Structural and electrical properties of Na$_2$ZnSiO$_4$ - Py$_{14}$TFSI hybrid solid electrolyte

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**Abstract**

Sodium-Ion Batteries has emerged as a potential alternative to the conventional Lithium-Ion Batteries, with current research focusing mainly on realising an all-solid-state battery system. In building a highly conducting hybrid solid electrolyte, Na$_2$ZnSiO$_4$ was synthesised using sol-gel method and then infused with ionic liquid Py$_{14}$TFSI. Crystal structure of Na$_2$ZnSiO$_4$ was characterized by X-ray diffraction and refined by Rietveld method, showing phase purity at almost 100%. FTIR and FESEM-EDX measurements indicated that the infused Py$_{14}$TFSI did not change the Na$_2$ZnSiO$_4$ structure and fill up the pores within the crystalline pellet. Highest conductivity value obtained by Na$_2$ZnSiO$_4$-Py$_{14}$TFSI hybrid solid electrolyte is 5.0 × 10$^{-3}$ S cm$^{-1}$ at 498 K. The activation energy values calculated for Pristine Na$_2$ZnSiO$_4$ and Na$_2$ZnSiO$_4$-Py$_{14}$TFSI hybrid solid electrolyte are $\Delta E_{ACT} = 0.23 \pm 0.02$ eV and $\Delta E_{ACT}$, respectively. By Jonscher’s power law, it was found that the ionic conduction in Na$_2$ZnSiO$_4$-Py$_{14}$TFSI hybrid solid electrolyte is primarily due to the diffusion of mobile ions instead of ionic hopping as per in Pristine Na$_2$ZnSiO$_4$.

1. Introduction

Conventional liquid aqueous electrolyte presents numerous setbacks that research interest has largely shifted towards solid-state electrolyte [1-4]. This is due to its enhanced safety, improved thermal and chemical stability, and wider electrochemical range. The compound of interest for this research is Na$_2$ZnSiO$_4$ (NZS), which is an oxide-based solid electrolyte, last reported by Grins in 1982. It was synthesised using the conventional solid state method which is known to be costly and highly susceptible to undesirable impurities and inhomogeneity [5-7] which can negatively affect long-term battery cycling and rate performance [5,8]. Modern materials science gave birth to sol-gel synthesis method, which is the method employed in this research. Its wet-chemistry initial processes [9,10] aid in delivering fine precursor powder, resulting in a higher purity inorganic compound produced at lower temperature in shorter time [6,11,12].

However, in general, conductivity obtained from compounds of pure-solid-state electrolytes are still considerably low and their electrochemical properties in a battery system is still poor. This is mainly due to the high interfacial resistance between solid electrolyte and solid electrode [13-15]. To address this issue, research direction in recent decade has gradually shifted towards creating a hybrid solid electrolyte (HSE) since the act of marrying different types of compound reportedly exhibits increased conductivity and electrochemical performance in solid-state battery, while at the same time tackling the problem of safety of aqueous electrolyte. Kim et al. [16] developed an HSE for sodium batteries by combining NASICON (Na$_3$Zr$_2$Si$_2$PO$_{12}$) ceramic powder with PVDHF-HFP polymer in sodium triflate TEGDMDE solution. The HSE achieved conductivity of 3.6 × 10$^{-3}$ S cm$^{-1}$ at room temperature. The high conductivity was reportedly achieved possibly through three mechanisms, i.e. Na$^+$ hopping, plasticizer transport, and cross ion transport [16]. On the other hand, de la Torre-Gamarra et al. [17] also reported a HSE that is based off a NASICON (Na$_3$Si$_2$Y$_{0.16}$Zr$_{1.84}$PO$_{12}$). They combined the ceramic powder with an ionic liquid (IL), N-buty1-N-methylpyrrolidinium bis(tri-fluoromethylsulfonyl)imide (Py$_{14}$TFSI) and obtained highest conductivity at the combination of 90% NASICON and 10% Py$_{14}$TFSI which gave the value of 3.6 × 10$^{-3}$ S cm$^{-1}$ at room temperature.

