Sodium ion conducting NaI-Na3PO4 solid electrolyte with PLLTMEDA as an additive for solid state batteries

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Abstract: In this work poly(L-leucine)1,3–diamino propane (PLLTMEDA) has been chosen as an additive to the binary compound sodium iodide (NaI) and sodium phosphate (Na3PO4). A small amount of PLLTMEDA was added to the optimum composition of the binary compound (0.5 NaI–0.5 Na3PO4). Results from EIS have proven this new compound is superionic with maximum conductivity of 1.12 × 10 –3 S cm –1. Fourier transform infrared spectroscopy (FTIR) analysis revealed the band of C=O at 1650 cm –1 experienced a shift, indicating that some interaction had occurred. The ionic transference number was found to be ≈1 for the optimum composition with maximum conductivity which suggests that the sample is ionic in nature. The optimum composition of the sample was used as solid electrolyte in solid state sodium battery. The sodium battery was tested by the discharged characteristic at a current of ≈1.0 µA. The solid state sodium batteries exhibited a discharge capacity of 173 mAh/g.

Keywords: sodium solid electrolyte; ionic conductivity; impedance spectroscopy; PLLTMEDA; NaI; Na3PO4.

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Biographical notes: Azizah Hanom Ahmad is a Professor in Physics with research interest focuses on developing materials with high ionic conductivity which is known as a super-ionic conductor solid electrolyte having fast ion motion. Conductive polymer, nano-composite and inorganic materials are chosen in preparing solid electrolyte by solid state reaction and also by solution cast method. She has secured Fundamental Research Grant of RM100K for research project on superionic conductors. She has won Gold and Double gold awards in international exhibitions (British Invention Show and Brussel Innovia Energy Exhibition) and with one patent titled Solid Polymer Electrolyte. Currently, she is the Deputy Dean (Research and Industry Linkages) of Faculty of Applied Sciences, Universiti Teknologi MARA.

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1 Introduction

Amid concerns over lithium supply, sodium has been proposed to be an alternative for many reasons. Researchers have concentrated on developing and improving Na+ ion conducting electrolyte for sodium batteries [1]. Sodium which is located below Li in the periodic table has very suitable redox potential \( E^0(\text{Na}^+/\text{Na}) = -2.71 \text{ V vs. standard hydrogen electrode; only 0.3 V above that of lithium} \) so has good energy storage. According to the Kim et al. [2], sodium exhibits similar chemical properties to lithium which indicates that Na chemistry could be applied to the same battery system.

Na+ ion conducting solid electrolytes have been developed for high energy density batteries next to Li+ ion because of their light weight and high electrochemical potential. It is also become the focus owing to the fact that it is very stable in solid state batteries [3]. According to nature of conducting species, Na+ is a fast ion conductor of solid electrolytes which exhibit high ionic conductivity \( (10^{-2} \text{ S cm}^{-1} \text{ to } 10^{-6} \text{ S cm}^{-1}) \), negligible electronic conductivity and a low value of activation energy for ion migration at temperatures below their melting point [4]. The smaller cation of Na+ next to Li+ ion travels faster and as a result, the high conductivity can be obtained. In addition, due to natural abundance, sodium is cheap and hazard free.

In our earlier work, binary system NaI–Na3PO4 has been prepared by ball milling and sintering method, and conductivity in the range of \( 10^{-4} \text{ S cm}^{-1} \) has been achieved [5]. Another report from Takada et al. [6] mentioned that iodides are the common solid electrolyte system with ionic conductivities as high as \( 10^{-3} \text{ S cm}^{-1} \). However, as iodide based materials are usually hygroscopic in nature, compounds such as ortho–oxosalts are usually added into iodides-containing systems to increase the stability against atmospheric attack as well as to increase the electrical conductivity [7–10]. The existence of corner–sharing PO4 tetrahedra is attributed to the formation of 3–D network tunnels as pathways through corner, edge or face sharing that help in ion migration which in turn enhances the conductivity [11,12]. Large anion immobilisation of iodide is another beneficial condition that can allow fast ion transport and contributes to high ionic conductivity [13–17].

