# **Electronic Supplementary Information**

# Enhanced Lithium Extraction from Brine Using Surface-Modified LiMn<sub>2</sub>O<sub>4</sub> Electrode with Nanoparticle Islands

### Experimental

Synthesis

The SnO<sub>2</sub> modified LMO material was prepared by the sol-gel method. First, 0.0233 g of SnCl<sub>4</sub>·5H<sub>2</sub>O was weighed and dissolved in 5 mL of deionized water. Next, 1.0 g of LMO was added to this solution and stirred mechanically for 2 h. Then, ammonia solution was slowly added dropwise during stirring (as a gelling agent) until a gel state formed. This gel was then vacuum dried at 80°C for 12 h, followed by calcination at 600°C for 2 h in an air atmosphere, resulting in LMO modified with 1.0 wt% SnO<sub>2</sub>. By adjusting the amount of SnCl<sub>4</sub>·5H<sub>2</sub>O added, SnO<sub>2</sub>-LMO with modified amounts of 0.5 wt%, 1.0 wt%, and 2.0 wt% were obtained, labeled as SnLMO-1, SnLMO-2, and SnLMO-3, respectively.

The preparation method of the SnLMO electrode is referred to in reference <sup>1</sup>. Firstly, graphite sheets were polished with 3000-grit and 5000-grit sandpaper to a smooth surface, followed by ultrasonic cleaning with water, and then dried in an 80°C oven for 8 h. Then, SnLMO-2, PVDF, Super P carbon, and NMP were mixed according to a mass ratio of 8:1:1:10 and stirred thoroughly to obtain electrode slurry. Finally, the slurry containing 10 mg of active material was drop-coated onto graphite sheets (10 ×  $20 \times 2$  mm) and dried in an 80°C oven for 12 h. In a three-electrode system, the delithiation electrodes of LMO and SnLMO were prepared using a current-time curve method with a run potential of 1.0 V and an electrolyte of LiCl for 3 h, resulting in the electrode surface changing from black to brown-black after lithium removal.

#### *Characterization*

The crystal structure was employed for X-ray diffraction (XRD, Shimadzu XRD-6100 Lab, Japan) with Cu Kα radiation 20 range of 10°~80° at the 7°/min, and quasiin suit characterization was performed with 3°/min. Raman spectra (DXR, Thermo Fisher, U.S.) with a laser length of 532 nm and X-ray photoelectron spectroscopy (XPS, K-Alpha Thermo, U.S.) were utilized to investigate the elemental composition. Scanning electron microscope (SEM, Thermo Fisher Apreo S HiVac, U.S.) and transmission electron microscope (TEM, FEI Tecnai G2 F20, U.S.) were utilized to study morphology. The N<sub>2</sub> adsorption–desorption isotherms and specific surface area of samples were measured by ratio surface and porosity analyzer (Micromeritics ASAP 2460, U.S.). An inductively coupled plasma-atomic emission spectrometry (ICP-AES, Vista-MPX, America) was employed for the concentration of cation ions. The electrochemical tests were employed in a Chenhua electrochemical workstation (CHI 760E, China).

## Electrochemical method

The three-electrode system consists of a working electrode, a reference electrode (vs. SCE), and a counter electrode (Pt sheet). The cyclic voltammetry method was used to investigate the selectivity and the diffusion rate of Li<sup>+</sup>. The cycling stability of the electrode material was examined using constant current charge-discharge curves in

LiCl solution.

Electrochemical impedance spectroscopy (EIS) was performed to investigate the electrochemical characteristics of the samples. The measurements were conducted using a frequency range of 0.1 Hz to 100 kHz with a sinusoidal voltage perturbation of 10 mV applied to the electrochemical cell (contained 1.0 mol L<sup>-1</sup> LiCl solution). The cell was composed of a working electrode (LMO and SnLMO), a reference electrode (SCE), and a counter electrode (platinum). Data acquisition was carried out using a electrochemical workstation (Gamry Interface 1010E), and the resulting impedance spectra were analyzed using an equivalent circuit model to extract parameters such as charge transfer resistance and double-layer capacitance.

Using SnLMO as the working electrode and Ag as the counter electrode, a 60 min discharge reaction (Li<sup>+</sup> insertion) was performed in simulated brine. Subsequently, the electrode was removed, rinsed with water, dried with filter paper, and then subjected to a 60 min charging reaction (Li<sup>+</sup> extraction) in 30 mL of 10 mmol L<sup>-1</sup> LiCl solution. Before and after the capture and release reactions, samples were taken with a syringe, diluted to volume, and tested for cation concentration. To determine the metal ion concentration, a certain volume of sample was taken according to the metal ion concentration, diluted, and then tested by ICP-AES.

