Novel halloysite based nanoionic Na$_2$ZnSiO$_4$ solid electrolyte: Structural and electrical properties

N.S.M. Johari$^a$, S.B.R.S. Adnan$^{b,*}$, N. Ahmad$^c$

$^a$ Institute of Advanced Studies, University of Malaya, 50603, Kuala Lumpur, Malaysia
$^b$ Centre for Foundation Studies in Science, University of Malaya, 50603, Kuala Lumpur, Malaysia
$^c$ Department of Chemistry, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia

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A B S T R A C T

Halloysite clay was acid-treated to obtain SiO$_2$ nanoparticles that were used as one of the starting reagents to synthesise clay-based Na$_2$ZnSiO$_4$ (Clay-NZS) through sol-gel method. XRD and FESEM results showed that the Clay-NZS produced a nanocrystalline structure, with grain sizes of 50–70 nm, in comparison to its synthetic counterpart (Synth-NZS) that had grain sizes of ~200 nm. BET measurements showed that Clay-NZS pellets pressed and sintered at the same condition as Synth-NZS were denser, allowing for a better grain-grain contact. Conductivity studies using EIS demonstrated superior conductivity of Clay-NZS in contrast to Synth-NZS due to the exponential reduction in grain boundary resistance, with calculated conductivity values of \( \sigma_{\text{Clay}} = 2.95 \times 10^{-3} \, \text{S} \cdot \text{cm}^{-1} \) and \( \sigma_{\text{Synth}} = 3.25 \times 10^{-4} \, \text{S} \cdot \text{cm}^{-1} \) at 500 °C. Activation energy required for ionic conduction was also found to be lower in Clay-NZS, \( \Delta E_{\text{Clay}} = 0.67 \pm 0.01 \, \text{eV} \) compared to \( \Delta E_{\text{Synth}} = 0.71 \pm 0.02 \, \text{eV} \), testifying that nanostructured ionic materials (nanoionics) provided easier diffusion pathway for ionic conduction in Clay-NZS.

1. Introduction

Halloysite clay belongs to the aluminosilicate group that has 1:1 ratio of alumina and silica layers. What makes halloysite unique from other types of clay is because the minerals are layered in rolls of nanotubes, where the silica form the outer layer and the alumina form the inner layer of the tubes [1–4]. Due to its natural nanotubular structure, halloysite nanotubes (HNT) caught the interest of many to serve a wide-ranging applications [3,5–8]. Numerous modifications are done onto halloysite to unlock its potential to serve a variety of purpose [5,9], with one involving a form of acid treatment to leach out the alumina from the inner layer of the nanotubes [2,10–12]. Depending on the strength of acid and the period of treatment, HNT can either undergo lumen enlargement [13,14] or disintegrate entirely [12,15]. Lumen enlargement allows for higher-volume loading whilst complete disintegration allows for the harvest of silica nanoparticles (SiNP).

Halloysite separates itself from its aluminosilicate sister, kaolinite, as the candidate to source nanoparticles via a simple extraction method. The yield of SiNP from HNT provides a promising output for dielectric materials. Zhou et al. [15] reportedly synthesised SiNP from halloysite to devise a high-performing anode for lithium-ion batteries. Meanwhile, Wang et al. [16] and Niu et al. [17] used the SiNP harvested from the acid treatment of halloysite to synthesise a macroporous Li$_4$SiO$_4$ carbon dioxide sensor that can absorb more carbon dioxide than the normal Li$_4$SiO$_4$. While HNTs have mainly been employed as nano-fillers in polymer electrolytes to improve their ionic conductivities [18–20], unfortunately to-date, no study has been done to see the effect of halloysite in a ceramic electrolyte.