The supportive roles of additives in solid electrolytes have been highlighted and witnessed an improvement in battery performance. Some commonly used additives by researchers are vinylene carbonate [18], vinyl ethylene carbonate [19] and vinyl ethylene sulphite [20]. These additives which are also known as functional materials for functional
electrolytes are reported to be fully utilised in developing battery design with improved electrochemical performance [21–24]. According to literature, zwitterionic polymer gave a great effect on ionic conductivity owing to structural modification during the preparation of the sample [25]. In binary salt composites, zwitterions play the role of dissociator and salts such as metal halide can be held by zwitterions helped to increase the mobility of the mobile charge carriers thus improving the conductivity [13,26,27].

Poly(L-leucine), 1,3-diaminopropane (PLLTMEDA) is classified as zwitterions. Amino acids such as poly(L-leucine) (PLL) are one of the best known examples of zwitterions. 1,3-Diaminopropane known as trimethylenediamine (TMEDA) is a simple diamine with the formula (CH₂)₃(NH₂)₂. In the present work, PLLTMEDA as an additive will be dispersed into binary system of NaI-Na₃PO₄ to enhance the electrical conductivity and to improve the performance of the sodium. PLLTMEDA is chosen because of its structure that assists in mobility of the Na⁺ when combined with inorganic salt of iodide. Thus, these studies will bring about new knowledge on solid based electrolytes and reveal the new information on structural properties and conductivity of NaI–Na₃PO₄–PLLTMEDA.

2 Experimental

Preparation of sample. Various compositions of PLLTMEDA in the range of 2–10 wt.% were added to the optimum binary sample (0.5 NaI–0.5 Na₃PO₄) with maximum conductivity of 1.02 × 10⁻⁴ S cm⁻¹ [5]. The mixture was milled using planetary ball mill (PM200) manufactured by Retsch GmbH (Germany) for 3 hours at a rate of 300 rpm and pelleted in a mould at 2000 psi using ENERPAC hydraulic press (max: 10,000 psi/700 bar). The thickness and diameter of the pellets were about 0.19 cm and 2.0 cm, respectively. Since the sample is hygroscopic and sensitive to moisture, the test tubes containing the samples were corked using glass wool before subjected to sintering process. Similar method can be found from literatures that is glass wool used to plug test tube during sintering process [28,29]. It is because that iodide salts will liberate I₂ vapour when heated. Then pelleted samples were sintered at 50°C for 72 h in a vacuum oven. Sintering in vacuum assisted in disposal of residual water in the pelleted samples [30].

Electrical measurement and structural characterisation. The real impedance (Zr) and imaginary impedance (Zi) over the frequency range from 50–10⁶ Hz and the bulk resistance, (Rb) were determined from the impedance spectra. Rb was used in calculating the electrical conductivity of the samples using equation (1)

$$\sigma = \frac{t}{R_b \cdot A}$$

where A is the contact area of pelleted sample, Rb is the bulk resistance of the samples and t is the thickness of the pelleted sample. FTIR measurements were carried out using Perkin Elmer FTIR Spectrometer Spectrum 2000 by KBr method in the transmission mode of 400 cm⁻¹ to 4000 cm⁻¹ at a resolution of 2 cm⁻¹. The morphological characteristics of the surface of NaI–Na₃PO₄–PLLTMEDA binary samples were examined and recorded using field emission scanning electron microscopy (FESEM), Zeiss SUPRA™ 40VP under 25,000X magnification. This study revealed the grain size
and the structural arrangement of the sample electrolytes. The ionic transference number was measured using Wagner’s polarisation technique [31]. The solid electrolyte was placed between two blocking electrodes. Current vs. time was monitored for a fixed applied dc potential until the current became constant. From this plot the electronic and ionic transference number can be determined by calculation using the equation (2).

$$t_{\text{ion}} = \frac{(I_i - I_f)}{I_i}$$

(2)

where $I_i$ and $I_f$ are the initial current and final residual current respectively.

