Sodium Ion Transport Mechanisms in Antiperovskite Electrolytes 
Na₃OBr and Na₄OI₂: An in Situ Neutron Diffraction Study

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Supporting Information

ABSTRACT: Na-rich antiperovskites are recently developed solid electrolytes with enhanced sodium ionic conductivity and show promising functionality as a novel solid electrolyte in an all solid-state battery. In this work, the sodium ionic transport pathways of the parent compound Na₃OBr, as well as the modified layered antiperovskite Na₄OI₂, were studied and compared through temperature-dependent neutron diffraction combined with the maximum entropy method. In the cubic Na₃OBr antiperovskite, the nuclear density distribution maps at 500 K indicate that sodium ions hop within and among oxygen octahedra, and Br⁻ ions are not involved. In the tetragonal Na₄OI₂ antiperovskite, Na ions, which connect octahedra in the ab plane, have the lowest activation energy barrier. The transport of sodium ions along the c axis is assisted by I⁻ ions.

INTRODUCTION

Medium- and large-scale stationary batteries are needed to match production and energy consumption from renewable sources like solar, wind, hydraulic electrogeneration, or even off-peak electrical energy from traditional power stations¹ in a safe, cost-affordable, and sustainable way. In portable electronic devices, lithium-ion batteries are currently the predominantly used secondary cell. The low abundance of lithium on Earth, combined with a continuously increasing demand, provides a formidable future challenge.² While lithium-based rechargeable batteries have the advantage of high energy density and durability,³⁻⁵ the sodium ion battery⁶⁻⁷ has a potential advantage when considering raw material abundance and cost. Today three types of sodium ion batteries are mainly used: the Na–S battery, which requires molten sodium and sulfur at 300–350 °C,⁷ the organic liquid electrolyte-based battery,⁹ and aqueous sodium ion batteries.¹⁰⁻¹² In nonaqueous sodium ion batteries, replacing the liquid or polymeric organic electrolyte¹³⁻¹⁵ with a cheap, safe, and stable solid electrolyte¹⁶⁻²⁰ will reduce the risk of leakage and ignition, as well as reducing cost. Currently, the existing sodium solid electrolytes can be broadly categorized into chalcogenides¹⁷,¹⁸ and the Na super ionic conductor (NASICON),¹⁹,²⁰ the latter suffers from a high grain-boundary resistance, which requires elevated sintering temperatures to overcome. Exploration of a new class of sodium solid electrolyte candidates could not only enhance the flexibility of full solid-state battery design, but also contribute to the requirements of large-scale energy storage and transportation in a safe and environmental friendly way.

The recent development of the antiperovskite electrolyte family²¹,²² derived from perovskites NaMgF₃ and (K,Na)MgF₃, received: February 26, 2016
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could be promising due to their structural tolerance and superionic conductivity. For example, through aliovalent substitution, the ionic conductivity of the compound Na2.9Sr0.05OBr0.6I0.4 reached 0.19 S m$^{-1}$ at 200 °C. However, fundamental scientific information, such as sodium ion transport and kinetic properties, must be obtained to successfully guide the synthesis of new Na-rich antiperovskites that perform at or above the desired level. Thus, an experimental investigation on the ionic transport mechanism within various antiperovskite-type electrolyte materials and an in-depth understanding of the structure–property relationship should be significant for future development of such antiperovskite materials. In this work, Na$_3$OBr$^{23}$ and Na$_4$OI$_2$$_{24}$ have been studied as two representatives of Na-rich antiperovskites for sodium ion transport investigations. These particular structures, albeit not with optimal ionic conductivities, have been selected to extract the fundamental transport mechanism without the confounding effects of doping or substitution, and to compare the transport in two distinct classes of antiperovskite crystals. Impedance spectroscopy and powder neutron diffraction measurements were performed as a function of temperature to study the sodium ionic transport.

