Electronic Supplementary Information:

A Solid-State Electrolyte Based on Electrochemical Active $LiMn_2O_4$ for Lithium Metal Batteries

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Materials

All of the chemicals mentioned in the synthesis steps were used directly without further treatment. $LiMn_2O_4$ (LMO) was purchased from Tmall. Ltd. Electrolyte (LB-315) was purchased from Zhangjiagang Guotai Huarong New Chemical Materials Co., Ltd. The anodes (lithium foils) were purchased from Guangdong Canrd New Energy Technology Co., Ltd. Poly(vinylidene difluoride) (PVDF), *N*-methyl pyrrolidone (NMP), dimethylacetamide (DMAc) and acetylene black were purchased from Sinopharm Group Co., Ltd.

Calculation

The ionic conductivity (σ) and activation energy (E_a) at different temperatures can be calculated from the following equation:

$$\sigma = \frac{L}{RS} = Aexp\frac{-E_a}{K_B T} \tag{S1}$$

where L is the electrolyte thickness, R is the bulk resistance, S is the contact area of the SSE and electrode, K_B is the Boltzmann constant, A is the pre-exponential factor, and T is the temperature.

The lithium ion transfer number (t_{Li+}) was obtained through calculation from the following equation:

$$t_{Li+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad \text{(S2)}$$

where I_0 and I_s are the initial current and steady-state current in the current curve respectively, ΔV is the transition potential (10 mV), R_0 and R_s are the AC impedance of the cell before and after polarization, respectively.

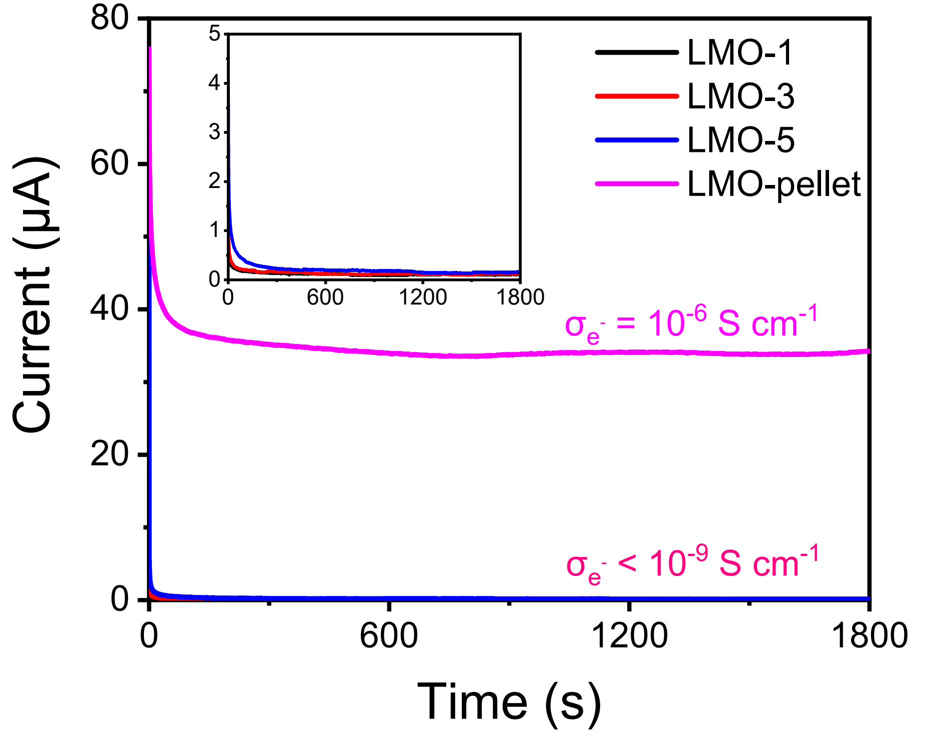

Figure S1. Chronoamperometry curve of electronic conductivity of LMO-X SSEs under 0.5 V.