IL poses as a good electrolyte candidate due to its low flammability, negligible vapour pressure, and wide electrochemical stability in addition to its high ionic conductivity [17-21]. Its inclusion in ceramic solid-state electrolyte to form HSE proved to have optimised the system’s overall conductivity. In a lithium-ion battery setting, Barpanda et al. [22] attempted to synthesise LiZnSO$_4$F in IL EMI-TFSI, which

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improved its conductivity by several magnitudes (from $10^{-11} \text{ S cm}^{-1}$ to $10^{-5.10^{-7}} \text{ S cm}^{-1}$ at room temperature). Meanwhile, Kim et al. [23] blended LiLa$_2$ZrO$_4$ ceramic particles with IL Py$_14$TFSI and gained conductivity of $10^{-2} \text{ S cm}^{-1}$ instead of $10^{-6} \text{ S cm}^{-1}$ at room temperature. With the promising performance demonstrated by HSE derived from IL, we combined NZS with Py$_14$TFSI in order to obtain highest conductivity of HSE. To the best of our knowledge, no studies have been reported in literature for such combination.

In this paper, the structural and electrical properties of NZS-Py$_14$TFSI HSE were investigated. We also compared the results with pristine NZS (no addition of IL) that acted as a control for this study. For characterisation purposes, the HSE was subjected to X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), field-emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller surface area analyser (BET), and electrical impedance spectroscopy (EIS) analysis.

2. Experimental procedure

2.1. Materials and methods

All analytical-grade chemical reagents, which are sodium acetate (CH$_3$COONa, Sigma-Aldrich), zinc acetate dihydrate ((CH$_3$COO)2Zn.2H$_2$O, Acros Organics), and tetraethyl orthosilicate ((CH$_3$CH$_2$O)$_4$Si, Sigma-Aldrich) were employed directly for sol-gel synthesis without any purification. The starting reagents were dissolved in deionised (DI) water to initiate hydrolysis reactions as per equations (1)–(3) below:

1. $(\text{CH}_3\text{COO})\text{Na}(s) + \text{H}_2\text{O}(aq) \rightarrow \text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq)$

2. $(\text{CH}_3\text{COO})\text{Zn}(s) + \text{H}_2\text{O}(aq) \rightarrow 2\text{CH}_3\text{COOH}(aq) + \text{Zn}(\text{OH})_2(s)\text{(aq)}$

3. $(\text{CH}_3\text{CH}_2\text{O})_4\text{Si}(s) + 2\text{H}_2\text{O}(aq) \rightarrow 4\text{CH}_3\text{CH}_2\text{OH}(aq) + \text{SiO}_2(s)$

Citric acid (C$_3$H$_5$O(COOH)$_3$, Sigma-Aldrich) was included to act as a chelating agent for the cations with molar ratio of 1:3 for Cit:Metal. The dissolved reagents were later mixed together to retrieve a mixture of desired ions with molar ratio of 2:1:1:1 for Na:Zn:Si:Cit. The citric acid was dissolved in DI water and stored at room temperature. Subsequent exothermic peaks at higher temperatures in DSC measurements, Fig. 1(b) shows the evolution of the XRD patterns of powders between 75-225 °C temperature range at 25 °C step within the frequency range of 4 MHz to 1 Hz ($\Delta V$ at 1000 mV).

3. Results and discussion

3.1. Crystallisation process

TGA-DSC measurements were initially employed on precursor powder of NZS to obtain the optimum thermal conditions to synthesise the polycrystalline. Fig. 1(a) shows the graph of TG and heatflow, where the TG line exhibits major decomposition between 238.7 °C and 518.0 °C ($\Delta m = 30.75\%$), with an exothermic peak at 338.3 °C. This decomposition occurs due to the burning off of the organic compounds used to facilitate the sol-gel process. Thus, the calcing step at 350 °C is necessary to ensure that the organic compounds are completely combusted to not interfere with the crystallisation process at higher temperature. Subsequent exothermic peaks at higher temperatures in Fig. 1(a) indicate that crystallisation process occur between 518.7 °C to 750.0 °C ($\Delta m = 4.74\%$), with the last peak at 741.1 °C. Temperatures higher than that show stabilisation of mass and heatflow. Therefore, 750 °C is deemed as the best sintering temperature as the crystallisation

The sintered pellet had a final weight of 0.3825 g, with diameter 13 mm and thickness 2.30 mm. The pellet was then soaked with IL Py$_14$TFSI (Sigma-Aldrich) for 48 h, achieving IL content $\sim 35\%$ weight ($\sim 0.2$ g), and later fired at 90 °C for 1 h to infuse the IL into the pores of the pellet, producing the desired NZS-Py$_14$TFSI HSE. The fired pellet was weighed again to ensure IL was retained within. Weight of the pellet before and after firing were determined to be equal, indicating no loss of IL during the process.