**Table 1. Refined Crystal Parameters for Na$_3$OBr and Na$_4$OI$_2$ at 300, 400, and 500 K**

<table>
<thead>
<tr>
<th>formula</th>
<th>lattice params (Å)</th>
<th>coordinates of equivalent positions</th>
<th>occupancy</th>
<th>thermal params</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_3$OBr</td>
<td>$a = 4.5674(1)$ 300 K</td>
<td>Na 0.5 0 0.5</td>
<td>0.989(2)</td>
<td>$U_{11}$ 0.015</td>
</tr>
<tr>
<td></td>
<td>$a = 4.5774(1)$ 400 K</td>
<td>Na 0.5 0 0.5</td>
<td>0.990(4)</td>
<td>$U_{11}$ 0.016</td>
</tr>
<tr>
<td></td>
<td>$a = 4.5858(3)$ 500 K</td>
<td>Na 0.5 0 0.5</td>
<td>0.992(6)</td>
<td>$U_{11}$ 0.018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 0.5 0.5 0.5</td>
<td>0.995(1)</td>
<td>$U_{11}$ 0.996(4)</td>
</tr>
<tr>
<td>Na$_4$OI$_2$</td>
<td>$a = 4.6902(3)$ 300 K</td>
<td>Na1 0 0.5 0</td>
<td>0.965(3)</td>
<td>$U_{11}$ 0.031</td>
</tr>
<tr>
<td></td>
<td>$c = 16.0086(10)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = 4.7053(3)$ 400 K</td>
<td>Na2 0 0 0.1425</td>
<td>1.0</td>
<td>$U_{11}$ 0.040</td>
</tr>
<tr>
<td></td>
<td>$c = 16.0536(12)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = 4.6729(1)$ 500 K</td>
<td>Na2 0 0 0.1425</td>
<td>1.0</td>
<td>$U_{11}$ 0.049</td>
</tr>
<tr>
<td></td>
<td>$c = 15.9556(5)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 0 0 0</td>
<td>0.983(2)</td>
<td>$U_{11}$ 0.062</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I 0 0 0</td>
<td>0.3468(2)</td>
<td>$U_{11}$ 0.0982(3)</td>
</tr>
</tbody>
</table>

“**The defect vacancies are both from Na$_2$O with ~1% Na$^+$ vacancies in Na$_3$OBr and ~3.5% Na$^+$ vacancies in Na$_4$OI$_2$.** The refined Rwp (Rp) for Na$_3$OBr at 300, 400, and 500 K are 3.30% (2.54%), 3.02% (2.48%), and 4.02% (2.69%), respectively; those for Na$_4$OI$_2$ at 300, 400, and 500 K are 4.01% (3.22%), 3.78% (2.93%), and 3.28% (2.48%), respectively. Firstly, all atomic occupancies were refined, and the results indicated that the occupancies of the halide sites and Na2 site stayed at 1, the others had occupancies less than 1; the occupancies of the halide sites and Na2 site were fixed during the following refinement.”

Figure 1. Neutron diffraction patterns of (a) Na$_3$OBr and (b) Na$_4$OI$_2$ at 300, 400, and 500 K (2$\theta$ = 66°). The experimental data are in black circles, the Rietveld fitting is the red line, and the blue ticks represent the peak positions; the arrows at 2.2 and 3.0 Å in part a indicate the peak positions of impurity NaBr phase, and the peak at ~2.7 Å in part b could come from some Na–O–I polymorph. (c) Normalized volumes and lattice parameters of Na$_3$OBr and Na$_4$OI$_2$ as a function of temperature in the range 300–500 K; Na$_4$OI$_2$ has an average thermal expansion coefficient of 10.1(4) × 10$^{-5}$ K$^{-1}$, larger than that for Na$_3$OBr 6.1(3) × 10$^{-5}$ K$^{-1}$. In the Na$_4$OI$_2$ structure, the thermal expansion along the a axis is larger than in the c axis direction.
conductivities and the potential Na⁺ transport pathways. The results provide new insight into the future design of these antiperovskite compounds. Chemical manipulations such as elemental doping, size-mismatch replacement, internal/external stresses, and structural manipulations may lead to enhanced sodium ionic conductivity to meet practical application demands.