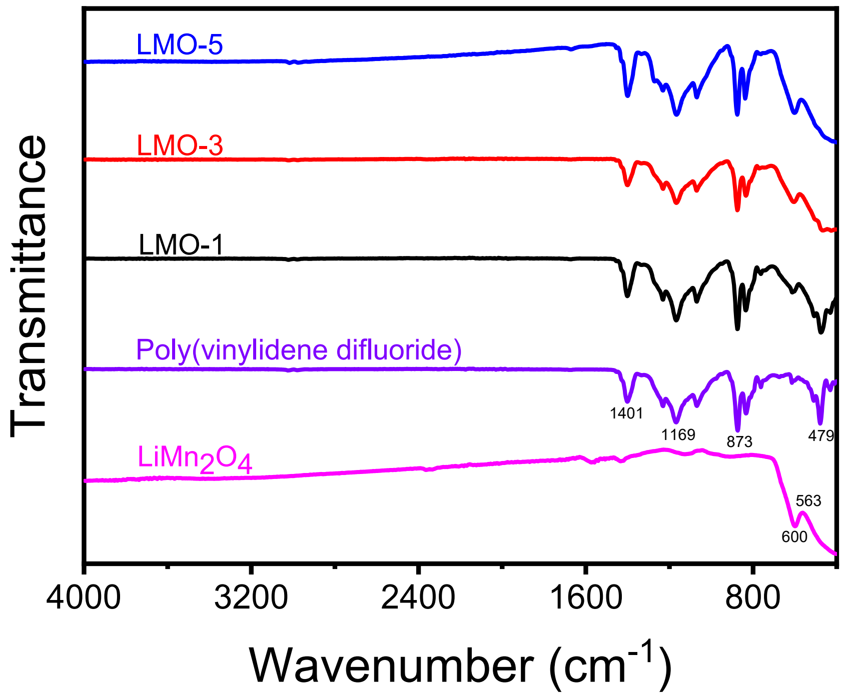

Figure S2. ATR-FTIR spectra comparison of LMO-X SSEs.

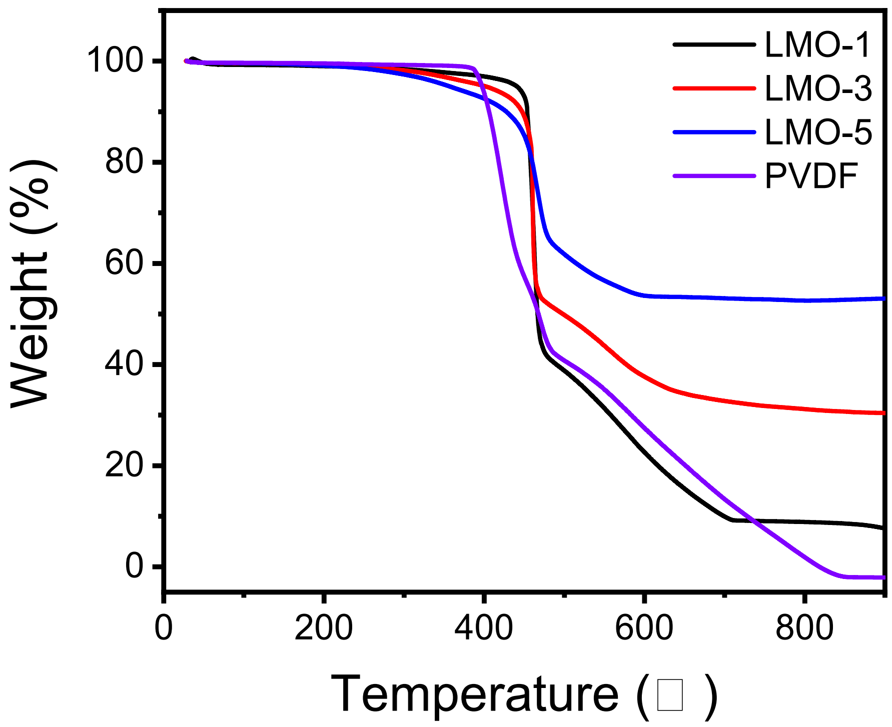

Figure S3. TGA image of LMO-X SSEs.

