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# Preparation of $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$ ( $0 \leq x \leq 0.5$ ) solid electrolyte and its application in all-solid-state Li-ion batteries

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$\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  ( $0 \leq x \leq 0.5$ ) solid electrolytes were synthesized using a mechanochemical method. XRD indicated that the prepared samples had a cubic structure. The lattice parameter was dependent on the value of  $x$ . The cold-pressed pellet of the sample with  $x = 0.45$  had an ionic conductivity of about  $2.4 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C and an activation energy of about 0.446 eV. The equivalence circuit and distribution of the relaxation time indicated that grain boundary resistance was the main component of the total resistance of the sample. The hot-pressed pellet of the sample with  $x = 0.45$  had an ionic conductivity of about  $9.2 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C and an activation energy of about 0.300 eV, which were comparable with those of the reported halide-based solid electrolyte. The solid-state cell employing the sample with  $x = 0.45$  as a solid electrolyte and bare  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  as the active material showed good cyclic ability at room temperature.

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## 1. Introduction

All-solid-state Li-ion batteries (ASS LIBs) have been investigated for a long time, and have been intensively studied from about 2010. At its most basic, an all-solid battery uses a solid electrolyte instead of an electrolyte solution. Replacement of an electrolyte solution by a solid electrolyte could make an all-solid battery able to operate at high temperatures and have a higher energy density than conventional batteries.<sup>1</sup> The solid electrolyte is the most important component when moving from a conventional LIB to an ASS LIB. Solid electrolytes can be divided into the following groups: oxides, sulfides, hydrides, halides and polymers.<sup>2</sup>

The biggest disadvantage of an oxide solid electrolyte is the very high sintering temperature, about 1000 °C, to bind the oxide particles. Meanwhile, the inter-particle adhesion of halide and sulfide solid electrolytes can take place under medium pressure (about 100–700 MPa) and room temperature. This is a huge advantage when applied to mass production. The sulfide solid electrolyte is unstable when in contact with the positive electrode active material that has a voltage greater than 2.80 V vs.  $\text{Li}/\text{Li}^+$ ; therefore, it is necessary to create a thin film to

separate the active material and the sulfidic solid electrolyte to prevent the reaction between the two materials.<sup>3</sup> In contrast, halide electrolytes ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ) are stable at high voltages, making them suitable for use in the positive electrode of ASS LIBs.

Halide solid electrolytes were studied in the early 1930s with  $\text{LiI}$  being the typical research object.<sup>4</sup> In 2018, high ionic conductivity  $\text{Li}_3\text{YCl}_6/\text{Li}_3\text{YBr}_6$  materials were successfully synthesized and their application in ASS batteries was reported.<sup>5</sup> The synthesis of  $\text{Li}_3\text{InCl}_6$  using an aqueous solution was first reported in 2019.<sup>6</sup> Since then, several members of this group have been extensively studied and reported.<sup>7,8</sup> The monoclinic  $\text{Li}_2\text{ZrCl}_6$  prepared at a high temperature exhibited a low  $\text{Li}^+$  conductivity of  $5.7 \times 10^{-6} \text{ S cm}^{-1}$ , but the mechano-chemically prepared hexagonal close-packed  $\text{Li}_2\text{ZrCl}_6$  showed a moderate  $\text{Li}^+$  conductivity of  $4.0 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C.<sup>9</sup> It was reported that the ionic conductivity of monoclinic  $\text{Li}_2\text{ZrCl}_6$  was improved from  $7.1 \times 10^{-6}$  to  $2.1 \times 10^{-3} \text{ S cm}^{-1}$  at 30 °C due to the aliovalent substitution of Zr by In.<sup>10</sup> High-energy ball-milling derived  $\text{Mn}^{2+}$  doped  $\text{Li}_2\text{ZrCl}_6$  had an ionic conductivity of  $8.0 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature, which was higher than that of bare  $\text{Li}_2\text{ZrCl}_6$ .<sup>11</sup> The disordered cubic spinel  $\text{Li}_{1.9}\text{Sc}_{0.7}\text{Cl}_4$ ,  $\text{Li}_{2.08}\text{Sc}_{0.64}\text{Cl}_4$  and  $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$  showed high ionic conductivities of  $1.09 \times 10^{-3}$ ,  $1.22 \times 10^{-3}$  and  $1.5 \times 10^{-3} \text{ S cm}^{-1}$ , respectively, at 30 °C.<sup>12</sup> The mechanochemically synthesized  $\text{LiAlCl}_4$  had a monoclinic structure and exhibited an ionic conductivity of about  $2.1 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature, which was about 20 times higher than the reported value of the material prepared by solid state reaction at a high temperature.<sup>13</sup>