## RESULTS AND DISCUSSIONS

Figure 1a,b shows the neutron diffraction patterns (2θ = 66°) of Na₃OBr and Na₄OI₂ at 300, 400, and 500 K, respectively. At room temperature (RT), Na₃OBr crystallizes into the cubic antiperovskite structure with space group \( Pn\overline{3}m \) and \( a = 4.5674(1) \) Å. The lattice is characterized by corner-sharing \( ONa₆ \) octahedra with \( Br^- \) ions located on the A-site.\(^{23} \) The layered intergrowth \( K₂NiF₄\)-type \( Na₄OI₂ \) is a tetragonal antiperovskite with space group \( I\overline{4}/m \) and lattice parameters \( a = 4.6729(1) \) Å and \( c = 15.9556(5) \) Å. The lattice is characterized by \( "NaOI₅" \) antiperovskite slabs and \"NaI\" rock-salt layers.\(^{24} \) All the refined parameters are listed in Table 1. The refined volume of Na₃OBr as a function of temperature gives an averaged thermal expansion coefficient of \( 6.1(3) \times 10^{-5} \) K⁻¹, while Na₄OI₂ has a slightly larger value of \( 10.1(4) \times 10^{-5} \) K⁻¹ with an anisotropic thermal expansion that is 11.5% greater along the \( a \) axis than along the \( c \) axis, as shown in Figure 1c. The larger expansion along the \( a \) axis could be the result of the dense packing in that direction. The two compounds are both nonstoichiometric. The defect vacancies are both from the dense packing in that direction. The two compounds are both nonstoichiometric.

In both sodium antiperovskite compounds, the Na⁺ ions are bonded to the O\(^{2-}\) ions forming \( ONa₆ \) octahedra. The octahedra in cubic Na₃OBr are connected to each other at the vertices, forming a three-dimensional (3D) octahedral array. The \( Br^- \) ions lie in the center of the eight nearest sodium atoms in Na₄OI₂. The octahedra in tetragonal Na₄OI₂ are also connected at the vertices in the \( ab \) plane, and the octahedra in the \( (001) \) and \( (002) \) planes relatively shift \( (1/2, 1/2, 0) \) each other with NaI layers separating the octahedral layers. The Na atoms in Na₄OI₂ are crystallographically equivalent.\(^{26} \) Cation transport in isostructural Na₄OI₂ occurs among nearest-neighbor Na⁺ sites (Na–Na atomic distance 3.2297(6) Å at RT) and vacancies along the edges\(^{26–31} \) within the \( ONa₆ \) octahedra, and through the oxygen ions as shown in Figure 3a and Figure 4. The missing overlap in the nuclear densities of sodium cations and bromine ions (Figure 3b) indicates that bromine ions are not involved in the Na⁺ ion migration process. This can be explained by the fact that the Na–O bond length is 2.2837(1) Å, and the Na–Br bond is 3.2296(1) Å at RT, with each O\(^{2-}\) ion carrying two electrons.

