravalent doping as Ge^{4+} occupies the zirconium position [16] or tantalum position [10], which provided an effective way to increase the Li-ion conductivity in all of these cases. In addition, Ga^{3+} doping on the La^{3+} site and Al^{3+} doping on the Zr^{4+} site helped to stabilize the cubic phase [11–15]. Pentavalent doping as Ta^{5+} and Nb^{5+} enhanced the ionic conductivity by increasing the concentration of Li-ion in the vacancy site [11,17]. For perovskite-type electrolytes, the system

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https://doi.org/10.1016/j.electacta.2018.06.085
0013-4686/

$Li_{3x}La_{2/3-x}TiO_3$ ($0 < x < 0.16$) was successfully prepared with perovskite structure. It exhibited a bulk Li-ion conductivity of 10^{-3} S cm^{-1} at room temperature; however, it also kept the large grain-boundary resistance due to which the Li-ion conductivity was reduced [22–26]. Chen et al. [22] demonstrated that the Li-ion intercalated into the structure at potentials below 1.8 V as Ti^{4+} showed instability with lithium metal and easily get reduced to Ti^{3+}. Further, Chen et al. [27] prepared an electrolyte $Li_{2x-y}Sr_{1-x}Ta_yZr_{1-y}O_3$ ($x = 3y/4$) with perovskite-type structure. The optimized composition of $Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O_3$ had been obtained with a highest total ionic conductivity of 8×10^{-5} S cm^{-1} at 30 °C. It showed the stability of electrolyte is stable above 1.0 V vs Li. Additionally, Inada et al. [28] obtained a solid oxide electrolyte $Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O_3$ with few secondary phases such as $SrTa_2O_6$ and $Sr_2Ta_2O_7$ by covering the same mother powder. Moreover Kimura et al. [29] synthesized $Li_{2x-y}Sr_{1-x}Ta_yZr_{1-y}O_3$ with different Ta contents ($y = 0.60$, 0.70, 0.75, 0.77 and 0.8) and also proved that $Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O_3$ as the optimized composition. However, the total Li-ion conductivity of Kimura's study was higher than 8×10^{-5} S cm^{-1} due to larger density and fewer impurity phases. Similarly, Yu et al. [30] replaced Ta to Nb and synthesized Li-Sr-Zr-Nb-O (LSZN) solid electrolytes with perovskite-type structure. They implicated that the optimal composition of $Li_{3/8}Sr_{7/16}Nb_{3/4}Zr_{1/4}O_3$ has a high total ionic conductivity of 2×10^{-5} S cm^{-1} at 30 °C. Furthermore, to study the influence of excess lithium ion electrical properties of $Li_{3/8}Sr_{7/16}Zr_{1/4}Nb_{3/4}O_3$, the 20 wt% of excess Li_2CO_3 was added and found that the total conductivity of solid electrolyte was improved [31].

In this paper, perovskite-type $Li_{3/8}Sr_{7/16-3x/2}La_xZr_{1/4}Ta_{3/4}O_3$ electrolytes were prepared with various La contents as $x = 0$, 0.025, 0.05, 0.10, 0.15 using a conventional solid-state reaction method. A-site vacancy ($C(\square) = 3/16 + x/2$) were increased with an increase of La_2O_3 doping. Meanwhile, the conductivity of electrolyte is related to the concentration of A-site vacancy, which assisted in improving the conductivity of ceramics to a certain limit. The samples were named as LSLZT-X, where X (1, 2, 3, 4, 5) represents the doping concentration. The amount of La_2O_3 was optimized and the subsequent influences of La_2O_3 on the microstructure, crystal structure, Li^+ conductivity, electronic conductivity and the chemical stability of the electrolytes were investigated.

2. Experimental

LSLZT with different La_2O_3 doping amounts ($x = 0$, 0.025, 0.05, 0.10, 0.15) were synthesized via a conventional solid-state reaction method. The nominal composition of lithium-ion and vacancy of five LSLZT samples are summarized in Table 1. The content of lithium-ion vacancy increased with an increase of x value. The raw materials Li_2CO_3 (20 wt% in excess, 99.0%, AR), $SrCO_3$ (99.5%, AR), La_2O_3(99.95%, AR), ZrO_2(99.5%, AR), Ta_2O_5 (99.5%, AR) were prepared according to the stoichiometric ratio. These raw materials were mixed with ethanol and grounded for 10 h using planetary ball milling with polyurethane ball and zirconia grinding media. Further, the wet raw materials were dried to remove alcohol at 120 °C in blast air oven. After grounding, the raw materials were followed with calcination at 1100 °C for 12 h in air using an alumina crucible. The calcined powders were grounded again, and then pressed into pellets (15 mm in diameter) at a pressure of 200 MPa by cold isostatic pressing. After that, the LSLZT pellets were placed into zirconia crucible and covered with the same mother powder. Finally, the pellets were sintered at 1300 °C for 12 h in air.