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Most of the reported halide solid electrolytes are based on rare earth elements.<sup>14–17</sup>  $\text{Li}_3\text{TiCl}_6$ ,  $\text{LiAlX}_4$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{Li}_2\text{ZnCl}_4$  are the reported solid electrolytes that employed earth-abundant elements.<sup>18–21</sup>  $\text{Li}_2\text{ZnCl}_4$  had a cubic spinel structure at low temperature and an olivine structure at temperatures higher than 215 °C.<sup>21</sup> The ionic conductivity of olivine  $\text{Li}_2\text{ZnCl}_4$  was about  $2.0 \times 10^{-4} \text{ S cm}^{-1}$  at 280 °C. The ionic conductivity of cubic spinel  $\text{Li}_2\text{ZnCl}_4$  was about  $10^{-7} \text{ S cm}^{-1}$  at 100 °C. Therefore, the improvement of the ionic conductivity of cubic  $\text{Li}_2\text{ZnCl}_4$  is an interesting issue. This study aimed to prepare a cubic  $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  ( $0 \leq x \leq 0.5$ ) solid electrolyte using mechanochemical synthesis. The as-prepared samples were subsequently heat-treated at 170 °C for 4 h in a dry argon atmosphere. The samples had a cubic structure. The resistance of cubic  $\text{Li}_2\text{ZnCl}_4$  was too large to be measured at room temperature. The ionic conductivity of the sample  $\text{Li}_{2.45}\text{In}_{0.45}\text{Zn}_{0.55}\text{Cl}_{4.9}$  ( $x = 0.45$ , hot-pressed) was about  $9.2 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C. The ASS cell employing  $\text{Li}_{2.45}\text{In}_{0.45}\text{Zn}_{0.55}\text{Cl}_{4.9}$  solid electrolyte and  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  as an active material showed good cyclic ability at room temperature.

## 2. Experimental

$\text{LiCl}$  (99.99% purity; Macklin),  $\text{ZnCl}_2$  (99.99% purity; Macklin),  $\text{InCl}_3$  (99.99% purity; Macklin) were purchased and used without further purification. In a typical batch (2 g of raw materials), appropriate amounts of the raw materials were weighed and mixed using a mortar and pestle for about 15 min and then placed in a zirconia pot (45 mL) with 30 g of zirconia balls

( $\varnothing$  5 mm). The pot was rotated at 360 rpm using a Pulverisette 7 (Fritsch) for 12 h. The obtained samples were recovered and heat treated at 170 °C for 4 h in a dry argon atmosphere.

The structures of the prepared powders were characterized by XRD (Bruker X8) and thermogravimetry–differential thermal analysis (TG–DTA; EVO II, Rigaku). TG–DTA data were obtained in a dry nitrogen flow at a heating rate of  $5 \text{ K min}^{-1}$ . The total resistivity of the prepared samples was recorded using alternating current impedance spectroscopy (PGSTAT302N, Autolab, Switzerland) from 1 MHz to 10 Hz under a dry  $\text{N}_2$  flow. The solid electrolyte pellets were made as previously reported.<sup>22</sup>

$\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  (MTI) (hereafter denoted as NCM) without any coating was employed as an active material in an ASS cell to study the stability of the prepared solid electrolyte. The positive electrode composites were prepared by manually mixing NCM, the sample  $\text{Li}_{2.45}\text{In}_{0.45}\text{Zn}_{0.55}\text{Cl}_{4.9}$  ( $x = 0.45$ , heat-treated at 170 °C), and Ketjen Black with a weight ratio of 68.5 : 28.5 : 3.0 using an agate mortar. The ASS cell composed of the prepared electrode composite (about 11.0 mg),  $\text{Li}_6\text{PS}_5\text{Cl}$  (about 100 mg) as separator, and a Li–In negative electrode was fabricated using the reported procedure.<sup>23</sup> About 100 mg of  $\text{Li}_6\text{PS}_5\text{Cl}$  were pressed in a polycarbonate mold (diameter of 10 mm) under 100 MPa for 1 min. About 11.0 mg of the electrode composite was dispersed on one side of the  $\text{Li}_6\text{PS}_5\text{Cl}$  layer and pressed under 330 MPa for 5 min. A piece of In metal foil (Aldrich, 99.995%, 8 mm diameter, 0.1 mm thickness) was placed on the other side of the  $\text{Li}_6\text{PS}_5\text{Cl}$ , followed by attaching a piece of Li foil (Aldrich, 99.999%, 4 mm diameter, 0.1 mm thickness) on the In foil. The cell was then pressed at 30 MPa