In contrast, in Na₄OI₂ there are two inequivalent Na positions in the structure, the one at \( (0, 0.5, 0) \) is denoted as Na1, and the other at \( (0, 0, z) \) is denoted as Na2; three possible sodium migration pathways are proposed: Na1–Na1 (3.3042(4) Å at RT), Na1–Na2 (3.2603(1) Å at RT) with the highest probability, and Na2–Na2 (4.7627(3) Å at RT) with the smallest migration probability. Therefore, differences in the sodium transport behaviors of Na₃OBr and Na₄OI₂ are expected. Na⁺ ions at Na1 position have a similar transport mechanism (in the \( ab \) plane) as in the Na₃OBr system, which is...
expected as the vertex-to-vertex connection geometry is similar. The sodium ions at the Na1 position show an elliptic-type nuclear density in the $ab$ plane, and have a smaller overlap with oxygen at 500 K as indicated in Figure 3c and Figure 5. The smaller overlap of the Na1 ions and O$_2^-$ ions is mainly due to the larger Na1–O bond length of 2.3364(1) Å as compared to that of the Na–O bond length 2.2837(1) Å in the Na$_3$OBr crystal. Furthermore, there is no obvious interaction between Na2 ions and I$^-$ ions in the $ab$ plane, similar to the Na$^+$ and Br$^-$ ions in Na$_3$OBr (Figure 3b). The anisotropic effect in tetragonal Na$_3$O$I_2$ is mainly expressed in the $c$ direction. As the activation energy of the nearest Na$_2$–Na$_2$ diffusion pathways (along $c$ axis) is >1 eV, and likely too great to overcome, the possibility of sodium ion transport along the $c$ axis could be via the I$^-$ ion. As shown in the (100) projected planes in Figure 3d and Figure 5, Na$^+$ ions at the Na2 position exhibit an elliptic nuclear density along the $c$ direction, which overlaps with the I$^-$ ions nuclear densities polarized toward the Na2 ion. This indicates that sodium ions have some likelihood to migrate among different octahedra along the $c$ axis, even though it is a minor migration probability compared with other directions. Interestingly, the polarized nuclear density distribution of the I$^-$ ion, and its overlap with Na2 ion as shown in Figure 3d, strongly suggests that the I$^-$ ion, not only the O$_2^-$ ion, acts as a pathway of a negative charge center facilitating sodium cation transport in the $c$ direction. It is expected that the ionic conductivity of Na$_4$OI$_2$ will be enhanced by doping with smaller radius anions, such as Br$^-$, Cl$^-$, or F$^-$, at the I$^-$ sites to shorten the jump distance of Na$^-$ ions between isolated octahedra. This ultimately corresponds to a reduction in the energy barrier bottleneck along the $c$ axis.

| Figure 3. Nuclear density distributions of Na$_3$OBr and Na$_3$OI$_2$ at 500 K deducted from MEM analysis. The isosurface level is between 0 and 0.05 fm Å$^{-3}$ in (001), (110) planes of Na$_3$OBr and (001), (100) planes of Na$_3$OI$_2$. The arrows indicate the preferable pathways in both structures, and the two colored arrows in Na$_3$OI$_2$ suggest the two transport mechanisms in the $ab$ plane and along the $c$ direction of the layered structure. |
| Figure 4. Upper panel shows the schematic crystal structure of Na$_3$OBr at 300, 400, and 500 K (from left to right) with anisotropic thermal vibration of sodium atoms at 80% probability; lower panel gives the nuclei density distributions from MEM analysis with an isosurface level of 0.03 fm Å$^{-3}$. |
| Figure 5. Upper panel shows the schematic crystal structure of Na$_4$OI$_2$ at 300, 400, and 500 K (from left to right) with anisotropic thermal vibration of sodium atoms at 80% probability; lower panel gives the nuclei density distributions from MEM analysis with an isosurface level of 0.03 fm Å$^{-3}$. |
The main sodium transport pathway in both Na3OBr and Na4OI2 has been synthesized via a solid-state reaction. Fresh Na2O is premade by reacting equal moles of Na metal with NaOH at 300 °C. Since the products are moisture sensitive, a 3% excess Na was employed to guarantee the anhydrous state of the products.

As both the electrolytes are moisture- and air-sensitive, electrochemical impedance spectra (EIS) were performed inside the same glovebox as the synthesis. The samples were melted between two pieces of Au foil electrodes forming symmetric cells. The cells were kept for 30 min after reaching the targeted temperature in a compact furnace at each set point before impedance measurement. A Solartron 1260A impedance/gain-phase analyzer was used for the EIS measurements with an applied ac voltage of 10 mV in a frequency range from 1 MHz to 1 Hz.