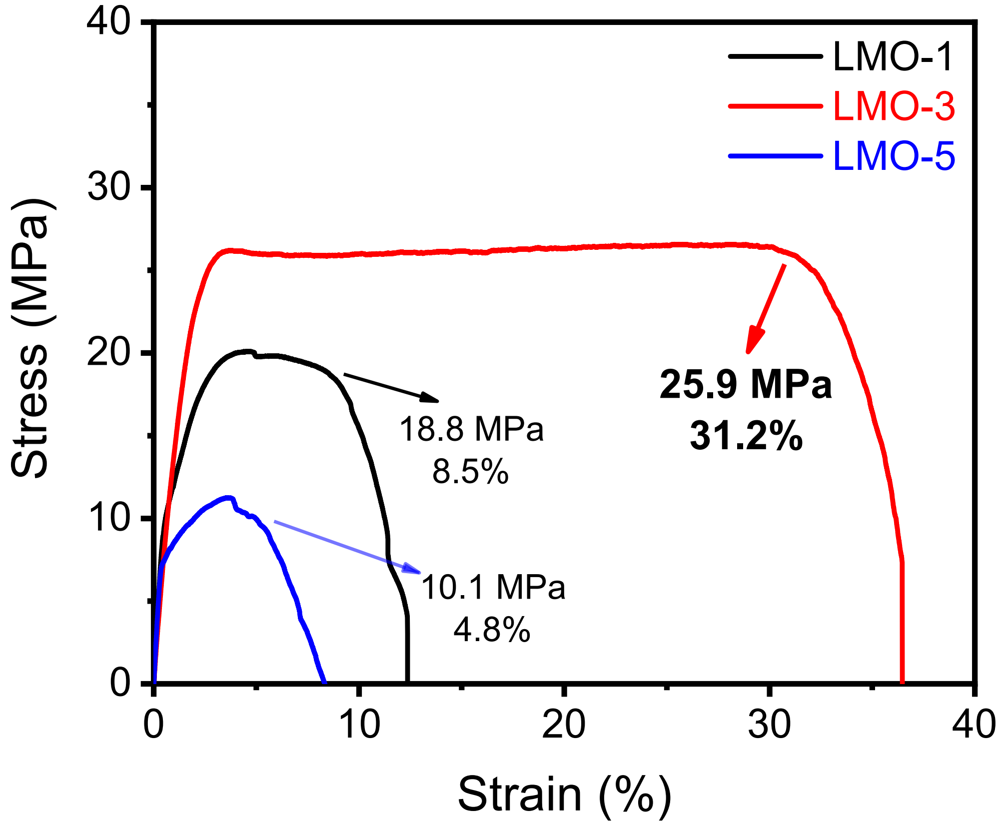

Figure S4. The stress–strain curves of LMO-X SSEs.

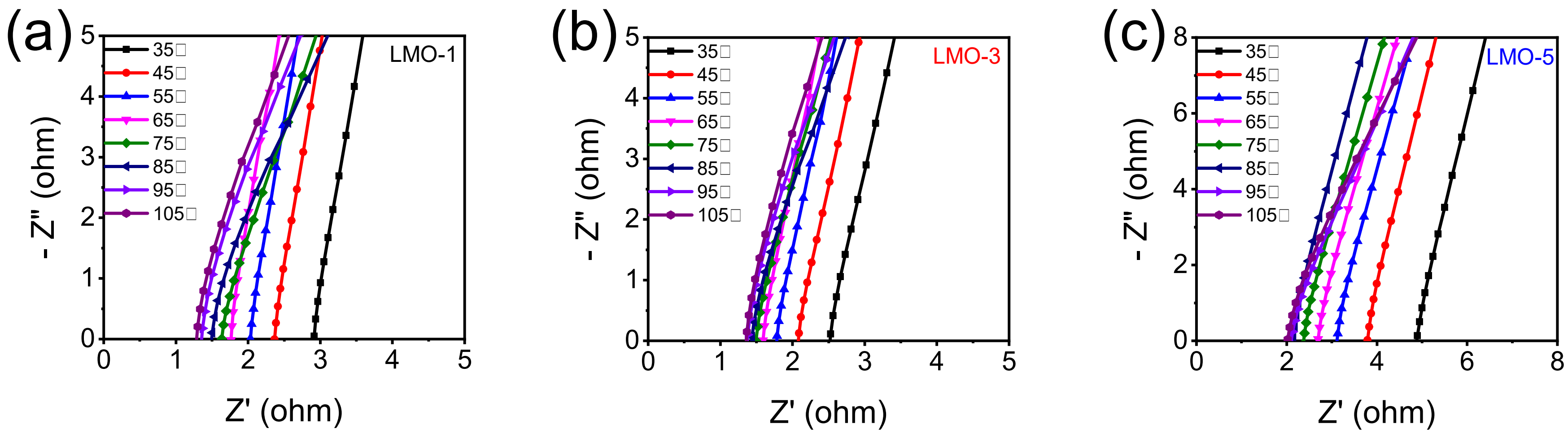

Figure S5. EIS test of LMO-1 (a), LMO-3 (b), LMO-5 (c) in SS||SS cells under different temperatures.