Notwithstanding, it is expected that SiNP involved in the synthesis of ceramic electrolyte will bring about nanoionics [21–24], which is a phenomenon for nanostructured ionic conductors. It was found that the resistance due to grain boundaries of a ceramic material is reduced significantly in nanoionics, resulting in a greatly enhanced overall ionic conductivity [25,26]. Ahmad [27] showed that his nanocrystalline Li$_3$La$_5$Nb$_2$O$_{12}$ (grain size 26 nm) exhibits conductivity value of 3.7 x 10$^{-3}$ S cm$^{-1}$ at 27 °C, one order magnitude higher than its normal crystalline (grain size 1–2 μm) counterpart. This provides a great basis to explore whether SiNP from HNT could catalyse the same effect on ionic transport of a ceramic electrolyte.

The subject of study for this project is the compound Na$_2$ZnSiO$_4$ (NZS), an understudied oxide-based ceramic electrolyte with a LISICON-type structure. It was last reported in the literature by Grins [28] in 1982, showcasing its potential as a solid electrolyte. Unfortunately, the system was not studied further due to the synthesis...
process being costly, and the difficulty to obtain a phase-pure compound using solid-state synthesis. With almost four decades gap, technological advancements allow NZS to become relevant again in the solid electrolyte scene. We have recently revived this system by changing the synthesis process to sol-gel method and hybridise it to further boost its performance [29]. This project serves as another attempt to improve the NZS system.

Henceforth, the scope of this paper is to study the structural and electrical properties of a novel halloysite-based nanoionic NZS ceramic electrolyte synthesised via sol-gel method. To the best of our knowledge, there is no study in the literature that uses halloysite clay as a base to synthesise NZS compound, let alone study its ionic conductivity. The samples were subjected to characterisation via X-ray fluorescence (XRF), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), surface area analyser (BET), and electrical impedance spectroscopy (EIS).

2. Experimental procedure

2.1. Materials and synthesis methods

Sulphuric acid was used to selectively etch Al2O3 in HNT. 250 ml of sulphuric acid (5 N, Sigma-Aldrich) was poured into a flask containing 10 g of halloysite nanoclay (Sigma-Aldrich) and stirred continuously with a magnetic stirrer for 20 h on a hotplate at 70 °C under reflux. The white suspension was then filtered and washed several times until the acidity level reduced to neutral. The obtained wet powder was dried in an oven for 48 h at 90 °C to retrieve a fine white powder of SiNP.

Subsequent steps for sol-gel synthesis and heat treatments were done as per the steps in Ref. [29] using analytical grade reagents consisted of sodium acetate (Sigma-Aldrich) and zinc acetate dihydride (Acros Organics). SiNP was dispersed in deionised (DI) water using ultrasonicator bath and added into the mixture of hydrolysed sodium acetate and zinc acetate to react and form Clay-NZS. A separate solution was made using tetraethyl orthosilicate (Sigma-Aldrich) as synthetic Si source to act as control (Synth-NZS). Citric acid (Sigma-Aldrich) was added into both mixtures to act as chelating agent to ensure homogeneous solutions. Subsequent heat treatments include drying at 150 °C for 24 h to remove water, and calcining at 350 °C for 6 h to remove acetate. After the calcining step, the sample powder was pressed using a hydraulic uniaxial press at 2 tonnes before being sintered at 700, 750, and 800 °C for 6 h to facilitate crystallisation process. The equation for the crystallisation process is as per equation (1) below:

\[2Na^+(s) + Zn^{2+}(s) + SiO_2(s) + O_2(g) \rightarrow Na_2ZnSiO_4(s) \]  

(1)

2.2. Characterisation techniques

The compounds were evaluated using FTIR (PerkinElmer Frontier) measurements obtained at 0.5 cm\(^{-1}\) resolution over the range of 600 – 4000 cm\(^{-1}\). The composition of different oxides in pure and acid-treated HNT was determined using XRF (Thermo Scientific) fitted with silicon drift detector. XRD (PanAnalytical) measurements were taken at room temperature using diffractometer equipped with CuKα radiation source, assembled using Bragg-Brentano configuration. The experimental XRD structural data were refined using Rietveld technique in HighScore Plus 3.0 programme and further processed using VESTA programme. The microstructures and elemental compositions were analysed using FESEM-EDX (Hitachi) with acceleration voltage of up to 50 kV, using cold field emission source. The surface area and pore volume of sintered pressed pellets were obtained using BET and BJH calculations respectively, from the N\(_2\) gas adsorption/desorption isotherm system surface analyser (Micromeritics). Degasging programme was set at 90 °C for 1 h and 200 °C for 4 h. The ionic conductivities of final systems were determined by impedance measurements taken using EIS (Solartron Analytical) done on two-blocking stainless steel electrode cells containing the sample pellets. The AC measurements were taken between 225 and 500 °C temperature range at 25 °C step within the frequency range of 10 MHz–100 Hz (ΔV at 1000 mV).