Fabrication of battery. The solid state cells with NaI–Na₃PO₄ solid electrolytes were constructed with the cathode material made up of V₂O₅, electrolyte, activated carbon, and PVdF with a weight ratio of 60 : 20 : 10 : 10. PVdF was added as a binder. The anode was made up of sodium metal. The electrolyte was sandwiched by the electrodes, and pressed to form a button cell. Thus, fabricated cell which comprised anode, electrolyte and cathode was loaded in a Teflon casing. The whole process was carried out in a glove box. A good mechanical contact was established by screwing the casing tightly. Sodium cells were prepared and the configurations are shown below:

$$\text{Na metal/NaI – Na}_3\text{PO}_4 – \text{PLLTMEDA/V}_2\text{O}_5 + \text{electrolyte + C.}$$

3 Results and discussion

3.1 Field emission scanning electron microscopy (FESEM)

Figure 1 shows the morphology 50 wt.% NaI–50 wt.% Na₃PO₄ and 4 wt.% of PLLTMEDA pellet samples at various conditions. Figure 1(a) shows unmilled and unsintered pellet sample. From the micrograph, a porous and non-homogenous microstructure with narrow grain size distribution was observed. Sintering at 50 ºC of unmilled pellet (Figure 1(b)) shows significant microstructural densification and grain growth. The number of pores was reduced as sample was sintered as a result of which the individual grains get closer to each other and the effective area of grain contact increased.

Figure 1(c) shows the grain boundaries of the sintered samples became clear along which the grains grew in straight line manner. Prominent features in this micrograph are the presence of less porosity and well-defined grains giving impression of grain growth. There is a facilitated grain growth in the samples in Figure 1(c) compared with the gradual increase of grain size in Figure 1(b). This result is in good agreement with Ahmad et al. [5], who stated that the sintering process can promote the growth of grain boundaries in a straight line manner and this could be owing to the conducting pathways forming at the interface of the materials. Upon sintering, these pathways can also grow in size and join with one another allowing fast ions to migrate throughout the materials thus enhancing the conductivity. Milling helps in breaking down into the sample into small fragments. Fine powders are expected to increase the surface-area-to-volume ratio and bring about the good interfacial contacts between the solid electrolyte and the electrode materials.
3.2 Electrical conductivity of NaI–Na$_3$PO$_4$–PLLTMEDA

The electrical conductivity of the NaI–Na$_3$PO$_4$–PLLTMEDA at room temperature was calculated using $R_b$ value obtained from impedance spectra in Figure 2 and the variation of electrical conductivity of the binary NaI–Na$_3$PO$_4$ with different wt.% of PLLTMEDA is tabulated in Figure 3. When the compositions of PLLTMEDA were added to binary solid, the conductivity of the sample increased as the composition of PLLTMEDA increased until maximum conductivity of $1.12 \times 10^{-3}$ S cm$^{-1}$ was achieved for the sample with 4 wt.% of PLLTMEDA.

Figure 2  Impedance spectra of the sample with different weight percent of PLLTMEDA (see online version for colours)
From the work conducted by Kaus et al. [32], Lil-PLLTMEDA system was found to have conductivity of $1.04 \times 10^{-3}$ S cm$^{-1}$ which was slightly lower compared to present study. The increase in conductivity could be owing to the presence of optimum electron donating atoms (O and N) in PLLTMEDA which can provide sites for the hopping mechanism of Na$^+$. Chelation of Na$^+$ could occur due to dissociating ability of the zwitterions in PLLTMEDA that leads to increase the mobility of mobile charge, thus enhancing the electrical conductivity [32]. At this concentration range, the rate of ion dissociation is higher than the rate of association. From another perspective, the enhanced conductivity could be owing to the fact that zwitterion anions offer a stronger coordination and create additional sites which improved the compatibility, dissociation of ions and conductivity. In addition, the zwitterionic forms of PLLTMEDA could act as a shield to the ionic interaction between the charges and prevent ion association.

