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Title: Nanoporous Ceramic-Poly(ethylene oxide) Composite Electrolyte for Sodium Metal Battery

Article Type: Short Communication

Keywords: Sodium-metal battery; polymeric composites; nanocomposites; nanoporous ceramic; conductivity.

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Abstract: The exploration of solid polymer electrolytes with both superior ionic conductivity and high mechanical stability for sodium-metal batteries still remains dramatical challenges. Herein, we report a composite electrolyte fabricated by sandwiching nanoporous ceramic with a poly(ethylene oxide) (PEO) base polymer electrolyte. This laminated configuration yields superior ionic conductivity of 1.6×10^{-4} S cm⁻¹ at room temperature, stable Na plating and stripping, as well as wide potential stability window of 4.2 V vs Na/Na⁺.

***Highlights (for review)**

Highlights

1. Nanoporous composite electrolyte for sodium metal battery is developed.
2. High room-temperature ionic conductivity of $1.6 \times 10^{-4} \text{ S cm}^{-1}$ is achieved.
3. Wide electrochemical stability window of 4.2 V vs Na/Na⁺ is illustrated.

1 Nanoporous Ceramic-Poly(ethylene oxide) Composite Electrolyte for Sodium
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3 Metal Battery
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44
45 **Abstract**

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1 temperature, stable Na plating and stripping, as well as wide potential stability
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3 window of 4.2 V vs Na/Na⁺.
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5 **Keywords:** Sodium-metal battery; polymeric composites; nanocomposites;
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7 nanoporous ceramic; conductivity.
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10 **1. Introduction**

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13 Since Na-ion batteries are in their early stage of development, there exist a lot of
14 challenges and tremendous difficulties in development of new electrodes and
15 electrolytes. Among many new electrode materials, P2-type Na_{2/3}[Fe_{1/2}Mn_{1/2}]O₂ can
16 deliver a high capacity of 190 mAh g⁻¹ with earth-abundant elements [1]. Contrary to
17 the numerous reports on sodium cathodes, only few low-voltage oxides have been
18 developed as the anodes, due mainly to the large ionic radius of Na⁺ [2]. Therefore, it
19 is particularly important to investigate anode materials. Titanate, TiO₂ has been used
20 as the anode for Li ion batteries due to cost effective, small volume expansion during
21 electronical cycling, and nontox. Therefore, it has garnered significant interests as a
22 material for Na⁺ anode applications [3]. However, it has been realized that TiO₂
23 possesses low electronic conductivity, limiting its application. To address this problem,
24 aligned TiO₂ nanotubes have been proposed to overcome this issue [4]. Although Na
25 metal has large theoretical reversible capacity of 1166 mAh g⁻¹, there are very little
26 real applications because the sodium metal is sensitive to carbonate electrolytes. One
27 of the viable solutions to use sodium metal as the anode is to adopt a solid electrolyte
28 with which sodium metal would not react. The research on sodium solid electrolytes
29 can benefit from their lithium counterparts [5,6]. A flexible solid-state lithium battery
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1 can be achieved by making use of a PEO-based composite polymer electrolyte [7].
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3 Moreover, it has showed enhanced compatibility with the lithium metal [8]. Therefore,
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5 PEO can be considered to be an ideal candidate in sodium system as well.
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9 However, low Na ionic conductivity of PEO at room temperature hinders its
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11 practical use. For example, PEO-NaClO₄ electrolyte was reported to have a
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13 conductivity of about 7×10^{-7} S cm⁻¹ [9]. Crosslinked polymer electrolyte consisting of
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15 PEO, NaClO₄, and propylene carbonate has been synthesized by photopolymerization
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17 technique [10]. The quasi-solid PEO-based electrolyte exhibits extremely high ionic
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19 conductivity exceeding 1 mS cm⁻¹ at room temperature. Compared with various
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21 technologies, the photopolymerization technique demonstrated an effective solution to
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23 prepare polymer electrolytes for safe Na-ion batteries [11].
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31 In addition to ionic conductivity, another key requirement is the ability to
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33 suppress sodium dendrites, which would lead to notorious short-circuits and safety
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35 issues. Solid electrolytes with sufficiently high modulus could mechanically block
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37 dendrites. Herein, we report for the first-time polymeric composites showing high
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39 conductivity and good modulus.
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42 43 44 45 **2. Experimental**

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47 All the chemical unless otherwise stated were purchased from Aladdin. The
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49 electrolyte was prepared *via* a mechanochemical approach [12]. In a typical
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51 processing, proportion of ether-oxygen to sodium was 20 : 1. The weight of SiO₂ and
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53 Emim FSI was 5% of the total weight of PEO₂₀-NaClO₄ and 70% of the total weight
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55 of PEO₂₀-NaClO₄-SiO₂, respectively. A Whatman Anodisc was dipped into the
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1 obtained slurry for 2 min, and then dried on a Teflon plate at 100 °C in vacuum.