Time-of-flight (TOF) neutron powder diffraction was performed at NOMAD (Nanoscale-Ordered Materials Diffractometer), SNS (Spallation Neutron Source), Oak Ridge National Laboratory. The samples were loaded in quartz capillaries with a diameter of 1 mm. About 2 cm length powder samples were loaded in the quartz capillary inside an argon protected glovebox, and then the capillary was sealed. The Cobra cryostream heating system was used to change temperature from 300 to 500 K. The advantage of using neutron diffraction at NOMAD is that neutron diffraction is not atomic-number-dependent and therefore can get a more accurate determination of the oxygen position than with X-ray diffraction. Additionally, multibank diffraction at NOMAD can cover larger d spacings with higher resolution. To map the sodium ion transport pathways, the nuclear density distributions of Na3OBr and Na4OI2 solid electrolytes over a range of temperatures were analyzed by a MEM/Rietveld refinement technique using data from five detector banks at 2θ = 154°, 122°, 66°, 30°, and 15° to gain the maximum d spacing range coverage as well as the high resolution at lower d spacings. The corresponding maximum d-spacing is in the range 0.5–9 Å (Supporting Information Figure S1). The observed structure factors, F, and standard uncertainties, ΔF, were estimated with Alchemy from relevant data in files output by GSAS+EXPGUI and analyzed by the MEM with Dynsorm. The unit cells of Na3OBr and Na4OI2 were divided into 100 × 100 × 100 voxels and 100 × 100 × 300 voxels, respectively. The detailed method for MEM analysis can be found in ref 33.

Sodium migration simulations were performed using CASTEP software (LST/QST) at the GGA level of theory. The crystal structures and lattice parameters of Na3OBr and Na4OI2 from neutron diffraction refinements were employed as the initial structure model to study the sodium migration within the two materials. For Na3OBr, a cubic 2 × 2 × 2 supercell of the perovskite unit cell containing 40 atoms was used to calculate the sodium migration enthalpy. While for Na4OI2, a 2 × 2 × 1 supercell containing 56 atoms was used. Sodium vacancies were generated by artificially removing one of the sodium atoms within the supercell. The shortest pathway for sodium ion was generated automatically from one Na site to the nearest vertex of ONa6 octahedron (vacancy). During the whole calculation process, the lattice vectors of the supercell were constrained to retain cubic symmetry, but internal ionic relaxations were allowed.

**EXPERIMENTAL METHODS**

Na-rich antiperovskites of Na3OBr and Na4OI2 have been synthesized via a solid-state reaction. The 0.05 mol portions of Na2O and NaBr (for Na3OBr: 0.05 mol Na2O and 0.1 mol NaBr) were weighed and ground for 20 min into well-mixed powder in an argon protected glovebox; the fine powder then was placed in a capped alumina crucible. The mixture was then heated in a compact furnace inside the same glovebox with a heating rate of 1.5 °C/min to 150 °C and then to 400 °C at a heating rate of 10 °C/min. Further reaction details can be found in ref 22. The entire reaction takes place under argon gas protection. The oxygen and moisture levels were both less than 10 ppm. The reaction is driven at 400 °C for 4 h, following the reaction pathway shown in Equations 1 and 2, and the products were subsequently allowed to cool to room temperature naturally.

\[
\text{Na}_3\text{O} + \text{NaBr} \rightarrow \text{Na}_3\text{OBr}
\]  
\[
\text{Na}_3\text{O} + 2\text{Na} \rightarrow \text{Na}_4\text{OI}_2
\]  

In conclusion, the main sodium transport pathway in both cubic Na3OBr and layered Na4OI2 is between the nearest Na+ ions in the NaO6 octahedra building block of the antiperovskite. The polarized nuclear densities of Na+ ions bridges the Na+ ions to the nearest Na+ ion in the NaO6 octahedra building block of the antiperovskite. The family of sodium-rich antiperovskites of Na3OBr and Na4OI2 have been synthesized to optimize the Na+ ions transport pathways and maximize the ionic conductivity.
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References