2.2. Characterisation techniques

Thermal behaviour study was done onto the precursor powder using TGA-DSC (Setaram) measurements with temperature range 25–850 °C at 10 °C/min under flowing N$_2$ gas. TGA measurements were also done on the final products to study their thermal stability. XRD (Panalytical) measurements were taken at room temperature on NZS powder using diffractometer equipped with CuKα radiation source, assembled using Bragg-Brentano configuration. The 29 range analysed was 18–80° with a step scan of 0.02° per 96 s. The experimental XRD structural data was refined using Rietveld technique in HighScore Plus 3.0 program, and further processed using VESTA program to obtain the Bragg peaks and schematic diagram of the structure. The microstructure and elemental composition of final pellets were analysed using FESEM-EDX (Hitachi) with acceleration voltage of 2.0 kV, using cold field emission source. Chemical compositions of the final products were compared through FTIR (PerkinElmer Frontier) spectra obtained at 0.5 cm$^{-1}$ resolution over the range of 500–4000 cm$^{-1}$. Based on the IUPAC classification [24], the types of pores in a sintered ceramic include macropores (width $>$ 50 nm), mesopores (intermediate size), and micropores (width $<$ 2 nm). The volume of macropores of sintered NZS pellet was evaluated using Archimedes method based on equation (7) below:

$$ V = \frac{m_{\text{pellet}} - m_{\text{dry}}}{\rho_{\text{water}}} $$

where $V$ is the macropore volume, $m_{\text{pellet}}$ is the mass of pellet after soaked in water, $m_{\text{dry}}$ is mass of pellet before soaking, and $\rho_{\text{water}}$ is the density of water. Meanwhile, the volume of mesopores and micropores were directly obtained via BJH and t-Plot methods respectively from BET surface analyser measurements (Micromeritics) using N$_2$ gas adsorption system. Degassing program of the surface area analyser was set at 90 °C for 1 h and 200 °C for 4 h. The ionic conductivities of final systems were determined by impendence measurements taken using EIS (Solartron Analytical) done on two-blocking stainless steel electrode cells sandwiching the sample pellet. The AC measurements were taken between 75-225 °C temperature range at 25 °C step within the frequency range of 4 MHz to 1 Hz ($\Delta V$ at 1000 mV).
the precursor powder, a small broad peak is seen around 20°. This signifies amorphousness in the compound, which is in agreement with the theory that in a citrate-assisted sol-gel synthesis, citrate-metal complex ligands form polymeric chains [6]. On top of that, data shows that after calcining the powder at 350 °C, the broad peak disappears, indicating the disintegration of the polymeric chain, thus combustion of the organic components in the compound are evident. Yet, crystallinity is only visible after the powder is heat-treated at 750 °C, agreeing with the theoretical peaks of NZS. According to those theoretical NZS peaks too, some of the peaks evidently disappear when compound is heated at 800 °C, making the ideal sintering temperature to be 750 °C.

### 3.2. Structural characterisation

The crystal structure of the polycrystalline Pristine NZS system was studied using XRD performed on NZS powder sintered at 750 °C, as shown by the black line in Fig. 2. Rietveld refinement was employed based on monoclinic P1c1 space group Na2ZnSiO4 structural pattern (ICSD ref code: 98-003-4565). The refinement resulted in a pattern shown by the red line in Fig. 2, with values Rwp = 3.664% and GOF (χ²) = 1.950. Lattice parameters of NZS were refined to be a = 5.24862 Å, b = 5.44474 Å, c = 8.76626 Å, α = γ = 90°, β = 126.6853°, and V = 200.8962 Å³.