3. Results and discussion

3.1. Extracting SiNP from HNT

Fig. 1 shows the XRD pattern of HNT before and after acid treatment which proves that the acid treatment has completely modified HNT to become amorphous SiO\(_2\) (broad peak across 2θ = 15.0° to 2θ = 31.5°) and crystalline SiO\(_2\) (sharp peaks at 2θ = 21.0°, 26.7°), confirming the yield of SiNP. From the XRF measurement, we found that Al\(_2\)O\(_3\) content in HNT was reduced from 27.4 ± 0.6% to 6.7 ± 0.4%, demonstrating a reduction of 21.0 ± 1.0% after the acid treatment. In spite of that, the concentration of SiO\(_2\) improved by only 13 ± 1% to become 83.5 ± 0.4%. This is due to the increased concentration of SO\(_3\) by 8.4 ± 0.2% caused by the reaction of HNT with sulphuric acid.

Meanwhile, Fig. 2 shows the FTIR spectra of HNT and SiNP. The characteristic peaks of HNT are seen to have diminished in SiNP, particularly for peaks at X\(_{\text{HNT}}\) = 3620 cm\(^{-1}\), 3695 cm\(^{-1}\), which represent
the O-H stretching vibrations in Al-OH groups \cite{30}. Instead, a broad peak around $X_{SiNP} = 3366 \text{ cm}^{-1}$ is present, indicating the remnants of water content after Al has been extracted. Absorption peaks at $X_{SiNP} = 1070 \text{ cm}^{-1}$ and $X_{SiNP} = 944 \text{ cm}^{-1}$ are assigned to Si-O-Si and Si-OH stretching vibration respectively \cite{31}. Not only do the FTIR data further prove the conversion of HNT to SiNP, the FTIR spectrum of SiNP is also characteristic to that of a silica nanoparticle \cite{32}.

3.2. Structural characterisation

Measurements of XRD were taken on the synthesised Clay-NZS compound sintered at 700, 750, and 800 °C. Fig. 3 shows the comparisons of the XRD spectra with Bragg peaks of Na$_2$ZnSiO$_4$ placed below the Clay-NZS-750 spectrum. At 700 °C, most of the peaks are not present, indicating that the crystallisation process is not yet completed at this temperature. In particular, the peaks at $2\theta = 23.5^\circ$, $25.3^\circ$, and $26.8^\circ$ are not present in 700 °C, but emerge at 750 °C and then reduced in intensity at 800 °C. Secondary phase impurity peaks at $2\theta = 31.8^\circ$ and $36.3^\circ$ are present at all temperatures. Furthermore, physically, grain growth was seen at 800 °C, which is the adverse effect undesired for this project. It is concluded that the best sintering temperature for Clay-NZS is 750 °C.

Both samples of Clay-NZS and Synth-NZS crystallise to the monoclinic structure of $P1c1$ space group Na$_2$ZnSiO$_4$ structural pattern (ICSD ref code: 98-003-4565). Rietveld refinement was performed on the XRD spectra of both samples sintered at 750 °C. Fig. 4 displays the refinement graph of Clay NZS and of Synth-NZS inset. Meanwhile, Table 1 shows the quantitative results obtained from the exercise on both compounds. It is found that under optimised refinement, there is no significant difference in the lattice parameters of both Clay-NZS and Synth-NZS. Instead, it can be seen in Fig. 4 that the peaks of Clay-NZS are substantially noisier and broader compared to Synth-NZS. The values in Table 1 justified that the noisier signals are due to the fact that the weight percentage of the Na$_2$ZnSiO$_4$ phase is a little bit less in Clay-NZS, whilst the broader peaks are due to the crystalline size of Clay-NZS being sizably smaller. Categorically, crystallite size of 406.89 nm denotes that Clay-NZS is nanosize.