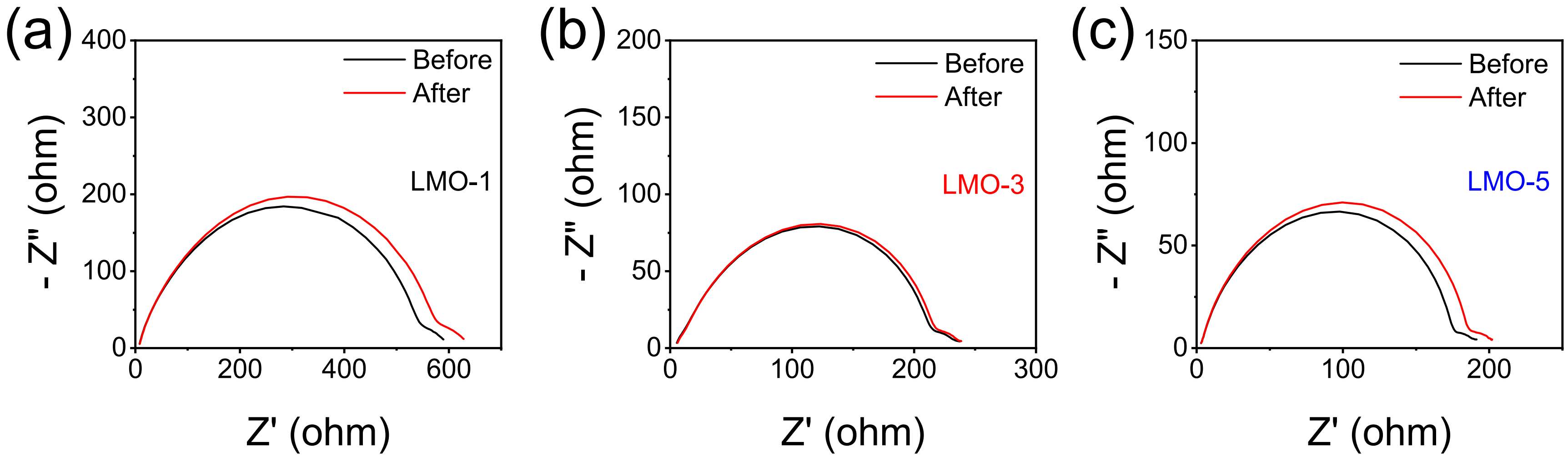

Figure S6. Impedance plots before and after Li^+ transfer number test.

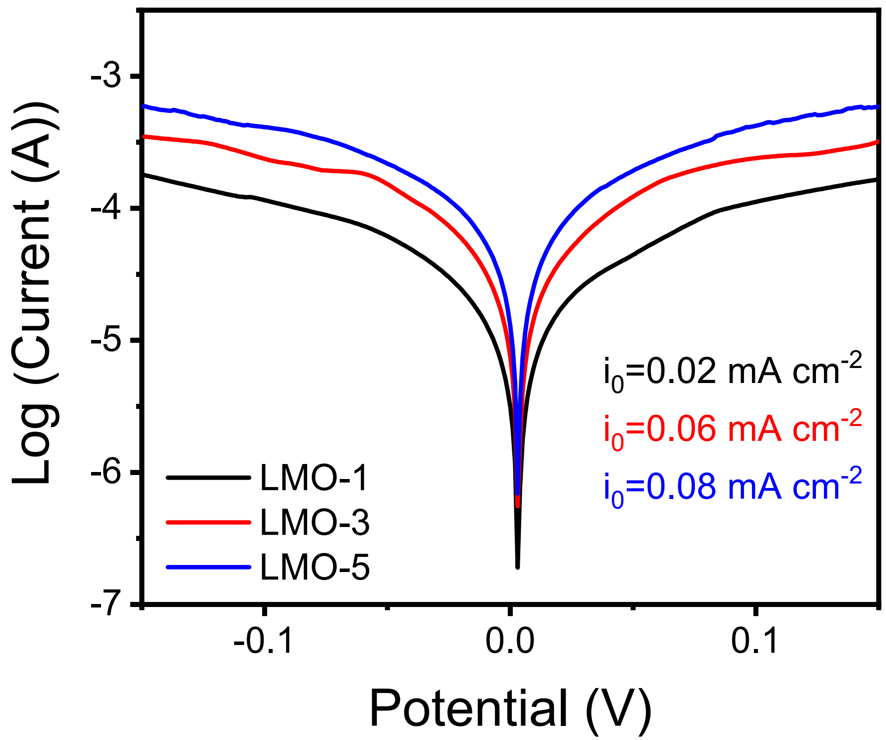

Figure S7. Tafel plots of symmetric cell Li|LMO-X|Li.