However, sudden drop in conductivity can be seen when wt.% of PLLTMEDA exceeds 4wt.%. This phenomenon can be explained owing to the addition of PLLTMEDA into the binary solid system leading to a decrease in the number of charge carriers per-unit volume, as the ratio of NaI and Na$_3$PO$_4$ was fixed. PLLTMEDA increases the dissociation at a certain concentration, beyond 4 wt.%, ion aggregation occurs at a faster rate than ion dissociation by PLLTMEDA. Therefore, the number of mobile ions available in the sample decreases and consequently reduces the conductivity. Another reason of the decreased conductivity could be due to the blocking effect [33]. At the optimum 4 wt.% of PLLTMEDA, the conducting pathways created are the highest and thus ion migrations will be increased. When the addition of PLLTMEDA exceed 4 wt.%, the conducting pathways are blocked such that no conducting pathways formed between binary compound and PLLTMEDA.

3.3 FTIR analysis

The infrared spectroscopy for pure poly(L-leucine) 1,3-diaminopropane, pure NaI and samples with varied compositions of PLLTMEDA are shown in Figure 4. In the pure PLLTMEDA spectrum, a peak can be seen at 1650 cm$^{-1}$ which is assigned to the C=O stretching vibration and the peak at 1539 cm$^{-1}$ is assigned to N–H stretching group. In the
binary sample spectrum, it can be seen that a peak at wavenumber 1618 cm\(^{-1}\) is assigned to NaI and the wavenumbers at 1010 cm\(^{-1}\) and 579 cm\(^{-1}\) are more likely from orthophosphate anion, PO\(_4^{3-}\) vibrations and P–O bending vibrations respectively [26,33,34]. It can be observed that peaks in the range of 3600–3400 cm\(^{-1}\) for 50 wt.% NaI (binary compound) are assigned to OH\(^-\) stretching vibrational model as the sample contains physisorbed water [29]. FTIR spectra of pure PLLTMEDA, binary compound (50 wt.% NaI) and samples with various weight percentages of PLLTMEDA are depicted in Figure 5(a) and (b). It is clearly seen that both compounds of PLLTMEDA, NaI and Na\(_3\)PO\(_4\) co-exist together.

From the spectra shown in Figure 5(a), the band at wavenumber 1650 cm\(^{-1}\) is assigned to C=O for pure PLLTMEDA. As the composition of PLLTMEDA is increased, the peak has shifted to higher wavenumber from 1650 cm\(^{-1}\) to 1687 cm\(^{-1}\). This could be owing to complexation as the cations (Na\(^+\)) interact with the polymer network or polymer lone pair. It is possible that chelation of Na\(^+\) may have occurred at oxygen atom [32]. From Figure 5(b), it can be seen that the band assigned to N–H at wavenumber 3287 cm\(^{-1}\) shifted to higher wavenumber, 3420 cm\(^{-1}\) with the addition of PLLTMEDA. This kind of shifting is owing to an interaction with the Na\(^+\) as the presence of electron donating atom (N) provide sites for the hopping mechanism of Na\(^+\).

**Figure 4** FTIR spectra of pure PLLTMEDA and NaI–Na\(_3\)PO\(_4\) with various compositions of PLLTMEDA (see online version for colours)

### 3.4 Transference numbers

The transference numbers for the NaI–Na\(_3\)PO\(_4\)–PLLTMEDA are calculated from plot of polarisation current vs. time Wagner’s polarisation method [31]. Figure 6 shows the polarisation current vs. time for the optimum composition 50 wt.% NaI–50 wt.% Na\(_3\)PO\(_4\)–4 wt.% PLLTMEDA.
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Figure 5 The (a) FTIR spectra of C=O band and (b) FTIR spectra of N–H band for pure PLLTMEDA and sample with different wt.% of PLLTMEDA (see online version for colours)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wavenumber (cm$^{-1}$) for C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g) Binary Compound</td>
<td>none</td>
</tr>
<tr>
<td>(f) 10 wt. % PLLTMEDA</td>
<td>1687</td>
</tr>
<tr>
<td>(e) 8 wt. % PLLTMEDA</td>
<td>1680</td>
</tr>
<tr>
<td>(d) 6 wt. % PLLTMEDA</td>
<td>1673</td>
</tr>
<tr>
<td>(c) 4 wt. % PLLTMEDA</td>
<td>1664</td>
</tr>
<tr>
<td>(b) 2 wt. % PLLTMEDA</td>
<td>1658</td>
</tr>
<tr>
<td>(a) Pure PLLTMEDA</td>
<td>1650</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wavenumber (cm$^{-1}$) for N–H</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g) Binary Compound</td>
<td>none</td>
</tr>
<tr>
<td>(f) 10 wt. % PLLTMEDA</td>
<td>3459</td>
</tr>
<tr>
<td>(e) 8 wt. % PLLTMEDA</td>
<td>3451</td>
</tr>
<tr>
<td>(d) 6 wt. % PLLTMEDA</td>
<td>3443</td>
</tr>
<tr>
<td>(c) 4 wt. % PLLTMEDA</td>
<td>3436</td>
</tr>
<tr>
<td>(b) 2 wt. % PLLTMEDA</td>
<td>3430</td>
</tr>
<tr>
<td>(a) Pure PLLTMEDA</td>
<td>3287</td>
</tr>
</tbody>
</table>