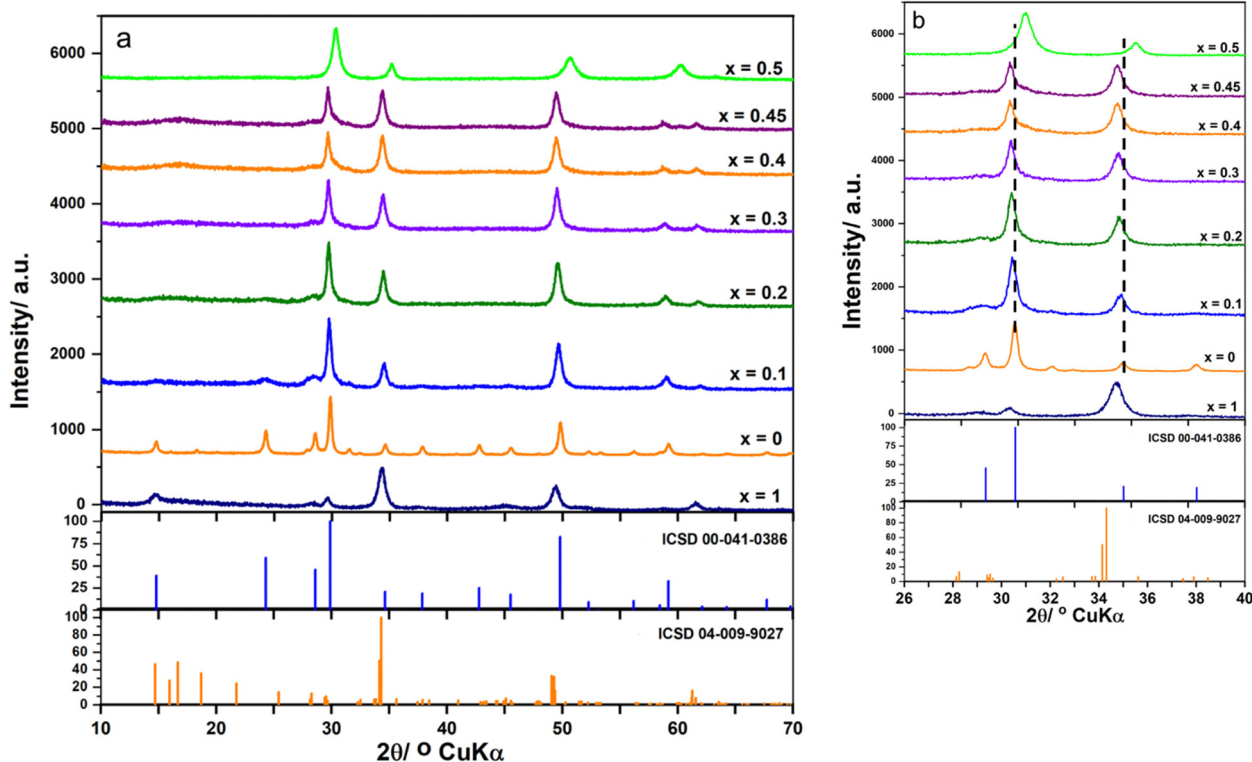


Fig. 1 (a) XRD patterns of the as-prepared  $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  ( $0 \leq x \leq 0.5$ ) samples; (b) enlargement of Fig. 1a.



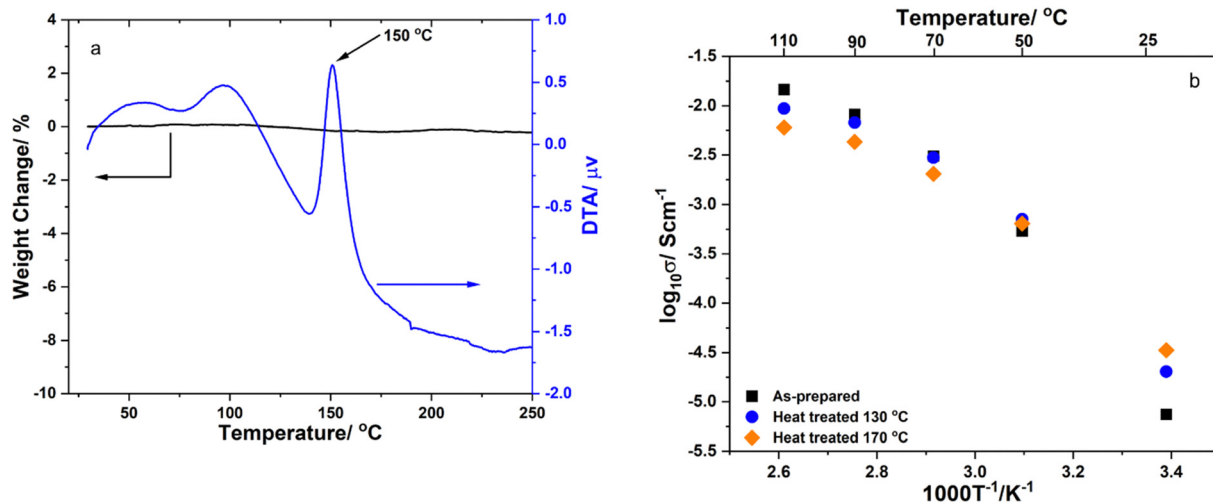


Fig. 2 (a) TG-DTA curves of the  $\text{Li}_{2.4}\text{In}_{0.4}\text{Zn}_{0.6}\text{Cl}_{4.8}$  sample; (b) temperature dependence of the ionic conductivity of the  $\text{Li}_{2.4}\text{In}_{0.4}\text{Zn}_{0.6}\text{Cl}_{4.8}$  solid electrolyte heat-treated at different temperatures.

for 30 sec. Stainless-steel rods with a diameter of 10 mm were used as a current collector (electrode area  $0.785 \text{ cm}^2$ ). The cell was rested at room temperature for 2 h before the cycling test. Galvanostatic testing of the cells involved cycles in CC mode ( $1\text{C} = 200 \text{ mA h g}^{-1}$ ) using a VMP3 (BioLogic) to study the stability of the sample with  $x = 0.45$ . The cut-off voltages were 3.70 and 2.40 V vs. Li-In. All electrochemical measurements were recorded at room temperature.