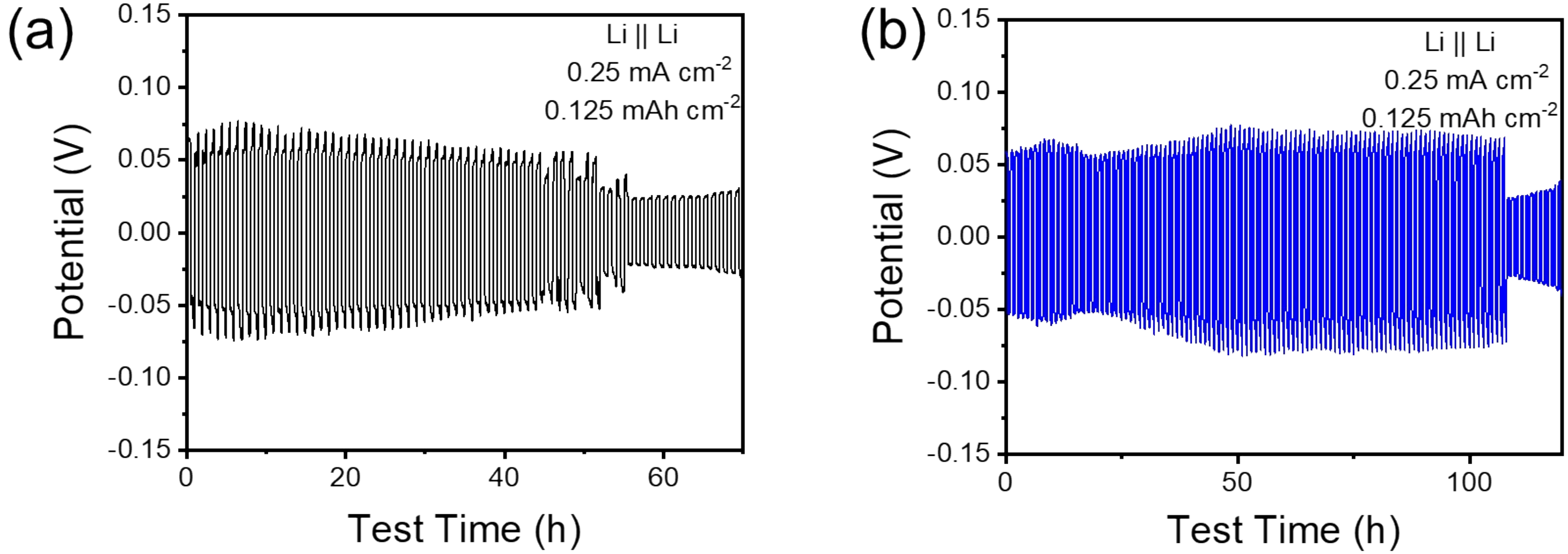

Figure S8. Galvanostatic cycling of lithium symmetric cells applying LMO-1 (a) and LMO-5 (b) in under 0.25 mA cm^{-2} to reach 0.125 mAh cm^{-2}.