Fig. 5 shows the crystal structure of Clay NKS generated through VESTA. The silicon and zinc ions form tetrahedra that share oxygen ions at their vertices. The tetrahedral rigid framework creates a bottleneck for the ionic migration pathway of sodium ions. The sodium ions migrate from one site to another via ionic hopping when the activation energy, $\Delta E_a$, is surpassed.

3.3. Microstructural and elemental characterisation

Micrographs from FESEM were taken on the evolution of the compounds to show the samples’ progress. Fig. 6(a) displays the renowned nanotubular structure of pure HNT, while Fig. 6(b) shows the remains of the nanotubes that were broken down through the acid leaching.
process to form SiNP. Both pictures were captured at the same magnification of ×40k. Meanwhile, Fig. 6(c) shows the Clay-NZS grains at ×90k magnification and Fig. 6(d) shows Synth-NZS grains at ×40k magnification. The scales of the final two pictures made evident that the spherical grains of Clay-NZS are much smaller than that of Synth-NZS, with the former ranging from 50 to 70 nm whilst the latter being about 200 nm. By definition, a particle that has a side of size < 100 nm is categorised as a nanoparticle. Therefore, this micrograph further solidifies the fact that Clay-NZS forms a nanocrystalline ceramic.

BET and BJH analyses were done onto the sintered pressed pellets of Clay-NZS and Synth-NZS. As shown in Table 2, both the surface area and the pore volume of Clay-NZS are calculated to be smaller than Synth-NZS and pure halloysite clay (Sigma Aldrich) [33]. This means that under the same pressing and sintering conditions, Clay-NZS is able to form a more densely packed ceramic compared to Synth-NZS. A denser pellet allows for a greater contact between grains, hence reducing the resistance due to grain boundaries. By this virtue alone, Clay-NZS is capable of having a higher conductivity than Synth-NZS.

Fig. 7 shows the comparison of EDX measurement done onto Clay-NZS and Synth-NZS on its inset. All peaks correspond to the atoms expected to be present in Na₂ZnSiO₄, with the exception of a small amount of Al traced in Clay-NZS. This shows that although the acid treatment is successful in yielding SiO₂, there is residual Al being carried forward to the synthesis of NZS. A denser pellet allows for a greater contact between grains, hence reducing the resistance due to grain boundaries. By this virtue alone, Clay-NZS is capable of having a higher conductivity than Synth-NZS.

As shown in Fig. 8, the Nyquist plot of both Clay-NZS and Synth-NZS at 500 °C. The plot corresponds with the equivalent circuit displayed at the inset of Fig. 8. For both compounds, the bulk resistance due to grain (Rg) is substantially smaller than the resistance due to grain boundaries (Rgb). It is apparent in Fig. 8 that Clay-NZS has a significantly lower Rgb than Synth-NZS.

From Ohm’s law [29], the conductivities of Clay-NZS and Synth-NZS at 500 °C were calculated to be $\sigma_{\text{Clay}(500)} = 2.95 \times 10^{-5} \text{ S cm}^{-1}$ and $\sigma_{\text{Synth}(500)} = 3.25 \times 10^{-5} \text{ S cm}^{-1}$ respectively. Noticeably, the difference between the two compounds is of one order magnitude at this temperature, which is believed to be due to the nano-size of particles in Clay-NZS. In dielectrics, thermodynamics require a space charge layer of several nanometres to form at the grain interfaces. At nanoscale, the grain-grain interface dominates the particle, allowing for high concentration of space-charge effect in the whole system [21]. At the contact of two nanosized grains, there will be a swift redistribution over both space-charge layers. This in turn reduces Rgb, significantly [35], which is the basis for nanoionics.