It can be seen that the initial total current which is due to ions and electrons decreases until it saturates at $1.92 \times 10^{-6}$ A. The residual current at saturation is only electronic current and the ionic transference number of the sample is obtained using the value of
saturated current. The value of the ionic transference number \( (t_{\text{ions}}) \) is 0.98. This indicates that charge transport in the electrolyte is predominantly due to ions and ionic conductor in nature.

Figure 6  Polarisation current as a function of time for 4 wt.% of PLLTMEDA

3.5 Fabrication of battery

Figure 7 shows the discharge characteristic of the sodium cell by using 50 wt.% NaI–50 wt.% Na₃PO₄–4 wt.% PLLTMEDA as the electrolyte. The cell was discharged at 1 µA of current at room temperature. The slight drop from 3.04 V followed by a plateau and then by a knee indicates a complete discharge of the cell. The discharge curve is stable over a long range of period with a plateau at ~2.35 V. After 173 h of discharge, the cell losses potential gradually and reaches a voltage of 0.5 V. The open circuit voltage (OCV) of 3.0 V was recorded at room temperature. The cell parameters obtained from the discharge characteristics are summarised in Table 1.

Figure 7  Discharge characteristics of Nametal+electrolyte+C+PVDF/NaI–Na₃PO₄–PLLTMEDA/V₂O₅+electrolyte+C+PVDF at room temperature
Table 1  Parameter of sodium cells from discharge characteristics of Nametal+electrolyte+C+PVDF/ NaI–Na3PO4–PLLTMEDA/ V2O5+electrolyte+C+PVDF

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NaI/Na3PO4–PLLTMEDA/V2O5</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV at r.t</td>
<td>3.0 V</td>
</tr>
<tr>
<td>Current(µA)</td>
<td>1.0</td>
</tr>
<tr>
<td>Discharge time (h) at room temp.</td>
<td>173 h</td>
</tr>
<tr>
<td>Discharge time at room temp. (µAh/g)</td>
<td>173 µAh/g</td>
</tr>
</tbody>
</table>

4 Conclusion

The maximum electrical conductivity of \((1.12 \pm 0.21) \times 10^{-3} \text{ S cm}^{-1}\) at room temperature was obtained for 50 wt.% NaI–50 wt.% Na3PO4–4 wt.% PLLTMEDA. The enhancement in the conductivity is owing to the increase in Na⁺ ions from NaI. High conductivity value is achieved effectively owing to the main charge carriers Na⁺ ions from the samples which resulted in more mobile ions and easy traverse along conducting pathway created from tetrahedral phosphate. Addition of PLLTMEDA provide electron donating atoms such as N and O which provide sites for the hopping of Na⁺. Chelation of Na⁺ could take place at oxygen atom owing to the dissociating ability of the zwitterions form of PLLTMEDA. FTIR revealed the C=O band shifted to higher wavenumber indicating chelation of Na⁺ has occurred at oxygen atoms. Transference number analysis confirms the optimum composition is ionic in nature. The Na/V2O5 cell showed a reasonably good performance at room temperature. The OCV obtained for sodium cell is 3.0 V. The discharge characteristic was done by using 1 µA of current. The result obtained showed performance up to 173 h.

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References

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