All the experiments were carried out in a glove box (Ar-filled,  $[\text{H}_2\text{O}] < 0.1 \text{ ppm}$ ) or an airtight sample holder.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared  $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  ( $0 \leq x \leq 0.5$ ) samples, and the standard patterns

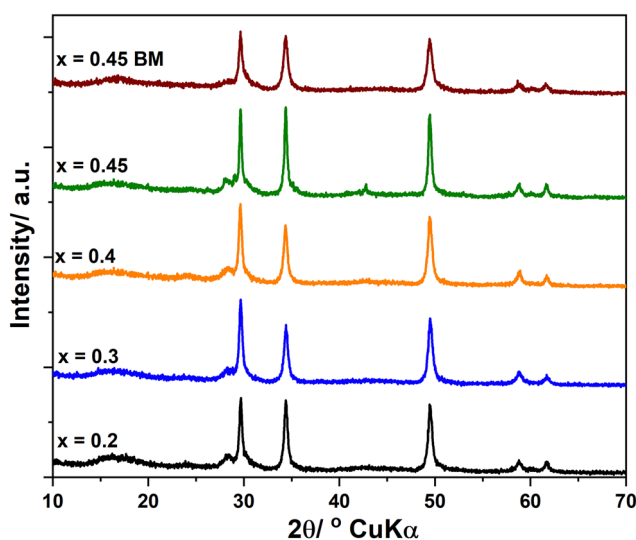


Fig. 3 XRD patterns of  $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  ( $0 \leq x \leq 0.5$ ) samples after heat-treatment at  $170 \text{ }^\circ\text{C}$  for 4 h and the sample with  $x = 0.45$  after ball milling ( $x = 0.45 \text{ BM}$ ).

of  $\text{Li}_2\text{ZnCl}_4$  and  $\text{Li}_3\text{InCl}_6$ . The peaks of the sample with  $x = 1$  were in agreement with those of  $\text{Li}_3\text{InCl}_6$  prepared by the high-energy ball-milling method and ICSD card number 04-009-4027.<sup>24</sup> The pattern of the sample with  $x = 0$  ( $\text{Li}_2\text{ZnCl}_4$ ) exhibited the formation of a nearly pure cubic spinel phase and is in agreement with ICSD card number 00-041-0386.<sup>12</sup> The samples with  $x = 0.1, 0.2, 0.3$  and  $0.4$  exhibited similar patterns to that with  $x = 0$ . The existence of a new peak at  $2\theta \approx 60^\circ$  in the pattern of the sample with  $x = 0.5$  suggested that the structure of this sample was different from that of cubic  $\text{Li}_2\text{ZnCl}_4$ . Fig. 1b shows that the peaks located at  $2\theta \approx 30.10$  and  $34.89^\circ$  for  $x = 0.1, 0.2, 0.3$  and  $0.4$  shifted to the left compared with those for  $x = 0$ . Considering that the ionic diameter of  $\text{In}^{3+}$  is bigger than that of  $\text{Zn}^{2+}$ , the left shift of those peaks indicated that  $\text{Zn}^{2+}$  was partly replaced by  $\text{In}^{3+}$  in the  $\text{Li}_2\text{ZnCl}_4$  cubic structure. This observation proved that a  $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  ( $x < 0.5$ ) solid solution was successfully prepared by the high-energy ball-milling method.

Fig. 2a illustrates the TG-DTA curves of the  $\text{Li}_{2.4}\text{In}_{0.4}\text{Zn}_{0.6}\text{Cl}_{4.8}$  sample. The TG curve showed only about 0.1% weight loss due to the desorption of adsorbed water on the sample's surface. There was a small endothermic peak from about  $50 \text{ }^\circ\text{C}$  to  $100 \text{ }^\circ\text{C}$  indicating the elimination of physically adsorbed water molecules. A sharp exothermic peak located at about  $150 \text{ }^\circ\text{C}$  indicated the crystallization of the sample. The peak started at about  $140 \text{ }^\circ\text{C}$  and ended at about  $170 \text{ }^\circ\text{C}$ . Thus, the sample  $\text{Li}_{2.4}\text{In}_{0.4}\text{Zn}_{0.6}\text{Cl}_{4.8}$  was heated at  $130$  and  $170 \text{ }^\circ\text{C}$  for 4 h to study the effect of heat treatment on its ionic conductivity at room temperature. The temperature dependence of the ionic conductivity of the  $\text{Li}_{2.4}\text{In}_{0.4}\text{Zn}_{0.6}\text{Cl}_{4.8}$  solid electrolyte heat-treated at different temperatures is depicted in Fig. 2b. The ionic conductivities at  $25 \text{ }^\circ\text{C}$  of the as-prepared sample, the sample heat treated at  $130 \text{ }^\circ\text{C}$  and the sample heat treated at  $170 \text{ }^\circ\text{C}$  were about  $2.0 \times 10^{-5}$ ,  $3.2 \times 10^{-5}$  and  $5.6 \times 10^{-5} \text{ S cm}^{-1}$ , respectively. Therefore, the other samples were also treated at  $170 \text{ }^\circ\text{C}$  for 4 h.