The graph of total conductivity of each compound against temperature is shown in Fig. 9. The graph depicts an exponential increase in conductivity with the increase of temperature, showcasing Clay-NZS’s exponential increase being much higher than Synth-NZS. This denotes a negative temperature coefficient of resistance (NTCR) behaviour, correlated to the increased mobility of the charge carrier as well.

### 3.4. DC conductivity

Typically, ceramic electrolytes have a very high resistance at room temperature and require thermal activation to ionically conduct. Oxides usually require temperatures of > 300 °C for the resistance to be low enough to be captured through EIS. Whilst this is true for Synth-NZS, evidently, Clay-NZS displays the characteristic Nyquist plot for a dielectric at a lower temperature, starting from 225 °C. Even so, both compounds show temperature dependence on conductivity.

EIS measurements were taken on both pellets at 225–500 °C, albeit no readings were recorded for Synth-NZS below 300 °C. Fig. 8 shows the Nyquist plot of both Clay-NZS and Synth-NZS at 500 °C. The plot corresponds with the equivalent circuit displayed at the inset of Fig. 8. For both compounds, the bulk resistance due to grain (Rg) is substantially smaller than the resistance due to grain boundaries (Rgb). It is apparent in Fig. 8 that Clay-NZS has a significantly lower Rgb than Synth-NZS.

Table 2

| Surface area and pore volume of sintered pressed pellets of Clay-NZS and Synth-NZS. |
|---------------------------------|------|------|
|                                 | Clay-NZS | Synth-NZS |
| BET Surface Area [m²g⁻¹]        | 2.33   | 3.18  |
| BJH Pore Volume [cm³g⁻¹]        | 0.0031 | 0.0071 |

*BET surface area of halloysite clay = 46.36 m²g⁻¹ (Sigma Aldrich) [33].

![Fig. 6. Micrographs of (a) pure HNT showcasing nanotubular morphology, (b) acid-treated HNT showing the disintegration of the nanotubular structure to form SiNP, (c) nanoparticulates of Clay-NZS, and (d) micrograins of Synth-NZS.](image-url)
temperature increases [36].

A plot of conductivity against temperature was charted for both compounds in Fig. 10 in order to calculate the activation energy required for ionic mobility. The Arrhenius relation used to construct the graph is as per equation (2) below:

$$\sigma_{\text{DC}} = \sigma_0 \exp\left(\frac{-\Delta E}{k_B T}\right)$$

where $\Delta E$ is activation energy, $k_B$ is Boltzmann constant, and $\sigma_0$ is pre-exponent value. The activation energies required for ionic mobility in Clay-NZS and Synth-NZS are calculated to be $\Delta E_{\text{Clay}} = 0.67 \pm 0.01$ eV and $\Delta E_{\text{Synth}} = 0.71 \pm 0.02$ eV respectively. The result of Synth-NZS is comparable to the $\Delta E_{\text{t}}$ of NZS reported by Grins [28]. The difference between $\Delta E_{\text{Clay}}$ and $\Delta E_{\text{Synth}}$ is relatively small, but still indicative that Clay-NZS requires smaller amount of energy to necessitate ionic conduction.

### 3.5. AC conductivity

The real impedance values were used to derive the frequency-dependent conductivity, $\sigma_{\text{AC}}$, across temperatures. The frequency dependent graph for Clay-NZS and Synth-NZS is shown in Fig. 11. Besides conductivity being increased with temperature, for both compounds, three regions are observed across frequencies. The first region is at the lower frequency range, where polarisation at electrode comes into effect, particularly prominent in Clay-NZS. The second region is at mid-range frequency, the plateau region which manifests $\sigma_{\text{DC}}$, where conductivity is independent of frequency. The third region, at higher range, is where conductivity increases with frequency as ions become mobile in variant to frequency. For both compounds, this region extends further to the right as temperature increases. The ionic conductivity in this region can be fitted with Jonscher’s [37] Universal Dynamic Response...
equation:

\[
\sigma_{\text{DC}}(\omega) = \sigma_{\text{DC}} + A\omega^S
\]  

(3)

where \( A \) is a pre-exponent constant and \( S \) is the exponent that corresponds to the ionic mobility behaviour. \( \sigma_{\text{DC}} \) abides by the Nernst-Einstein relation,

\[
\sigma_{\text{DC}} = e\text{n}_c\mu
\]  