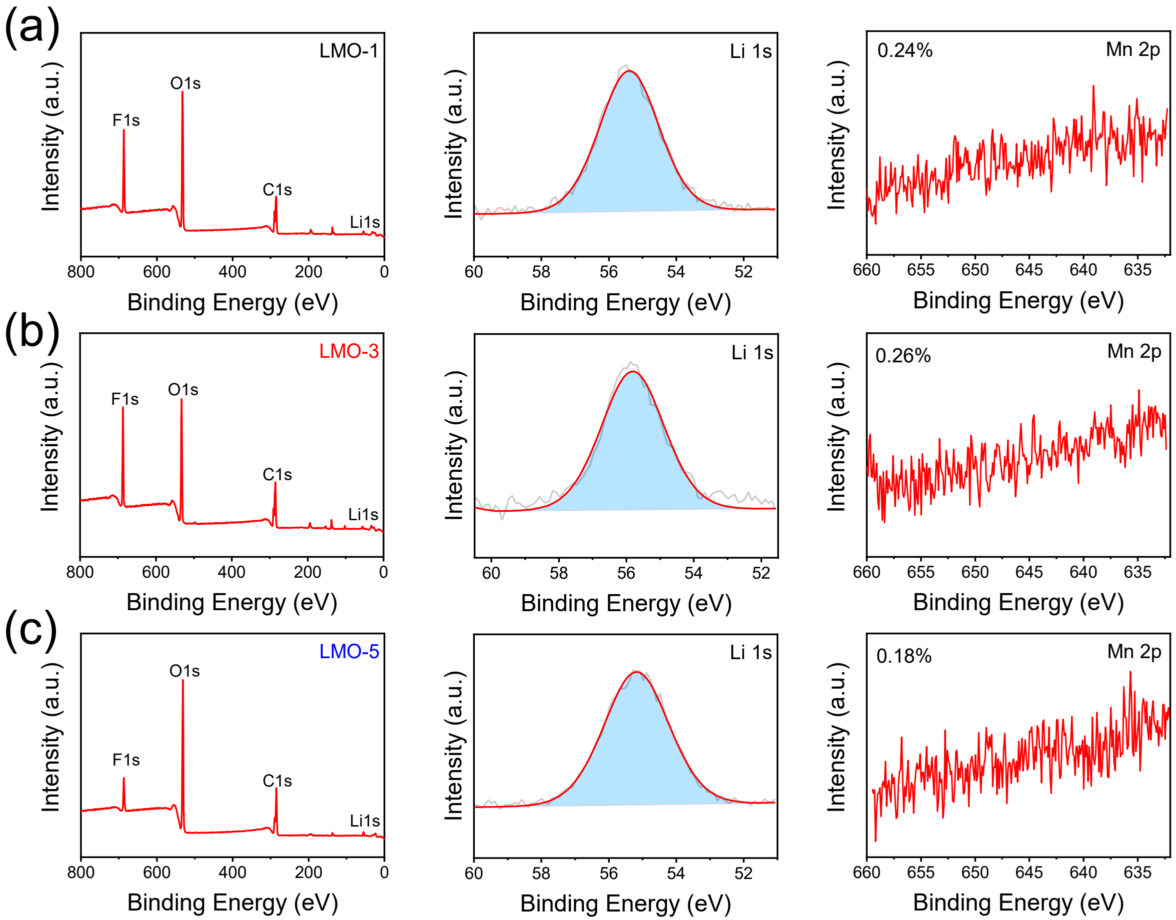

Figure S9. XPS profiles of Li||Li symmetric cells after cycling under 0.25 mA cm^{-2} and 0.125 mAh cm^{-2} with varying SSEs. (a) LMO-1, (b) LMO-3, and (c) LMO-5.

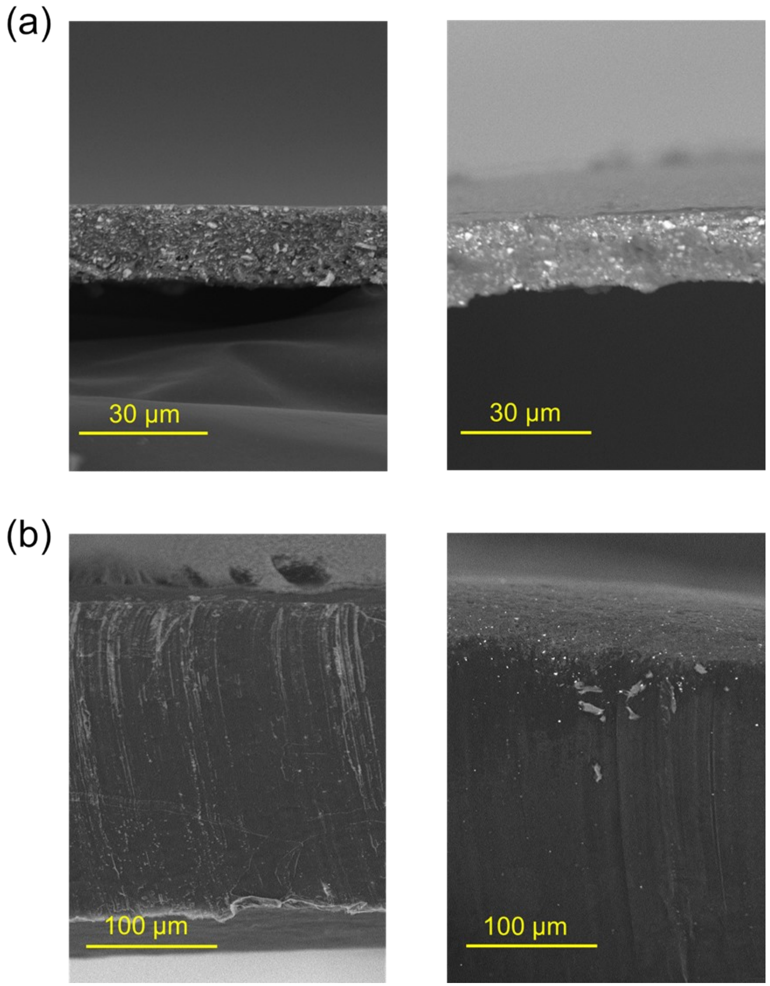

Figure S10. Cross-section SEM images of Li|LMO-3|Li symmetric cell before and after cycling under 0.25 mA cm^{-2} and 0.125 mAh cm^{-2}. (a) LMO-3 and (b) Li anode metal.

