

Electronic Supplementary Information

Low-cost anodic catalyst of transition metal oxide for lithium extraction from seawater

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Experimental Procedures:

Material synthesis

50 mg of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was dissolved in 100 mL of ethylene glycol with the addition of 80 mg of Super P. The solution was uniformly mixed through an ultrasonic bath and refluxed for 3 h at 170 °C. After cooling down, the supernatant was removed and the remnant mixture was centrifuged with deionized water and ethanol several times. The resulting products were dried in a vacuum oven at 80 °C for 12 h to obtain Ru@SP catalyst material.

2 mmol of NaOH and 1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\text{Co}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$) were dissolved in 70 mL of H_2O with the addition of 70 mg of Super P. The solution was uniformly mixed through an ultrasonic bath and kept at 180 °C in an autoclave for 18 h. After cooling down, the solid product was centrifuged with deionized water and ethanol several times. The resulting products were kept at 250 °C (500 °C) for 3 h under the gas of argon to obtain NiO@SP (CoO@SP) catalyst material.

0.6 mmol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 0.4 mmol of KMnO_4 were dissolved in 70 mL of H_2O with the addition of 70 mg of Super P. The solution was uniformly mixed through an ultrasonic bath and kept at 180 °C in an autoclave for 18 h. After cooling down, the solid product was centrifuged with deionized water and ethanol several times. The resulting products were dried in a vacuum oven at 80 °C for 12 h to obtain MnO_2 @SP catalyst material.

Electrode fabrication

The catalyst material (70%), Super P (20%) and polytetrafluoroethylene (PTFE) binder (10%) were mixed and rolled into a 0.6 cm × 0.8 cm thin film. The thin film was then pressed on carbon paper and used as the catalyst anode electrode. Super P (85%) and polytetrafluoroethylene (PTFE) binder (15%) were mixed and rolled into a 0.6 cm × 0.8 cm thin film. The thin film was then pressed on carbon paper and used as the Super P anode electrode.

LAGP membrane fabrication

The definite stoichiometric ratio of chemical precursors (Li_2CO_3 , Al_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, GeO_2) were mixed and ball milled. The mixture were kept at 600 °C with the heating rate of 2 °C·min⁻¹ for 1 hour. After cooling down, the products were ball milled, followed by a solid-state reaction through sintering heat treatments under the temperature of 900 °C with the heating rate of 2 °C·min⁻¹ for 6 hours. The products were ball milled and compressed into film followed by sintering heat treatments under the temperature of 900 °C to obtain LAGP membrane.

Lithium extraction device assembly

The photographic image of the lithium extraction device is shown in Fig. S6a. It is composed with an anode electrode, a cathode compartment, a seawater container and the solar power constant current source (Fig. S2b). The anode electrode was immersed in the seawater. In the cathode compartment, the LAGP membrane was

sticked on one side of a glass tube. 0.5 M LiClO₄ in propylene carbonate (PC) was used as the electrolyte in the cathode compartment. A piece of copper foil was partially immersed in the electrolyte as the cathode. The head space of the compartment was filled with Ar, and a silica gel stopper was used to seal the glass tube. Simulated seawater with a LiCl concentration of 1.038 mg·L⁻¹ and a NaCl concentration of 26.845 g·L⁻¹ was used as the electrolyte in the anode side of the device. The solar power constant current source was connected to the anode and cathode to supply constant current.

Electrochemical testing and material characterization

The electrochemical testing was performed on electrochemical workstation CHI 760E (Chenhua Shanghai). XRD characterisation was performed on a D8 Advance X-ray diffractometer (Bruker). SEM images were obtained with a Hitachi SU8010 scanning electron microscope. In situ GC-MS analysis of the seawater electrolysis process was conducted with a homemade device connected to the equipment (Clarus 680 and SQ 8S). The mass of the lithium deposits was measured through an ICP-MS test on an ELAN 9000 inductively coupled plasma source mass spectrometer.

Measurement of the lithium deposition

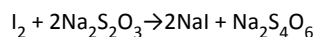
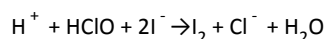
The copper foil in the cathode compartment was transferred to an Ar-filled glove box after electrolysis and rinsed with glycol dimethyl ether to dissolve the soluble lithium salt. The copper foil was heated at 60 °C for 12 hours in the glove box after the rinsing procedure. Then, the copper foil was immersed in a certain amount of a 0.1 M HCl solution. The grey deposit rapidly disappeared, and bubbles were generated. The resulted solution was examined by ICP-MS to evaluate the Li⁺ concentration. The mass of the lithium deposits on the copper foil could be calculated by multiplying the Li⁺ concentration by the volume of the HCl solution. The energy consumption could be calculated by integration of the potential through the following formula.

$$\text{Energy consumption} = I \cdot \int_0^t V(t) \cdot dt$$

Where I is the current applied to the cell, V is the potential during electrolysis and t is the electrolysis time.