(4)

where \( e \) is ionic charge, \( n_c \) is charge concentration, and \( \mu \) is ionic mobility. From the Nernst-Einstein relation, the ionic mobility can also be described by its hopping frequency, \( \omega_H \), since \( \mu \propto \omega_H \). Because the mobility of ions in both compounds is temperature dependent, Arrhenius relation from equation (2) can be used to find energy required for hopping, \( \Delta E_H \). The hopping frequency, \( \omega_H \), at each temperature is obtained by measuring the \( \omega \) value from the graph in Fig. 11 when \( \sigma_{\text{DC}}(\omega) = 2\omega_{\text{DC}} \) [38]. The values of \( \omega_H \) at each temperature are plotted against 1000/\( T \) as shown in Fig. 12. It is found that both compounds have two ranges of temperature with which the \( \Delta E_H \) are of different values. For both compounds, \( \Delta E_H \) at the higher temperature range is lower than the lower temperature range. This means that despite having a constant \( \Delta E_H \) throughout operable temperatures, less energy is required to move the ions at higher temperature.

Besides having two values of \( \Delta E_H \) across temperatures, the fact that \( \Delta E_{\text{Clay}} \neq \Delta E_{\text{Synth}} \) are in both compounds means that NZS's increased conductivity with temperature is not only due to increase in \( \omega_H \), but also due to increase in \( n_c \). This is in accordance with equation (4) above.

\[
\Delta E_A = \Delta E_C + \Delta E_H
\]  

(5)

Table 3 shows the overall energy values for Clay-NZS and Synth-NZS. In every circumstance, less energy is needed for the mobile ions in Clay-NZS to be created, hopped, and conducted. This is in agreement with the works of Maier [21,22,24,26] that demonstrate how nanionics allow for easier diffusion pathway, simply because its size allows for space charge effect to dominate.

4. Conclusion

XRF, XRD, and FTIR measurements testify that SiNP were successfully extracted from HNT. The SiNP was used as one of the starting reagents to synthesise Clay-NZS. Clay-NZS was found to have a significantly smaller crystallite size than its Synth-NZS counterpart, which was calculated from XRD refinement to be 406.89 nm and measured from FESEM to be about 50–70 nm. This confirms that Clay-NZS formed a nanocrystalline.

Conductivity studies show that Clay-NZS demonstrates a substantial reduction in \( R_{gb} \) across temperatures due to the reduction of its particle size to nano-region, thus showcasing an exponential increase in
conductivity when compared to Synth-NZS. At 500 °C, the ionic condu-
tivities were calculated to be $\Delta E_{\text{Clay}} = 2.95 \times 10^{-6}$ cm$^{-1}$ and $\Delta E_{\text{Synth}} = 3.25 \times 10^{-6}$ cm$^{-1}$. The activation energy of Clay-NZS was calculated to be lower than Synth-NZS, with values $\Delta E_{\text{Clay}} = 0.67 \pm 0.01$ eV and $\Delta E_{\text{Synth}} = 0.71 \pm 0.02$ eV respectively. The frequency-dependent conductivities demonstrate that the hopping of ions in the compound is thermally activated. It was found that at every circumstance, all values of $\Delta E_{A}$, $\Delta E_{C}$, and $\Delta E_{Clay}$ in Clay-NZS are considerably lower than Synth-NZS. Therefore, it can be concluded that Clay-NZS is a nannion that has an easier ionic diffusion pathway compared to its synthetic counterpart, granting a sizable gain in con-
ductivity.

Declaration of competing interest

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

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Table 3 Energy values of Clay-NZS and Synth-NZS with respect to different temperature regions.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\Delta E_{A}$ (eV)</th>
<th>$\Delta E_{C}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>$0.67 \pm 0.01$</td>
<td>$0.71 \pm 0.02$</td>
</tr>
<tr>
<td>High</td>
<td>$0.67 \pm 0.01$</td>
<td>$0.71 \pm 0.02$</td>
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