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3 X-ray diffraction, SEM, electrochemical impedance spectroscopy, linear cyclic
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X-ray diffraction, SEM, electrochemical impedance spectroscopy, linear cyclic voltammetry and galvanostatic cycling were performed to examine the crystal structure and electrochemical performance of the composite electrolyte.

3. Results and Discussion

As shown in Fig. 1a, the nanocomposites are fabricated by immobilizing the polymer electrolyte in nanoporous alumina. This configuration leads to a composite membrane with dramatically higher mechanical stability, in contrary to the sticky nature of the single polymer membrane (Fig. 1b).

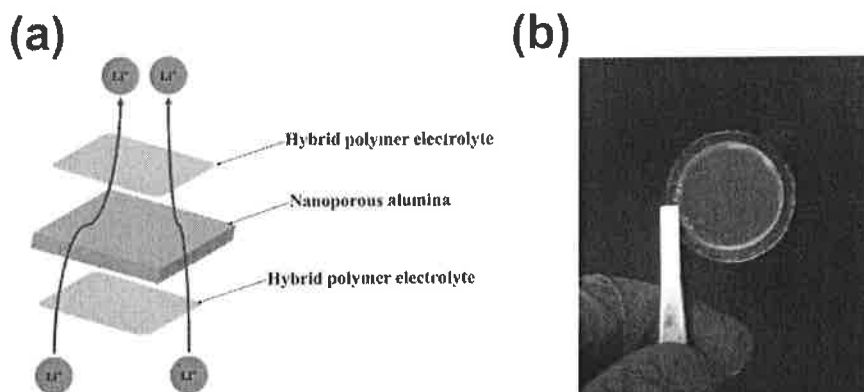


Fig. 1

The alumina has a uniform distribution of nanometer-sized through holes of 0.1 μm (Fig. 2a). As shown in Fig. 2b and c, the surface of the composite electrolyte is smooth, indicating an amorphous structure [13]. The cross-sectional SEM image shows that the composite electrolyte presents a laminated structure in which the top and bottom layers are composed of a PEO base polymer and the middle layer is alumina (Fig. 2d).

