Supplementary Information

Li-Rich Anti-Perovskite Li_3OCl Films with Enhanced Ionic Conductivity

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Experimental details

Target preparation and film deposition:

To prepare Li_3OCl 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_3OCl powders (with some hydroxyl radicals) was pressed to 2000 psi and annealed at 300 ^oC to obtain compact pellet which was used as the target for pulsed laser deposition of Li_3OCl films.

The Li_3OCl 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_3OCl films deposition on LAO, a protective layer of TiO_2 was further deposited

on top of Li_3OCl films to prevent Li_3OCl 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_3OCl/Ag and Li/Li_3OCl/Li were deposited (without breaking the vacuum) to study the ionic conductivity and long-term cyclability of the Li_3OCl 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_3OCl 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_3OCl films were derived from the impedance spectra. The Li/Li_3OCl/Li and Ag/Li_3OCl/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.

Films	Li_3OCl layer	TiO_2 layer	Li layer	Ag layer
LAO/Li_3OCl/TiO_2	175 °C, 60 min, 20 Hz, 4.0 J cm^{-2}, vacuum	175 °C, 30 min, 20 Hz, 5.0 J cm^{-2}, vacuum	N/A	N/A
Li/Li_3OCl/Li	175 °C, 60 min, 20 Hz, 4.0 J cm^{-2}, vacuum	N/A	175 °C, 30 min, 20 Hz, 2.0 J cm^{-2}, vacuum	N/A
Ag/Li_3OCl/Ag	175 °C, 60 min, 20 Hz, 4.0 J cm^{-2}, vacuum	N/A	N/A	225 °C, 60 min, 20 Hz, 6.5 J cm^{-2}, vacuum

Figures

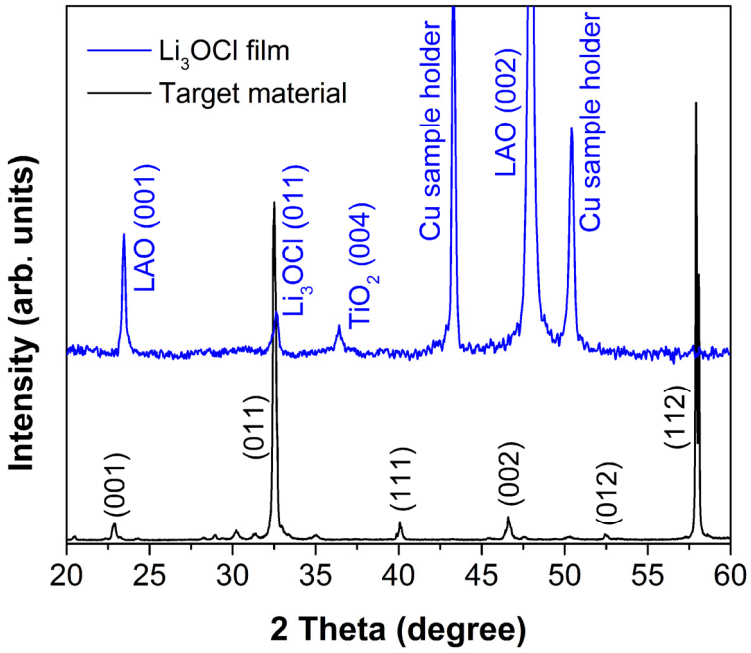

Fig. S1 XRD patterns of Li_3OCl target material and the as-deposited film.

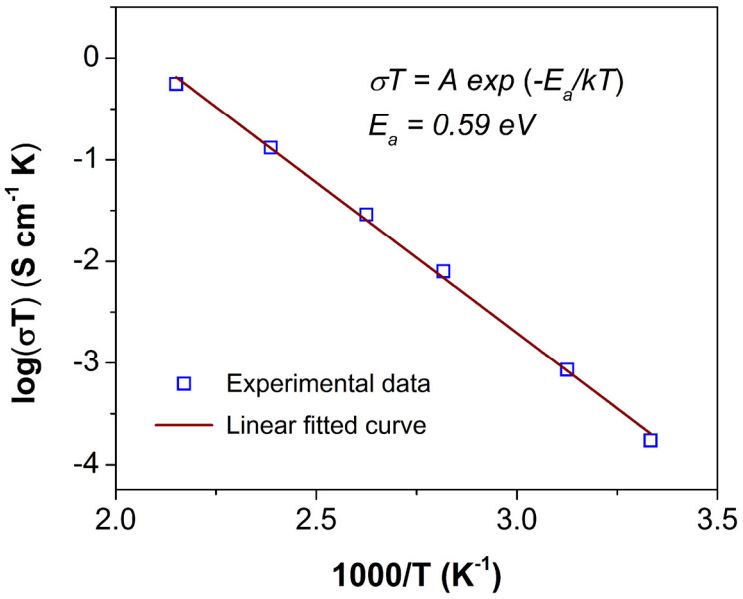

Fig. S2 Arrhenius plot for bulk Li_3OCl (target material). The activation energy E_a is derived by the slope of the linear fitting of log(σT) versus 1000/T.

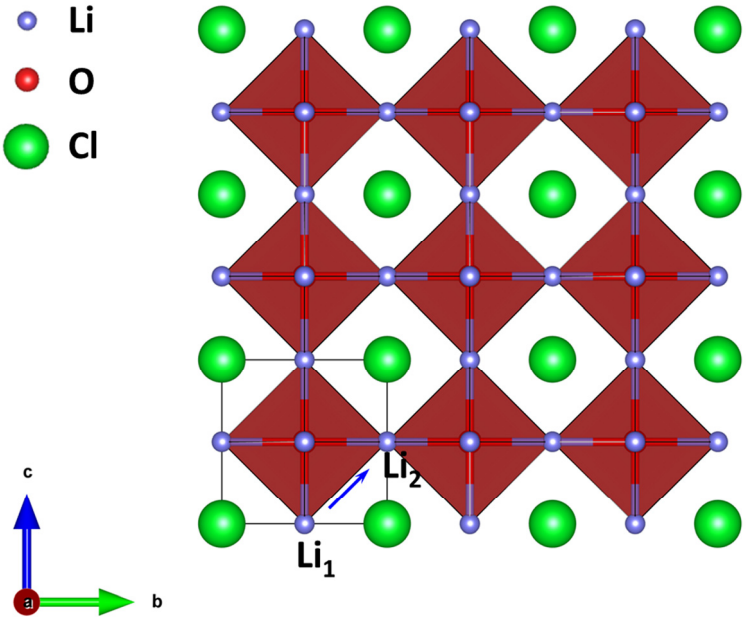

Fig. S3 The crystal lattice of cubic Li_3OCl with the label of Li-ion transport pathway along (011) planes.