Table 1
Nominal composition of lithium-ion and vacancy of $Li_{3/8}Sr_{7/16-3x/2}La_xZr_{1/4}Ta_{3/4}O_3$ ($x = 0$, 0.025, 0.05, 0.10, 0.15) prepared in this study. Symbol $\square$ represents the expected content of A-site vacancy.

Code	x	$C(Li^+)$	$C(\square)$
LSLZT-1	0	0.375	0.1875
LSLZT-2	0.025		0.2000
LSLZT-3	0.05		0.2125
LSLZT-4	0.10		0.2375
LSLZT-5	0.15		0.2625

The identification of the crystal phase of LSLZT samples with different doping amounts was characterized by X-ray diffraction (XRD, Ultima IV, RIGAKU) using Cu Kα radiation ($\lambda = 0.15418$ nm), with a measurement angle range of $2\theta = 5$–$90°$ and a step interval of 0.02°. The X-ray diffraction(XRD) data was used to compute the lattice sizes of LSLZT samples. A scanning electron microscope (SEM, JEM-7800F, JEOL) was used to observe the cross-section microstructure of samples. The density of samples was calculated by Archimedes principle following the equation $\rho = (m_1 \cdot \rho_{water})/(m_1 - m_2)$, where, ρ is the density of samples, m_1 is the weight of samples in air and m_2 is the weight of samples in distilled water, $\rho_{water} = 1$ is density of distilled water. Additionally, the theoretical density of electrolytes following the equation $\rho_{theory} = m/V$, where m is the weight of the single unit cell and V is the volume of the single unit cell. Ion conductivity of each sample was tested by AC-impedance technique (S1 1260 Impedance/Grain-Phase analyzer, Solartron) with frequency ranging from 1 Hz to 10 MHz and polarization voltages of 0.1 V. Both sides of samples were coated with a conducting Au ink layer (dried at 800 °C for 2 h) as blocking electrode before testing. Electronic conductivity was evaluated by potentiostatic polarization measurement (V3 electrochemical workstation, Princeton) at 30 °C with scanning time of 30 min and applied voltage of 4 V.

Electrochemical window of LSLZT-1 and LSLZT-2 were measured by a cyclic voltammetry using Li/LSLZT-1 or LSLZT-2/Au. To reduce the interface impedance, liquid electrolyte was added between solid electrolyte and the lithium foil. The cyclic voltammetry (CV) test was carried out on an electrochemical work-station (V3 electrochemical workstation, Princeton) with a voltages ranging between 0 and 4.5 V at a scanning rate of 0.5 mV s^{-1}. To evaluate the capacity of solid electrolyte, the sample LSLZT-2 was sintered at 1300 °C, crushed to powder and were made into electrode laminates. The weight ratio of electrolyte powder: carbon black: polyvinylidene (dissolved in N-methyl-2-pyrrolidone) was taken as 80 wt%: 15 wt%: 5 wt%. The mixed materials were coated onto an aluminum current collector and dried under vacuum at 80 °C overnight. After punched and weighed, CR 2032 coin cell was made using LSLZT-1 or LSLZT-2 powder as cathode, 1 M $LiPF_6$ in EC: DMC = 1:1 (volume ratio) as an electrolyte and lithium foil as anode, and the cells were assembled in a glovebox. Charge-discharge measurement was performed with a Li-ion battery testing system (CT2001A, LAND) at 0.1 C rate over the potential range of 1–2.5 V at 25 °C. In some literature [32,33], the solid electrolyte has been used as a separator. To test the performance of LSLZT-2 solid electrolyte, commercial $LiFePO_4$ powder was used as the cathode. The preparation method of $LiFePO_4$/Li half-cell is the same as mentioned above. Except for the difference that the weight ratio of $LiFePO_4$: carbon black: polyvinylidene was selected as 80 wt%: 10 wt%: 10 wt% and charge-discharge measurement was performed at 0.2 C rate over the potential range of 2.5–4.2 V.

3. Results and discussion

3.1. Crystal structures and microstructures

Fig. 1 demonstrated the XRD patterns of LSLZT samples sintered at 1300 °C with heat preservation for 12 h. For LSLZT-1, LSLZT-2 and