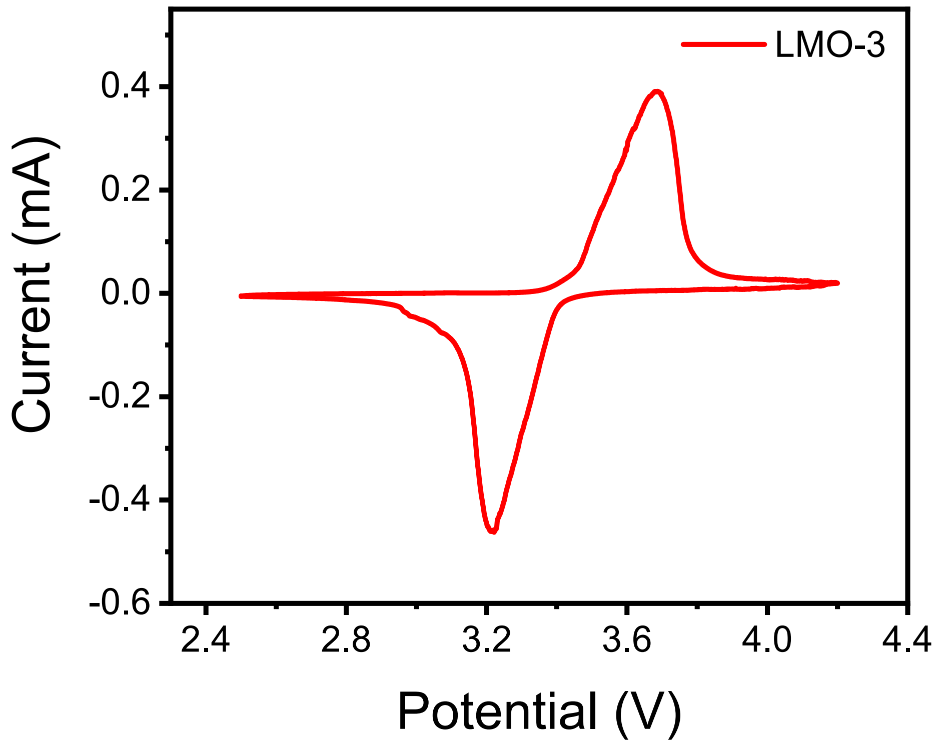

Figure S11. Cyclic voltammetry curve of the Li|LMO-3|LFP cell.

