**Supplementary Information**

**Li-Rich Anti-Perovskite Li$_3$OCl Films with Enhanced Ionic Conductivity**

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**Experimental details**

**Target preparation and film deposition:**

To prepare Li$_3$OCl target for pulsed laser deposition (PLD), LiOH and LiCl powders (Aldrich, > 99% purity) with appropriate ratios were mixed and ground. The mixed powders were sintered in a quartz tube (connected to a roughing pump) at 300 °C for 48 hours. The obtained Li$_3$OCl powders (with some hydroxyl radicals) was pressed to 2000 psi and annealed at 300 °C to obtain compact pellet which was used as the target for pulsed laser deposition of Li$_3$OCl films.

The Li$_3$OCl films were deposited on LaAlO$_3$ (LAO), Ag or Li coated stainless steel substrates by PLD (KrF laser, 248 nm, 20 Hz) under vacuum using the as-prepared target. For the Li$_3$OCl films deposition on LAO, a protective layer of TiO$_2$ was further deposited.
on top of Li$_3$OCl films to prevent Li$_3$OCl from direct exposure to air during XRD test.
The Ag and Li layers were also deposited by PLD using the similar processing parameters. The detailed PLD parameters for the deposition of different materials are shown in Table S1. The tri-layer films of Ag/Li$_3$OCl/Ag and Li/Li$_3$OCl/Li were deposited (without breaking the vacuum) to study the ionic conductivity and long-term cyclability of the Li$_3$OCl films.

Characterizations and electrochemical measurements:

The structure and morphology of the films were studied by X-ray diffraction (XRD, Rigaku Ultima III) and scanning electron microscopy (SEM, FEI Inspect F). The thickness of the Li$_3$OCl film was measured using a Bruker Dectak XT Profilometer. Electrochemical measurements were carried out using a specially designed air-tight cell. AC impedance spectroscopy measurements were conducted in the frequency range from 1 Hz to 1 MHz with an amplitude of 10 mV by using an electrochemical system (PARSTAT 2273, Princeton Applied Research). The temperature for the electrochemical measurement was controlled from room temperature to 140 °C. The ionic conductivities of the Li$_3$OCl films were derived from the impedance spectra. The Li/Li$_3$OCl/Li and Ag/Li$_3$OCl/Ag symmetric cells were cycled by applying a constant current of 100 μA with periodically changed polarity using a battery test station (Arbin BT-2000) at room temperature.
Table S1. PLD parameters used for deposition of different materials.

<table>
<thead>
<tr>
<th>Films</th>
<th>Li3OCl layer</th>
<th>TiO2 layer</th>
<th>Li layer</th>
<th>Ag layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAO/Li3OCl/TiO2</td>
<td>175 °C, 60 min, 20 Hz, 4.0 J cm⁻², vacuum</td>
<td>175 °C, 30 min, 20 Hz, 5.0 J cm⁻², vacuum</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Li/Li3OCl/Li</td>
<td>175 °C, 60 min, 20 Hz, 4.0 J cm⁻², vacuum</td>
<td>N/A</td>
<td>175 °C, 30 min, 20 Hz, 2.0 J cm⁻², vacuum</td>
<td>N/A</td>
</tr>
<tr>
<td>Ag/Li3OCl/Ag</td>
<td>175 °C, 60 min, 20 Hz, 4.0 J cm⁻², vacuum</td>
<td>N/A</td>
<td>N/A</td>
<td>225 °C, 60 min, 20 Hz, 6.5 J cm⁻², vacuum</td>
</tr>
</tbody>
</table>

Figures

![XRD patterns of Li3OCl target material and the as-deposited film.](image)

Fig. S1 XRD patterns of Li3OCl target material and the as-deposited film.
Fig. S2 Arrhenius plot for bulk Li$_3$OCl (target material). The activation energy $E_a$ is derived by the slope of the linear fitting of $\log(\sigma T)$ versus 1000/T.

$$\sigma T = A \exp \left(-\frac{E_a}{kT}\right)$$

$E_a = 0.59$ eV

Fig. S3 The crystal lattice of cubic Li$_3$OCl with the label of Li-ion transport pathway along (011) planes.