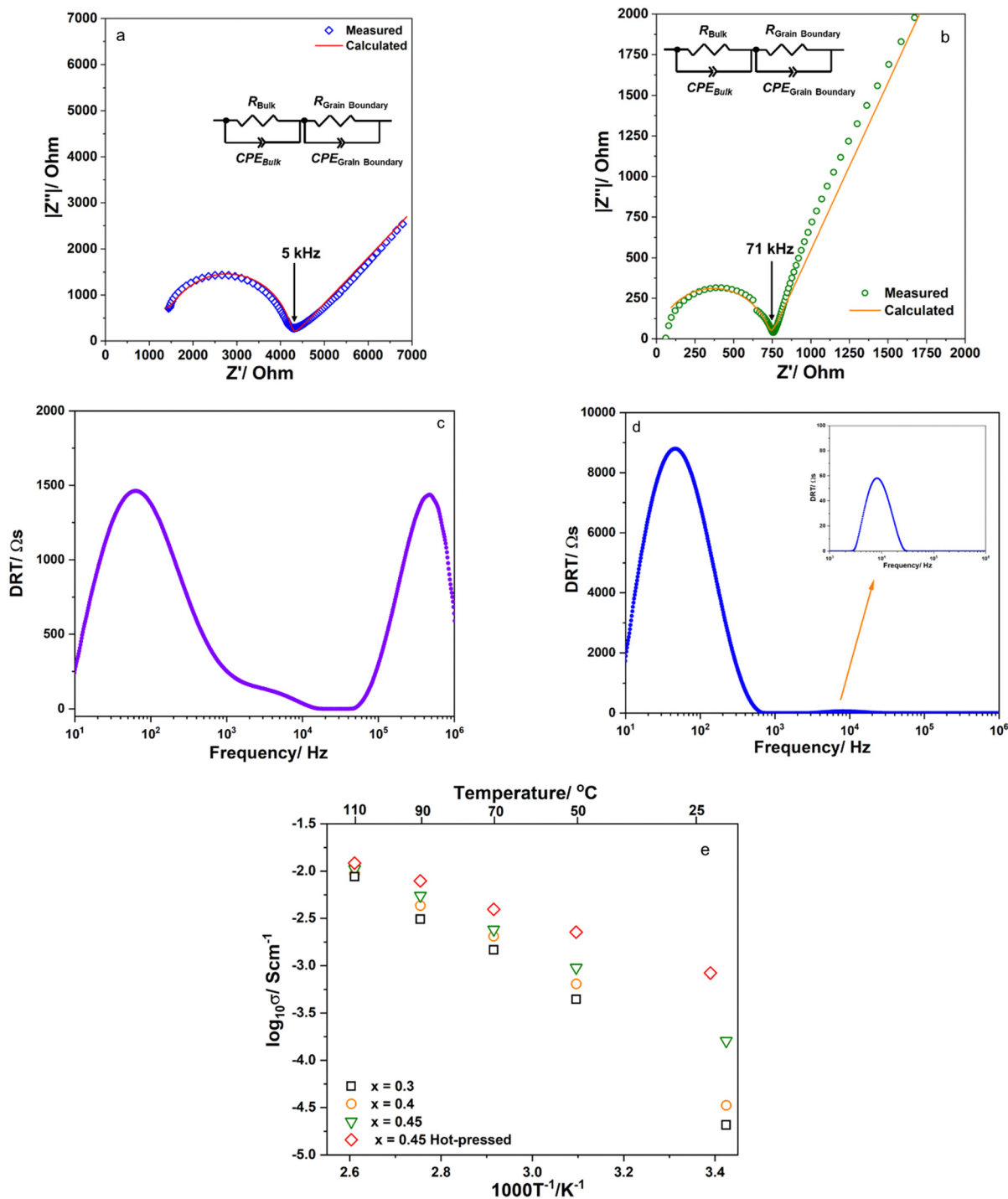


Fig. 4 (a) and (b) Nyquist plots and fitting curves for  $x = 0.3$  and  $0.45$ , respectively. The insets show the equivalence circuits. (c) and (d) The distributions of the relaxation times for  $x = 0.3$  and  $0.45$ , respectively. (e) Temperature dependence of the ionic conductivity for  $x = 0.3, 0.4$  and  $0.45$  solid electrolytes heat-treated at  $170\text{ }^{\circ}\text{C}$  for 4 h.