# Data processing

The lithium ion purity  $({}^{P_{Li}})$  was calculated using the following formula (1):

$$P_{Li}(\%) = \frac{C_{Li}}{\Sigma C_i} \times 100\%$$
<sup>(1)</sup>

The lithium adsorption capacity (Q) was determined by the equation (2):

$$Q = \frac{C_0 V_0 - C_s V_s}{m} \tag{2}$$

The manganese dissolution loss  $(R_{Mn})$  was assessed as:

$$R_{Mn} = \frac{c \times V}{m \times w \times 10^3} \times 100\%$$
(3)

where  $C_{Li}$  and  $C_i$  are the concentration of Li<sup>+</sup> and other cation ions (mg L<sup>-1</sup>) in the final simulated brine, respectively;  $C_0$  and  $C_s$  are the concentration of Li<sup>+</sup> (mg L<sup>-1</sup>) in the initial and final simulated brine respectively;  $V_0$ , V and  $V_s$  are the volume (L) of the corresponding electrolyte; m (mg) is the weight of active materials on the electrode; cis the concentration (mg L<sup>-1</sup>) of Mn<sup>2+</sup> in the electrolyte; W is the mass fraction of the element an electroactive material.

Figures



Fig. S1 Particle size distribution of LMO in SEM images



Fig. S2 Mapping images and energy spectra of SnLMO-1.



Fig. S3 SEM (a, b), mapping images (c-f) and energy spectra (g) of SnLMO-2.



Fig. S4 SEM (a, b), mapping images (c-f) and energy spectra (g) of SnLMO-3



Fig. S5 TEM (a, b) and HRTEM (c) images of SnLMO-1



Fig. S6 Cyclic voltammograms curve of SnLMO-1 electrode in different solutions.



Fig. S7 Discharge curves of SnLMO-1 electrode in different solutions



Fig. S8 Cyclic voltammograms curve of LMO, SnLMO-2 and SnLMO-3 in different scan rate (a-c); Linear relationship between  $v^{1/2}$  and corresponding with redox peak

current (d-f)



Fig. S9 Experimental Nyquist plot of the LMO and SnLMO electrode.



Fig. S10 The N<sub>2</sub> adsorption-desorption isotherms of the LMO and SnLMO powder.

Materials	Equation	R <sup>2</sup>
LMO	$I_{pal}=0.32v^{1/2}-0.0019$	0.9560
	$I_{pa2}=0.37v^{1/2}-0.0018$	0.9966
	$I_{pcl}$ =-0.24 $v^{1/2}$ +0.0009	0.9291
	$I_{pc2}$ =-0.31 $v^{1/2}$ +0.0017	0.9998
SnLMO-1	$I_{pal}=0.43v^{1/2}-0.0022$	0.9992
	$I_{pa2}=0.53v^{1/2}-0.0024$	0.9986
	$I_{pcl}$ =-0.41 $v^{1/2}$ +0.0017	0.9993
	$I_{pc2}$ =-0.51 $v^{1/2}$ +0.0038	0.9917
SnLMO-2	$I_{pal}=0.35v^{1/2}-0.0016$	0.9992
	$I_{pa2}=0.47v^{1/2}-0.0023$	0.9943
	$I_{pcl}$ =-0.35 $v^{1/2}$ +0.0014	0.9999
	$I_{pc2}$ =-0.48 $v^{1/2}$ +0.0034	0.9863
SnLMO-3	$I_{pal}=0.31v^{1/2}-0.0015$	0.9976
	$I_{pa2}=0.41v^{1/2}-0.0019$	0.9934
	$I_{pcl}$ =-0.29 $v^{1/2}$ +0.0010	0.9961
	$I_{pc2}$ =-0.40 $v^{1/2}$ +0.0029	0.9891

Table S1 Equation for solving diffusion coefficient and correlation coefficient.

 G. Luo, L. Zhu, X. Li, G. Zhou, J. Sun, L. Chen, Y. Chao, L. Jiang and W. Zhu, Electrochemical lithium ions pump for lithium recovery from brine by using a surface stability Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> coated LiMn<sub>2</sub>O<sub>4</sub> electrode, *J. Energy Chem.*, 2022, 69, 244-252.