The schematic diagrams of the NZS crystal structure are shown in Fig. 3(a–d). It is found that not all Na atoms assemble themselves to form tetrahedral coordination with neighbouring atoms. Instead, only Na atoms occupying Na2 sites form a four-coordinate polyhedra whilst Na atoms occupying Na1 sites form five-coordinate polyhedra. Furthermore, the Na1 polyhedra share edges with Na2 (seen in Fig. 3(c)), Si (seen in Fig. 3(c)), and also Zn (seen in Fig. 3(d)). By Pauling’s rules [25], such assembly is not a stable ionic structure because the cations are “unreasonably close”. In fact, the most stable structure for Na2ZnSiO4 was determined by the computational work of Persson [26] using density functional theory (DFT) calculation, where all cations form tetrahedral coordination with neighbouring anions [26]. In addition, XRD peaks in Fig. 2 at ~32° and ~36° indicate small amount of ZnO impurity, determined as 4.2% by Rietveld refinement. Therefore, it can be deduced that the minute ZnO content is necessary to stabilise the whole structure of synthesised NZS due to the unstable ionic assembly [25]. Because the NZS is still near phase-pure, henceforth the compound’s conductivity and other properties should not be affected by the presence of ZnO.

### 3.3. Chemical and elemental characterisation

Table 1 shows the volumes obtained for each type of pores for Pristine NZS. The porosity of the pellet obtained from the ratio of total pore volume and apparent pellet volume is 0.51. To determine the maximum weight of IL Py14TFSI that can be infused within the pores of the pellet, the density of IL Py14TFSI was measured using automatic density meter. Density obtained was 1.3949 g cm⁻³, which is in agreement with the literature [27]. Therefore theoretically, the total weight of IL Py14TFSI that can be infused into the pores of sintered NZS pellet is 0.21 g. The empirical weight of IL Py14TFSI infused into the pellet after soaking was measured to be ~0.20 g. This means that at 35% weight, the pores of the pellet were almost completely filled with IL Py14TFSI.

Once sintered NZS pellet was infused with IL Py14TFSI to form NZS-Py14TFSI HSE, its chemical and elemental compositions were compared with Pristine NZS by means of FTIR and EDX. Fig. 4 depicts that upon addition of IL, the original peaks of NZS are not altered. Instead, the primary peaks are furnished with secondary peaks that are related to the bonds within Py14TFSI [28]. This shows that Py14TFSI does not change the structure of NZS crystalline.

Meanwhile, Fig. 5(a–b) shows the EDX elemental spectra and composition of Pristine NZS and NZS-Py14TFSI HSE respectively. The ratio obtained for Pristine NZS is close to the stoichiometric ratio of Na2ZnSiO4 by one significant figure, while in NZS-Py14TFSI HSE, additional content of C, F, N, and S present in Py14TFSI are observed, albeit the ratio of Na:Zn:Si:O is still preserved. This further strengthens the argument that infused Py14TFSI does not react with NZS crystalline, nor cause any effect to its composition and structure. Therefore, it is established that Py14TFSI simply bathe the crystalline particles within the pellet.

Fig. 6(a–b) and Fig. 6(c–d) show the micrographs from FESEM of Pristine NZS and NZS-Py14TFSI HSE respectively. As displayed in Fig. 6(a), the sintering effect between the particles is clearly seen. The
fusing of particles is significant in solid-state electrolyte to reduce the resistance due to grain boundaries. On the other hand, Fig. 6(c-d) showcased that Py14TFSI fill up the pores within the pellet. Due to the fact that the crystalline particles are bathed with Py14TFSI, it is expected that movement of ions in NZS-Py14TFSI HSE will largely be contributed by the flowing liquid instead of the NZS grains.