Fig. 3 shows XRD patterns of  $\text{Li}_{2+x}\text{In}_x\text{Zn}_{1-x}\text{Cl}_{4+2x}$  samples ( $0.2 \leq x \leq 0.45$ ) after heat-treatment at  $170\text{ }^{\circ}\text{C}$  for 4 h and the sample with  $x = 0.45$  after ball milling ( $x = 0.45$  BM). The patterns illustrate that the cubic structure of the prepared samples was still preserved after heating at  $170\text{ }^{\circ}\text{C}$ . It can be

seen that the patterns of the sample with  $x = 0.45$  before and after heat treatment were similar; however, the peaks of the heat-treated sample were sharper than those of the as-prepared sample. This indicated that the crystalline size increased after the heat treatment process. The patterns had three main peaks



at  $2\theta \approx 29.64, 34.37, 49.49, 58.82$  and  $61.77^\circ$ . The lattice parameters were obtained at each diffraction angle  $\theta$  using the Bragg equation.

$$n\lambda = 2d \sin \theta \quad (1)$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (2)$$

The results obtained from (1) and (2) confirmed that the prepared samples had a cubic structure and the mentioned peaks were assigned to the [222], [400], [440], [622] and [444] planes, respectively. The Nelson–Riley equation was employed to determine the lattice parameter  $a_0$ .<sup>25</sup>

$$a \approx \frac{1}{2} \left( \frac{\cos \theta^2}{\sin \theta} + \frac{\cos \theta^2}{\theta} \right) \quad (3)$$

$a_0$  was determined from a linear fit equation, which was derived from a plot with  $a$  as the  $y$ -axis and  $\frac{1}{2} \left( \frac{\cos \theta^2}{\sin \theta} + \frac{\cos \theta^2}{\theta} \right)$  as the  $x$ -axis. The obtained lattice parameters for the samples with  $x = 0.2, 0.3, 0.4$  and  $0.45$  were 10.379, 10.401, 10.425 and 10.45 Å, respectively.

Fig. 4a and b show the Nyquist plots and fitting curves for  $x = 0.3$  and  $0.45$  recorded at room temperature. The insets show the equivalent circuits. The plots are composed of a semicircle and a low-frequency tail consistent with  $\text{Li}^+$  blocking at the stainless-steel electrodes, demonstrating ionic conduction properties. The parallel-plate capacitor model was used to estimate the capacitance  $C$  of the grain boundary and bulk:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d} = C_0 \varepsilon_r \quad (4)$$

where  $\varepsilon_r$  is the value of the inflection point in the plot of  $\varepsilon'$ . The real part of the permittivity,  $\varepsilon'$ , was calculated using the following equation:

$$\varepsilon' = -\frac{Z''}{\omega C_0 (Z' + Z''^2)}$$

where  $C_0 = \varepsilon_0(A/d)$  is the free space capacitance of the cell,  $\varepsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-14} \text{ F m}^{-1}$ ), and  $A$  and  $d$  are the surface area and thickness, respectively, of the sample pellet. For the sample with  $x = 0.3$ , the capacitance of the grain

boundary and bulk were approximately 1.1 nF and 4.7 pF, respectively. For the sample with  $x = 0.45$ , the capacitance of the grain boundary and the bulk were approximately 0.6 nF and 1.3 pF, respectively. The resistance components for  $x = 0.3$  and  $0.45$  were double-checked using the distribution relaxation time (DRT).<sup>26</sup> The results are illustrated in Fig. 4c and d for the samples with  $x = 0.3$  and  $0.45$ . The DRT spectrum for  $x = 0.3$  (Fig. 4c) consists of two peaks located at low ( $10^3$ – $10^4$  Hz) and high frequency ( $10^5$ – $10^6$  Hz) regions, indicating the contribution of the grain boundary and bulk resistance to the ionic conductivity of this sample. The DRT spectrum for  $x = 0.45$  (Fig. 4d) shows the major peak in the low frequency ( $\sim 10^4$  Hz) region and an almost negligible peak in the high frequency region. Thus, the grain boundary gave rise to the major resistance of this sample. The temperature dependence of the ionic conductivity of the  $x = 0.3, 0.4$  and  $0.45$  solid electrolytes heat-treated at  $170^\circ\text{C}$  for 4 h are plotted in Fig. 4d. The ionic conductivities at  $25^\circ\text{C}$  of the samples with  $x = 0.2, 0.3$  and  $0.45$  were  $4.6 \times 10^{-5}, 7.4 \times 10^{-5}$  and  $2.4 \times 10^{-4} \text{ S cm}^{-1}$ , respectively. It could be seen that  $\log_{10} \sigma$  exhibited an almost linear dependence on the inverse temperature and therefore followed the Arrhenius equation  $\sigma = \sigma_0 \exp(-E_{a,\text{DC}}/(k_B T))$ . The calculated activation energies  $E_{a,\text{DC}}$  were 0.632, 0.590 and 0.446 eV for the samples with  $x = 0.3, 0.4$  and  $0.45$ , respectively. These results proved that the ionic conductivity at room temperature of cubic  $\text{Li}_2\text{ZnCl}_4$  was greatly improved due to the solid solution formation with  $\text{Li}_3\text{InCl}_6$ . The results from equivalent circuit and DRT tests (Fig. 4b and d) show that the grain boundary resistance was the main issue in the ionic conductivity at room temperature of the sample with  $x = 0.45$ ; therefore, a pellet of this sample was prepared by hot-pressing at  $170^\circ\text{C}$  and 30 MPa for 1 h to reduce the grain boundary resistance. The temperature dependence of the ionic conductivity of the hot-pressed pellet is plotted in Fig. 4e and denoted as ' $x = 0.45$  Hot-pressed'. It could be seen that the ionic conductivity at room temperature was greatly improved because the grain boundary resistivity was reduced. The ionic conductivity at  $25^\circ\text{C}$  was about  $9.2 \times 10^{-4} \text{ S cm}^{-1}$  and the activation energy was about 0.300 eV. The ionic conductivity for  $x = 0.45$  is comparable to that of the reported halide solid electrolytes as shown in Table 1.