Iodine titration

After electrolysis, the electrolyte (5 mL) was transferred to a beaker. Then, 1 mL of 0.5 M acetic acid and 1 mL of a 2% KI solution were added to the beaker. The colour of the electrolyte became yellow due to the formation of I₂. A 5 mM Na₂S₂O₃ solution was added dropwise using a burette. When the colour of the solution faded to pale yellow, 0.5 mL of a 1% starch solution was added, turning the mixture blue. Then, the titration of Na₂S₂O₃ was continued until the colour disappeared. The quantity of oxidised chloride species and the charge transfer ratio of CER could be calculated according to the following reactions and formula:



$$\text{CTR}_{\text{CER}} = \frac{C_{\text{Na}_2\text{S}_2\text{O}_3} \cdot V_{\text{Na}_2\text{S}_2\text{O}_3} \cdot F}{I \cdot t}$$

Where $C_{\text{Na}_2\text{S}_2\text{O}_3}$ is the concentration of the Na₂S₂O₃ solution, $V_{\text{Na}_2\text{S}_2\text{O}_3}$ is the volume of the Na₂S₂O₃ solution, F is Faraday constant, I is the current applied to the cell and t is the electrolysis time.

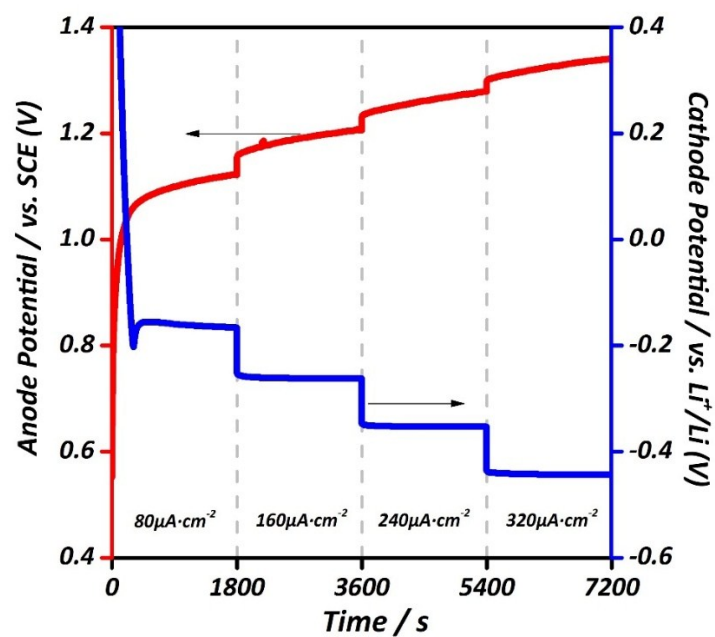


Fig. S1. Characterization of the absolute potential of the cathode and anode during lithium extraction. Potential of the anode versus SCE and the cathode versus Li^+/Li during electrolyzing under the current density of 80, 160, 240 and $320 \mu\text{A}\cdot\text{cm}^{-2}$ using the lithium extraction electrolyze cell.

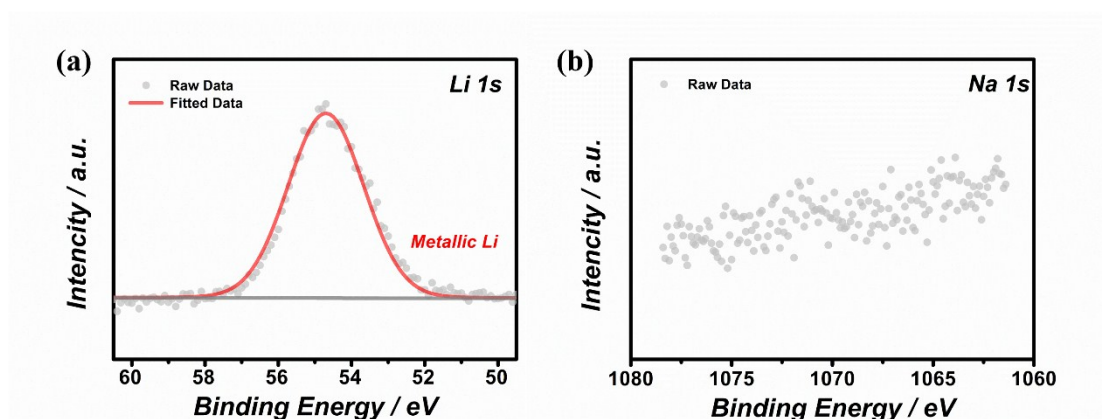


Fig. S2. XPS characterization of the extracted lithium metal on copper foil. (a) Li 1s orbital and (b) Na 1s orbital after Ar-ion etching.