### Table 1

<table>
<thead>
<tr>
<th>Type of pore</th>
<th>Pore volume per weight (cm$^3$g$^{-1}$)</th>
<th>Total pore volume (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macropore</td>
<td>0.398562</td>
<td>0.152450</td>
</tr>
<tr>
<td>Mesopore</td>
<td>0.008652</td>
<td>0.003309</td>
</tr>
<tr>
<td>Micropore</td>
<td>0.000822</td>
<td>0.000314</td>
</tr>
</tbody>
</table>

Fig. 4. FTIR spectra comparison between pristine NZS sample and NZS soaked with IL Py14TFSI

Pristine NZS and NZS-Py14TFSI HSE were initially subjected to TGA to determine their operable temperatures for conductivity measurement. From Fig. 7, besides the weight loss due to water at $\sim$100 °C for both systems, Pristine NZS is stable across a wide range of temperature, as expected. Meanwhile, NZS-Py14TFSI experience a steep drop in weight ($\sim$25%) starting from temperature 300.0 °C–513.4 °C, due to the combustion of Py14TFSI. This is in agreement with the work of Valderrama et al. [27] who calculated the boiling temperature of Py14TFSI to be 486.65 °C [27]. Therefore, it is determined that the operable

### 3.4. DC conductivity

Fig. 5. EDX elemental spectra and composition ratio of (a) Pristine NZS and (b) NZS-Py14TFSI HSE.
temperature of NZS-Py14TFSI HSE is up to 300 °C, which is a broad potential window for commercial use.

EIS were performed on pellets of Pristine NZS and NZS-Py14TFSI HSE at their most stable temperatures, 75–225 °C. Their Nyquist plots at lowest and highest selected temperatures are shown in Fig. 8(a–d) with their indicative equivalent circuits at the inset of each graph.

Pristine NZS’s Nyquist diagram at 75 °C (Fig. 8(a)) plots a typical R|C circuit, suggesting a dielectric behaviour, common in ceramics [29]. As temperature increase (Fig. 8(b)), a decrease in bulk resistance, $R_b$ (grain), is seen, unveiling the higher resistance component due to grain boundary, $R_b$ (gb). The equivalent circuit is therefore $R | C$ at high temperature. Furthermore, a slope is seen at low frequency, indicating a diffusion response in the circuit, hence the additional CPEd component connected in series.

On the other hand, the Nyquist diagrams of NZS-Py14TFSI HSE indicate a very different behaviour. At low temperature, Fig. 8(c) suggests the Randles circuit [29], which is usually synonymous of a liquid electrolyte. Unlike Pristine NZS, the bulk resistance at high frequency is not accompanied by a capacitance value, hence the absence of a semicircle. Therefore, the bulk resistance in NZS-Py14TFSI HSE is deduced to be due to the solution of IL, instead of grain of NZS, thus labelled $R_b$ (sol). In addition, the slope at low frequency is inclined at 45°, which is characteristic of Warburg diffusion element although at higher temperatures, the inclination decreases, indicated by a normal diffusion element, CPEd.

Therefore conductivity, $\sigma$, is calculated from Ohm’s Law, $\sigma = \frac{d}{RA}$ (8), where $d$ is thickness of pellet, $R$ is the measured resistance value, and $A$ is pellet’s surface area. Since $\sigma$ is inversely proportional to $R$, total conductivity, $\sigma_{tot}$, is calculated using equation (9) below:

$$\frac{1}{\sigma_{tot}} = \frac{1}{\sigma_{(grain)}} + \frac{1}{\sigma_{gb}}$$

(9)

Fig. 9(a) shows the graph of $\sigma_{tot}$ against temperature for both systems, depicting an exponential increase in conductivity with the increase of temperature. This denotes a negative temperature coefficient of resistance (NTCR) behaviour, correlated to the increased mobility of the charge carrier [30]. The difference in conductivity between Pristine NZS and NZS-Py14TFSI HSE is consistently big throughout, with up to $10^{-6}$ S cm$^{-1}$ difference at low temperature. Highest $\sigma_{tot}$ recorded is of NZS-Py14TFSI HSE at 225 °C, with value $5.0 \times 10^{-3}$ S cm$^{-1}$.

Subsequently, the activation energy for ionic mobility in the systems is calculated using the modified Arrhenius equation:

$$\sigma_{tot} = -\left(\frac{\Delta E_i}{1000k_B}\right) \left(\frac{1000}{T}\right) + \log \sigma_0$$

(10)

where $\Delta E_i$ is activation energy, $k_B$ is Boltzmann constant, and $\log \sigma_0$ is the y-intercept. Fig. 9(b) shows the activated temperature dependence in an Arrhenius plotting. Line of fit based on equation (10) were plotted on both the data points for Pristine NZS and NZS-Py14TFSI. The activation energy values calculated for Pristine NZS and NZS-Py14TFSI HSE are $\Delta E_{i,\text{NZS}} = 0.33 \pm 0.02$ eV and $\Delta E_{i,\text{HSE}} = 0.12 \pm 0.03$ eV respectively. These low activation energy values indicate that the systems
make for a desirable electrolyte.

