Supporting Information

Reassessing the bulk ionic conductivity of solid state electrolytes

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Experimental

Materials

Li(OH), La_2O_3, Al_2O_3, and ZrO_2 were purchased from Sigma-Aldrich Chemical Co. LLC. The Al_2O_3 was 13nm particle size. All precursors were reagent grade. Li(OH) and La_2O_3 were kept in an Argon filled glovebox to avoid air and moisture exposure. Isopropyl alcohol was purchased from Fisher Scientific Inc. (70% v/v) and used as it is. For comparison, a commercial LLZO was also used which was collected from Toshima Manufacturing Co. Ltd., Japan (purity 99.9%).

Synthesis of the Solid-State Electrolyte

Li(OH), La_2O_3, Al_2O_3, and ZrO_2 were mixed in isopropyl alcohol in a stoichiometric ratio of $Li_7La_3Zr_2O_{12}$, with 0.2 mol.% of Al replacing Zr and an excess of 60 wt.% Li(OH) to compensate Li loss during the calcination. The mixing was obtained in a planetary mill using zirconia jars and balls. The mixing time was 12 hours, and the ball to powder ratio was maintained as 20:1. The slurry was spray dried (Yamato GB-22) with inlet and outlet temperature of 175 °C and 90 °C respectively. The powder was calcined in an alumina crucible at 900 °C for 12 hours, and further ball milled to obtain the LLZO powder. Pellets were made by pressing LLZO powder with 10-ton pressure for 15 mins. The diameter of the pellet was 19 mm, and the thickness was 1– 1.5 mm.

Materials and Electrochemical Characterizations

Phase analysis was done using an X-ray diffractometer (Bruker AXS) using Cu Kα radiation. Morphology of the LLZO powders were studied using a field emission SEM (Carl Zeiss Auriga-BU). For the EIS measurements, the pellet was placed between two gold-coated copper plates in air (ion blocking electrode) or two lithium foils in argon environment (non ion-blocking electrode) with glass slides on the outer sides. EIS was performed with an electrochemical workstation (Bio-Logic SP300) from different HFL to 10 Hz with a 500 mV perturbation amplitude at different temperatures. From the Nyquist plot of impedance, the ionic conductivity was calculated by using the equation: $\sigma = d / (R_b \times A)$; where σ is the ionic conductivity in S/cm, d is the thickness of the pellet in cm, R_b is the bulk resistance in Ω, and A is the area of the pellet in cm^2.

Table S1: Frequency limit and corresponding ionic conductivity of different solid-state electrolytes. The list is merely comprehensive, and only represents a brief overview of the current state-of-the-art solid electrolyte studies in lithium ion batteries.

Sl. No.	Name of the Solid-State Electrolyte (SSE)	Higher Frequency Limit (kHz)	Lower Frequency Limit (Hz)	Ionic Conductivity (S/cm)	Type of the SSE	Year	Ref.
1	$Li_{7-x}La_3Zr_2O_{12-1/2x}$	1.0E+03	1.0E-01	5.7E-04	Garnet	2011	1
2	$Li_7La_3Zr_2O_{12}$	7.0E+03	1.0E+00	4.0E-04	Garnet	2011	2
3	$Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$	1.0E+03	1.0E+00	8.7E-04	Garnet	2012	3
4	$Li_{6.15}La_3Zr_{1.75}Ta_{0.25}Ga_{0.2}O_{12}$	1.0E+03	1.0E+00	8.7E-04	Garnet	2012	3
5	t-$Li_7La_3Zr_2O_{12}$	1.0E+03	1.0E+00	2.3E-05	Garnet	2012	4
6	$Li_7La_3Zr_2O_{12}$	1.0E+03	1.0E+01	1.7E-04	Garnet	2012	5
7	$Li_{7-x}La_{3-x}Ce_xZr_2O_{12}$	8.0E+02	1.0E+01	1.4E-05	Garnet	2013	6
8	$Li_7La_3Zr_2O_{12}$	8.0E+02	1.0E+01	4.0E-04	Garnet	2013	7
9	$Li_{6.16}Al_{0.28}La_3Zr_2O_{12}$	1.5E+04	2.0E+01	6.1E-04	Garnet	2014	8
10	$Li_7La_3Zr_2O_{12}$	1.0E+02	1.0E+00	2.5E-04	Garnet	2014	9
11	$Li_7La_3Zr_2O_{12}$	1.0E+03	5.0E-02	4.9E-04	Garnet	2014	10
12	$Li_7La_3Zr_2O_{12}$	1.0E+03	1.0E-01	5.2E-04	Garnet	2014	11
13	$Li_7La_3Zr_2O_{12}$	7.0E+03	1.0E+00	4.6E-04	Garnet	2016	12
14	$Li_7La_3Zr_2O_{12}$	5.0E+03	1.0E+02	2.0E-04	Garnet	2016	13
15	Li_3ClO	5.0E+03	1.0E-01	2.5E-02	Halide	2014	14
16	$LiGe_2(PO_4)_3$	1.0E+03	1.0E-02	1.0E-04	NASICON	1997	15
17	$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$	1.0E+04	1.0E-01	7.3E-04	NASICON	2007	16
18	$Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$	1.0E+03	1.0E-01	1.1E-03	NASICON	2008	17
19	$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$	1.0E+03	1.0E-02	5.1E-03	NASICON	2008	18
20	$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$	1.0E+02	1.0E-02	1.0E-04	NASICON	2013	19
21	$Li_2S.GeS_2.P_2S_5$	1.0E+03	1.0E-01	2.2E-03	Sulfide	2001	16
22	$80Li_2S{\cdot}20P_2S_5$	1.5E+04	1.0E+02	7.2E-04	Sulfide	2003	20
23	$Li_2S.P_2S_5$	8.0E+03	1.0E+01	3.2E-03	Sulfide	2005	21
24	$Li_{10}GeP_2S_{12}$	1.0E+03	1.0E-01	1.2E-02	Sulfide	2011	22
25	$Li_2S.P_2S_5.P_2S_3$	8.0E+03	1.0E+01	5.4E-03	Sulfide	2011	23
26	Li_2S-P_2S_5-Li_3N	1.0E+03	1.0E-01	1.4E-03	Sulfide	2017	24
27	$Li_{10+\delta}[Sn_ySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$	1.5E+04	1.0E+01	1.2E-02	Sulfide	2017	25