Fig. 5a and b show the charge–discharge curves and cyclic properties of the prepared solid-state cell. The cells were cycled

Table 1 Summary of the ionic conductivity of some reported halide solid electrolytes

Solid electrolyte	Structure	Ionic conductivity/ $\text{S cm}^{-1}$	Activation energy/eV	Preparation method	Ref.
$\text{Li}_3\text{YBr}_6$	$C2/m$	$1.7 \times 10^{-3}$ (RT)	0.37	Ball milling and heat treatment	5
$\text{Li}_3\text{InCl}_6$	$C2/m$	$1.49 \times 10^{-3}$ ( $25^\circ\text{C}$ )	—	Ball milling and heat treatment	27
$\text{Li}_3\text{InCl}_6$	$C2/m$	$2.04 \times 10^{-3}$ ( $25^\circ\text{C}$ )	0.347	Aqueous solution	6
$\text{Li}_2\text{ZrCl}_6$	$C2/m$	$4.0 \times 10^{-4}$ ( $30^\circ\text{C}$ )	0.37	Ball milling	9
Mn-doped $\text{Li}_2\text{ZrCl}_6$	$C2/m$	$8.0 \times 10^{-4}$ ( $30^\circ\text{C}$ )	0.326	Ball milling	11
$\text{LiAlBr}_4$	$P2_1/c$	$1.7 \times 10^{-4}$ ( $30^\circ\text{C}$ )	0.437	Ball milling	19
$\text{Li}_3\text{YbCl}_6$	$P\bar{3}m1$	$1.06 \times 10^{-4}$ ( $30^\circ\text{C}$ )	0.51	High temperature solid state reaction	28
$\text{Li}_3\text{YBr}_{5.7}\text{F}_{0.3}$	$C2/m$	$2.04 \times 10^{-3}$ ( $25^\circ\text{C}$ )	0.378	High temperature solid state reaction	29
$\text{Li}_3\text{InCl}_{4.8}\text{F}_{1.2}$	$C2/m$	$5.1 \times 10^{-4}$ ( $30^\circ\text{C}$ )	—	Ball milling and heat treatment	30
$\text{Li}_3\text{TiCl}_6$	$C2/m$	$1.04 \times 10^{-3}$ ( $25^\circ\text{C}$ )	0.32	Ball milling and heat treatment	18
$\text{Li}_3\text{ErI}_6$	$C2/c$	$6.5 \times 10^{-4}$ (RT)	0.37	Ball milling	17
$\text{Li}_{2.45}\text{In}_{0.45}\text{Zn}_{0.55}\text{Cl}_{4.9}$	$Fd\bar{3}m$	$9.2 \times 10^{-4}$ ( $25^\circ\text{C}$ )	0.300	Ball milling and heat treatment	This work