3.5. AC conductivity

The frequency-dependent conductivity, $\sigma_{AC}$, is calculated from the impedance values at various temperatures and its plotting against frequency, $\omega$, is shown in Fig. 10 and Fig. 11 for Pristine NZS and NZS-Py$_{14}$TFSI HSE respectively. The lines are fitted with Jonscher’s [31] Universal Dynamic Response equation:

$$\sigma_{AC}(\omega) = \sigma_{DC} + A_1 \omega^{S_1} + A_2 \omega^{S_2}$$

where $A_1$ and $A_2$ are constants, and $S_1$ and $S_2$ are exponents corresponding to low and high frequency region, and $\sigma_{DC}$ is the y-intercept. The expression $A_2 \omega^{S_2}$ is not applicable in the fitting of NZS-Py$_{14}$TFSI.
AC conductivity of Pristine NZS across frequencies at different temperatures. Inset table provides the exponent values for each curve at low frequencies, $S_1$, and high frequencies, $S_2$.

AC conductivity of NZS-Py$_14$TFSI HSE across frequencies at different temperatures. Inset table provides the exponent values for each curve, $S$.

HSE system as the curve in Fig. 11 indicates one power factor only. The exponent $S$ represents the degree of interactions between mobile ions with the environment surrounding them. Exponent values of $0.5 < S < 1$ generally indicate that conductivity occurs through hopping [31]. In the Pristine NZS system, $S_1$ values are higher than $S_2$ across different temperatures, albeit obeying the limiting values. Meanwhile, $S$ values in NZS-Py$_14$TFSI HSE are generally lower than 0.5, which signify that ionic conduction in the system is not due to hopping. Almond and West [32] theorised that the energy needed for ionic conduction is due to ionic hopping and the diffusion of mobile ions, therefore relating activation energy to be:

$$\Delta E_A = \Delta E_D + \Delta E_H$$

(12)

where $\Delta E_D$ is energy needed for the diffusion of mobile ions and $\Delta E_H$ is energy needed for hopping of ions.

The hopping frequency, $\omega_H$, of Pristine NZS at each temperature is obtained by measuring the $\omega$ value from the graph in Fig. 10 when $\sigma_{AC}(\omega) = 2\sigma_{DC}$ [32]. The values of $\omega_H$ are plotted against 1000/T as per equation (10), resulting in $\Delta H_{NZS} = 0.27 \pm 0.02$ eV. Using equation (12), $\Delta E_C$ is calculated to be $0.06 \pm 0.04$ eV, which shows that the bulk of the ionic conduction in Pristine NZS is due to ionic hopping. Meanwhile, in NZS-Py$_14$TFSI HSE, $\Delta E_H$ cannot be obtained empirically, thus it can be deduced that the ionic conduction in NZS-Py$_14$TFSI HSE is mainly due to the diffusion of mobile ions.

4. Conclusion

Na$_2$ZnSiO$_4$ (NZS) was successfully synthesised by sol-gel method and infused with IL Py$_14$TFSI to form the desired NZS-Py$_14$TFSI HSE system. NZS-Py$_14$TFSI HSE was characterised alongside Pristine NZS using TGA-DSC, XRD, FTIR, FESEM-EDX, and EIS. Rietveld refinement of XRD measurements on NZS shows optimum phase purity obtained at sintering temperature 750 °C. IL Py$_14$TFSI was found to completely fill up the pores of the NZS pellet and bathe the NZS crystals within the pellet without disturbing the NZS crystal structure.

Conductivity studies show that NZS-Py$_14$TFSI HSE exhibit much superior ionic conductivity compared to Pristine NZS at all temperatures. Activation energy calculation proposes that ionic conductivity in NZS-Py$_14$TFSI HSE is largely contributed by the diffusion of highly mobile ions within the ILs, as oppose to ionic hopping in Pristine NZS.

Declaration of competing 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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