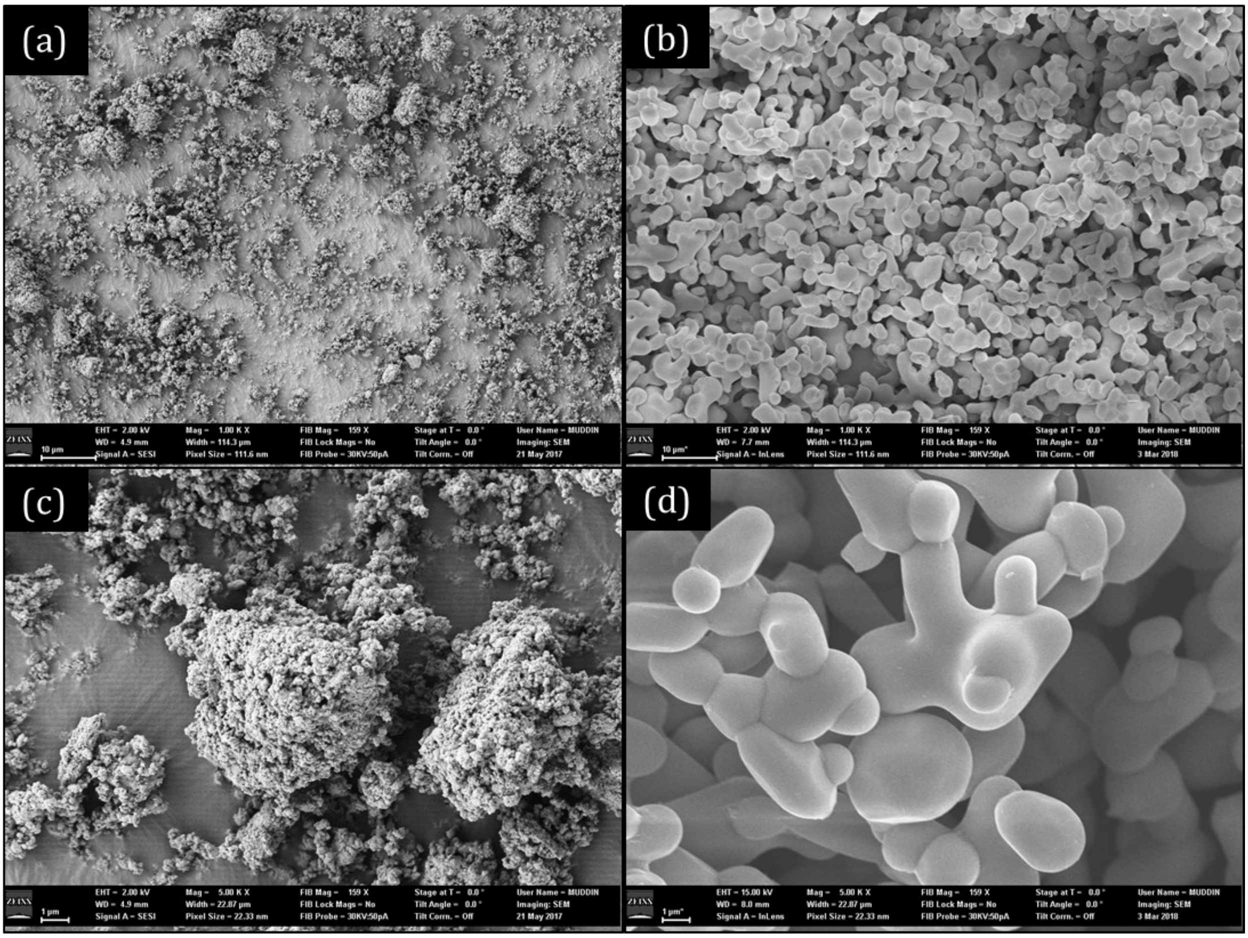

Figure S1: SEM micrograph of (a) experimental LLZO powder and (b) commercial LLZO powder, (c) higher magnification of (a) and (d) higher magnification of (b)

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