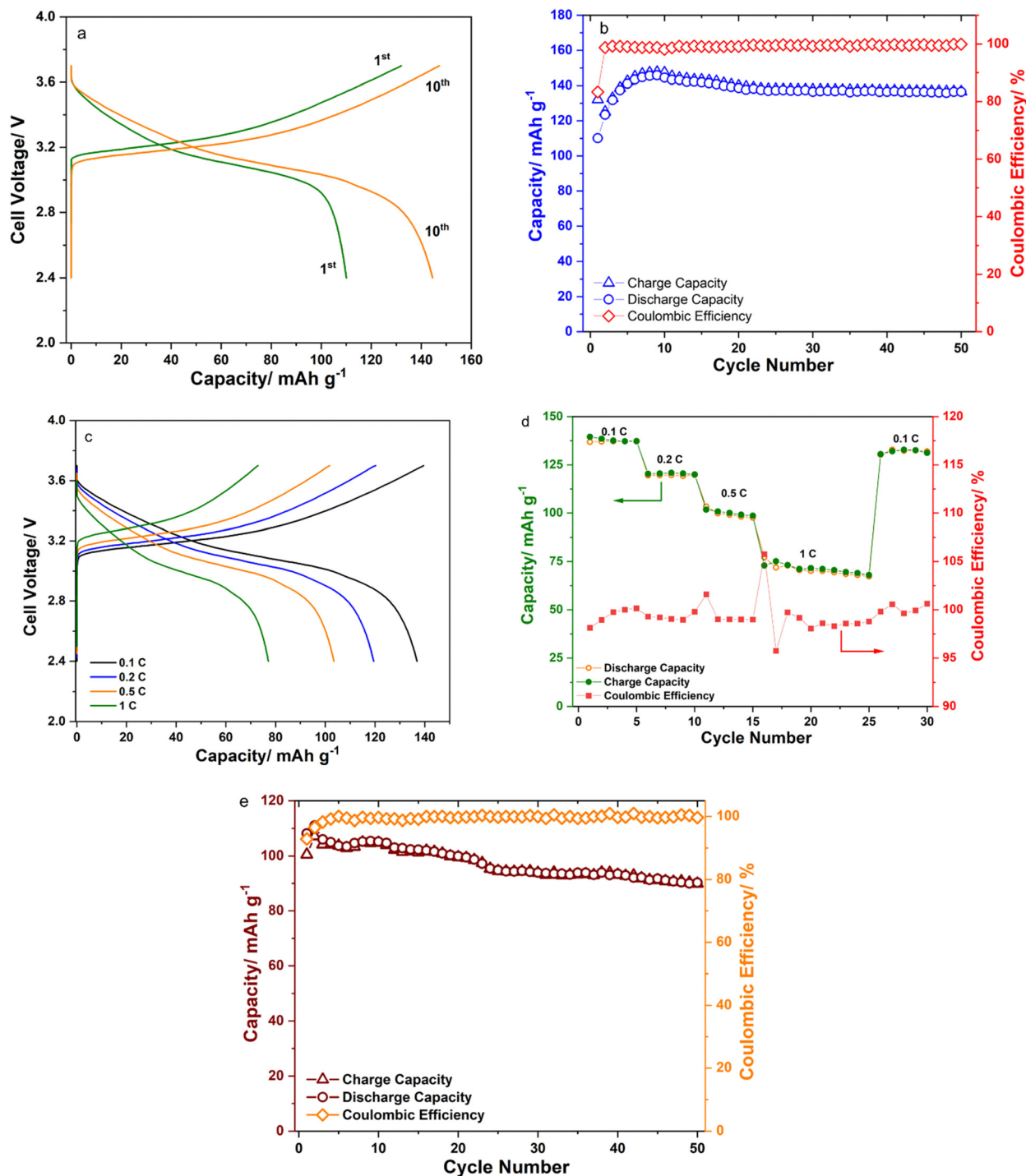


Fig. 5 (a) The 1st and 10th charge–discharge curves at 0.1C; (b) cyclic properties at 0.1C; (c) and (d) rate capability at 0.1, 0.2, 0.5 and 1C; (e) long-term cycling at 0.5C of the fabricated ASS cell.

in constant current mode at 0.1C. The initial charge–discharge capacities were 132.9 and 110.1 mA h g<sup>-1</sup><sub>NMC</sub>. The charge–discharge capacities were improved and reached 147.4/144.7 mA h g<sup>-1</sup><sub>NMC</sub> at the 10th cycle. The initial coulombic efficiency (CE) was about 83.6%. At the 2nd cycle, the CE was about 98.72%. From the 3rd cycle, the CE was higher than 99.5%. The cell was stable after 50 cycles and the charge–

discharge capacities were still maintained at 136.6 and 136.5 mA h g<sup>-1</sup><sub>NMC</sub>. The cell exhibited acceptable rate capability as shown in Fig. 5c and d. The average discharge capacities were 138, 118, 98 and 70 mA h g<sup>-1</sup><sub>NMC</sub> when the cell was cycled at 0.1, 0.2, 0.5 and 1C, respectively. High reversible capacity remained after the rate performance indicated that the structure of the cell was not affected by this process. The long-term



cycling at 0.5C was also investigated to study the cell's stability at a high rate. The result is shown in Fig. 5e. The cell maintained a good discharge capacity of about 90 mA h g<sup>-1</sup><sub>NMC</sub> and a coulombic efficiency of about 99.8%. Thus, the results suggested that the prepared solid electrolyte was compatible with the high Ni active material LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub>.

## 4. Conclusion

Li<sub>2+x</sub>In<sub>x</sub>Zn<sub>1-x</sub>Cl<sub>4+2x</sub> (0 ≤ x ≤ 0.5) solid electrolytes were successfully prepared by mechanochemical synthesis. XRD results proved that the prepared samples had a cubic structure and the lattice constant was dependent on the x value. The sample with x = 0.45 had an ionic conductivity of about 2.4 × 10<sup>-4</sup> S cm<sup>-1</sup> at 25 °C and the grain boundary resistance was the main component of the total resistance of the sample. The hot-pressed pellet (x = 0.45) exhibited a decent ionic conductivity of about 9.2 × 10<sup>-4</sup> S cm<sup>-1</sup> at 25 °C and a low activation energy of about 29 kJ mol<sup>-1</sup>. The all-solid-state cell was stable after 50 cycles indicating that the prepared solid electrolyte was compatible with bare LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub>.

## Data availability

All the data presented in this article are present in the form of figures and tables in the manuscript itself.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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