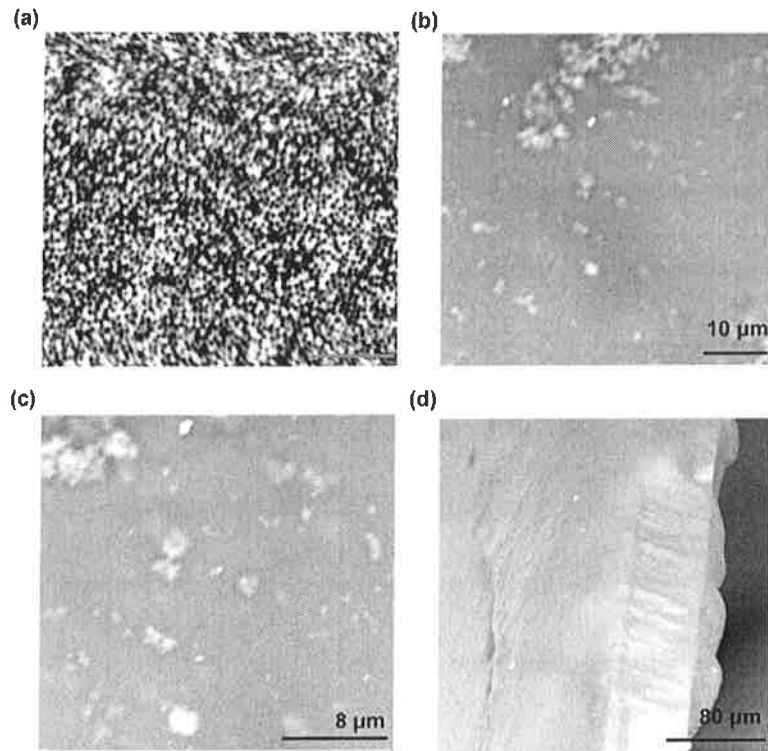


Fig. 2

It has been known that the PEO suffers from low crystallization temperature below 60 °C, which in turn decreases the conductivities by more than two orders of magnitude [14]. As shown in Fig. 3a, the raw PEO characterizes two distinct diffraction peaks at 19.2° and 23.4° (2-theta). The composite electrolyte shows an amorphous structure at room temperature, which will facilitate the Na-ions transport. The electrochemical impedance spectroscopy (EIS) shows a semicircle at high frequency and a tail at low frequency (Fig. 3b), which represent a bulk relaxation and a double layer capacitance, respectively. The total conductivity is $1.6 \times 10^{-4} \text{ S cm}^{-1}$ that is about three orders of magnitude higher than those of reported PEO–NaX polymer electrolytes [15], according to the interception of the tail on the real axis.

The composite electrolyte possesses an electrochemical stability window of 4.2

1 V vs Na/Na^+ , which can couple sufficiently with most sodium cathodes (Fig. 3c). Fig.
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 3 3d shows the time-dependent voltage profile of the symmetric cell cycling over 50 h
 4 with a current density of 0.02 mA cm^{-2} at a temperature of $80 \text{ }^\circ\text{C}$. The cell's voltage is
 5 stabilized at 0.6 V after the first 10 h. The stable d.c. Na plating and stripping implies
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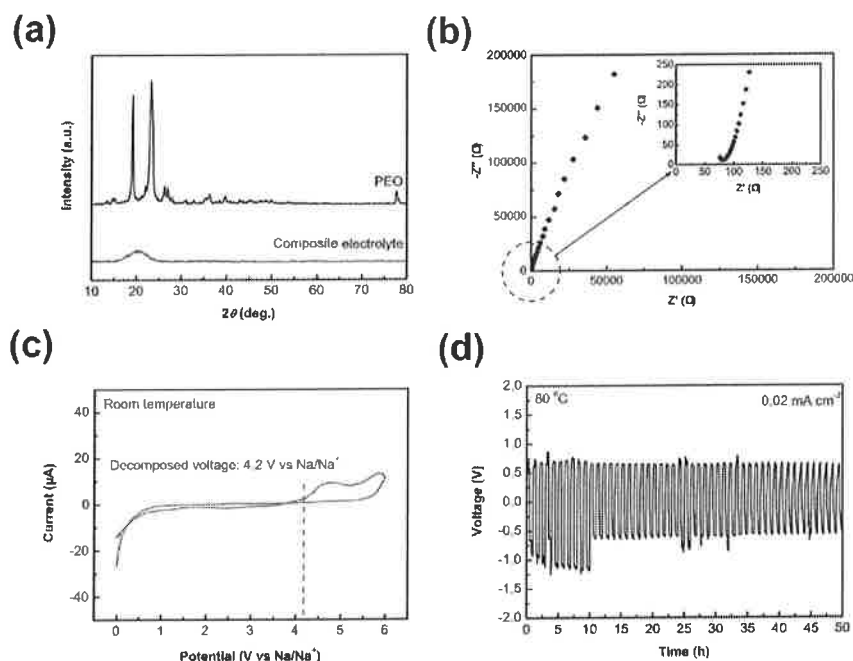


Fig. 3

4. Conclusions

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 45 We report a nanoporous ceramic-polymer composite electrolyte, in which the
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 47 nanoporous alumina is sandwiched with PEO. The composite electrolyte exhibits
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 49 superior ionic conductivity of $1.6 \times 10^{-4} \text{ S cm}^{-1}$, wide electrochemical stability window
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 51 of 4.2 V vs Na/Na^+ , as well as robust dendrite blocking. This configuration offers a
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Acknowledgments

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Figure captions

Fig. 1. (a) Schematic illustration for the composite electrolyte. (b) Typical composite electrolyte membrane obtained after solidifying.

Fig. 2. (a) SEM image of the nanoporous ceramic. (b & c) Top SEM images of the composite electrolyte. (d) Cross-section SEM image of the composite electrolyte.

Fig. 3. Structural and electrochemical characterization of the composite. (a) XRD patterns. (b) EIS profiles. (c) Current–potential curve. (d) Galvanostatic cycling.