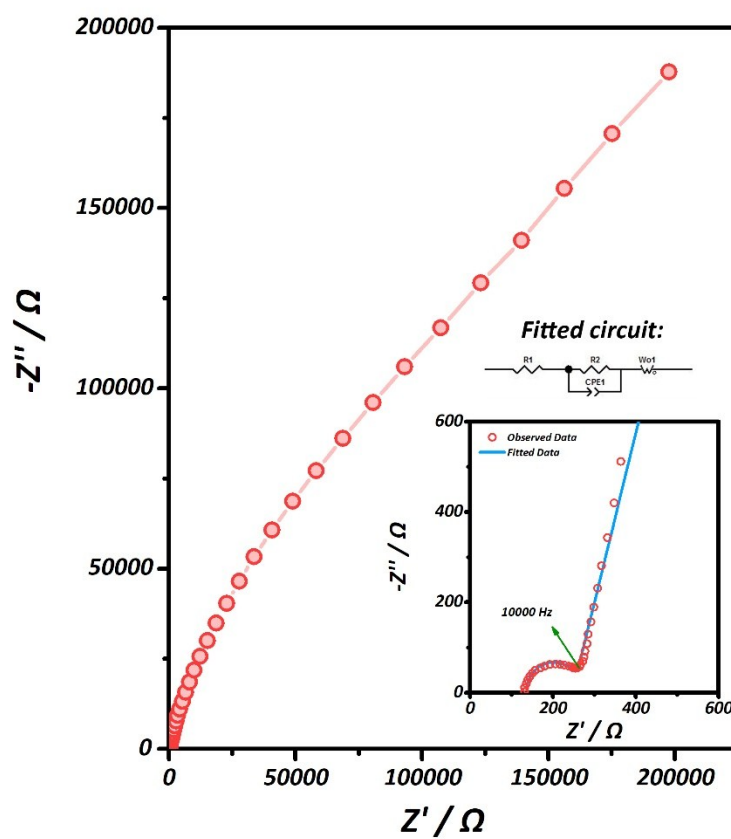


Fig. S3. Electrochemical performance of the LAGP solid-state electrolyte. Electrochemical impedance spectroscopy (EIS) of the LAGP solid-state electrolyte. The inset figure shows the experimental (red circle) and fitting (blue line) data and the equivalent circuit.

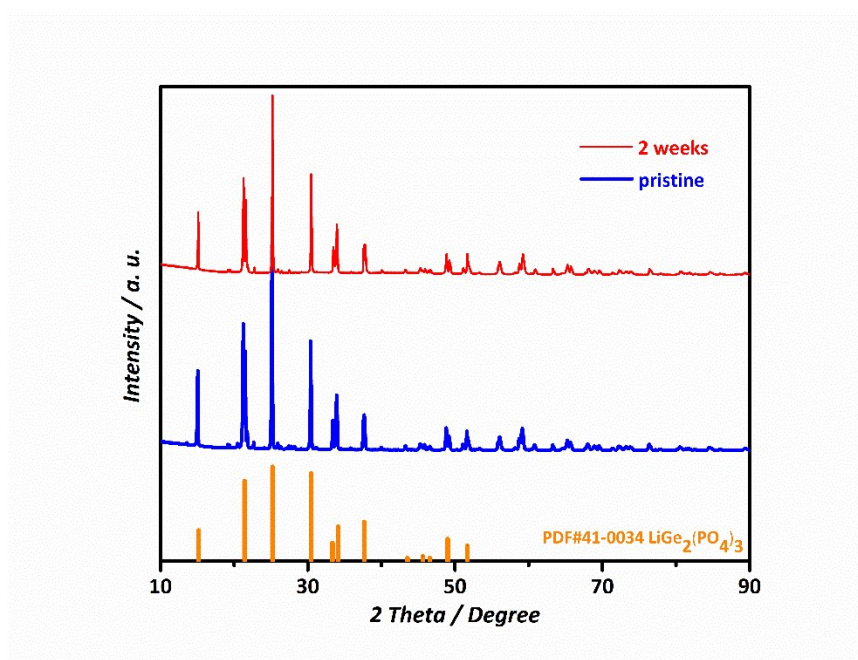


Fig. S4. XRD characterization of the pristine LAGP solid-state electrolyte and the immersed LAGP solid-state electrolyte.