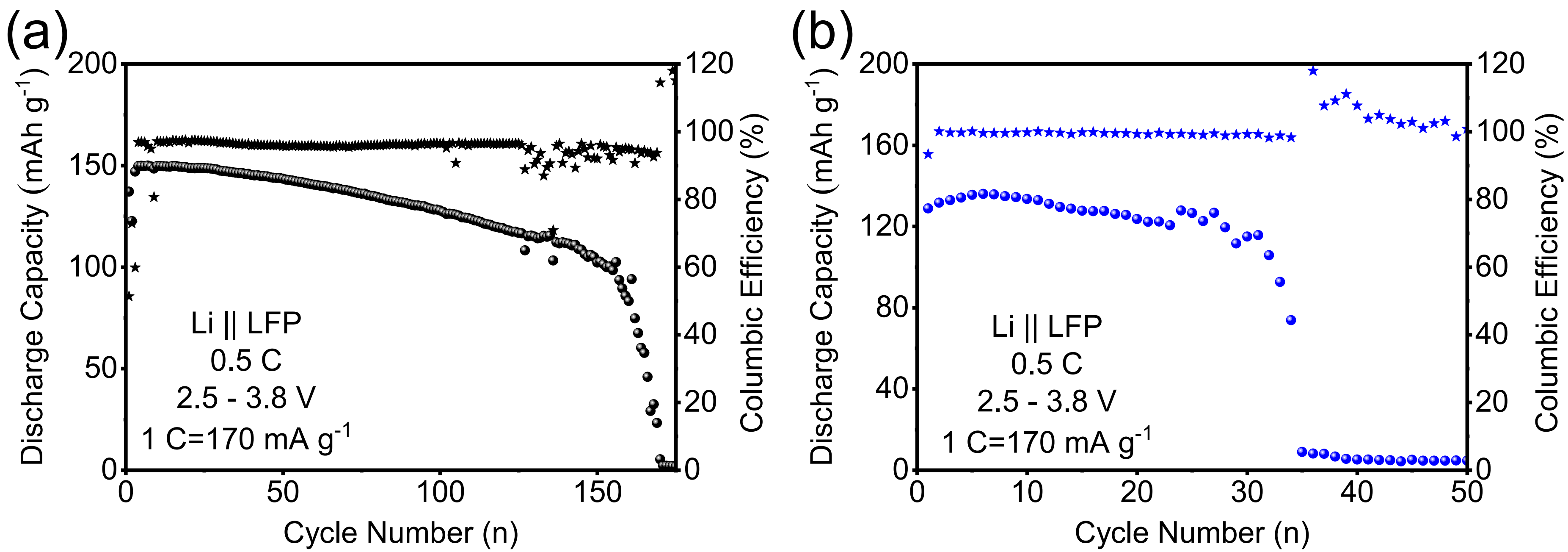

Figure S12. Cycling performance of Li||LFP cells with LMO-1 (a) and LMO-5 (b) at 0.5 C.

Table S1. The vibration modes corresponding to each infrared absorption peak.

Absorption peak (cm^{-1})	**Stretching vibration modes**
1401	CH_2 wagging vibration
1169	CF_2 asymmetric stretching vibration
873	C-C skeletal vibration
600, 563	MnO_6 asymmetric stretching vibration
479	CF_2 bending vibration

Table S2 Comparison of ionic conductivities and cycling performance for SSEs.

Solid State electrolyte	**Thickness (μm)**	**Conductivity (S cm^{-1})**	**Cathode material**	**Cycling performance**	**Ref.**
PVDF/30 wt.% LMO	~20	5.17×10^{-4} at 35 ℃	LFP	147.7 mAh g^{-1} after 200 cycles under 0.5C at 35 ℃	This work
PEO/VAVS/LiTFSI		1.89×10^{-4} at 25 ℃	LFP	110.7 mAh g^{-1} after 200 cycles under 0.5C at 35 ℃	[1]
PE/SN/PEGDA/1% wt.%$LiNO_3$/LiTFSI	~16	1.08×10^{-4} at room temperature	LCO	110.6 mAh g^{-1} after 385 cycles under 0.2C at room temperature	[2]
PEO/ZiF-67/LITFSI		1.0×10^{-4} at 25 ℃	LFP	124.0 mAh g^{-1} after 200 cycles under 0.2C at 60 ℃	[3]
PEO/10 wt.% LLZO/LITFSI	~40	2.39×10^{-4} at 25 ℃	LFP	107.0 mAh g^{-1} after 200 cycles under 0.1C at 60 ℃	[4]
PEO/LiTFSI/wheat flour electrolyte	~300	2.62×10^{-5} at 25 ℃	NCM811	62.9 mAh g^{-1} after 60 cycles under 0.1C at 25 ℃	[5]
PEO/10% SiO_2/$LiClO_4$	~200	4.4×10^{-5} at 30 ℃	LFP	100.0 mAh g^{-1} after 80 cycles under 0.1C at 60 ℃	[6]
P(PO/EM)/LITFPFB		1.55×10^{-4} at 70 ℃	$LiFe_{0.2}Mn_{0.8}PO_4$	125.6 mAh g^{-1} after 100 cycles under 0.1C at 70 ℃	[7]
QSCE-PH/GPFIL3/P	~21	3.24×10^{-4} at room temperature	LFP	117.0 mAh g^{-1} after 350 cycles under 0.5C at 30 ℃	[8]
PEO/10 wt.% LLZTO/LITFSI	~70	1.17×10^{-4} at 30 ℃	LFP	127.0 mAh g^{-1} after 200 cycles under 0.2C at 55 ℃	[9]

1. W. Tang, S. Tang, X. Guan, X. Zhang, Q. Xiang and J. Luo, *Adv. Funct. Mater.*, 2019, **29**, 1900648.
2. B. Yuan, B. Zhao, Q. Wang, Y. Bai, Z. Cheng, Z. Cong, Y. Lu, F. Ji, F. Shen, P.-F. Wang and X. Han, *Energy Storage Mater.*, 2022, **47**, 288-296.
3. Y. Zou, Z. Ao, Z. Zhang, N. Chen, H. Zou, Y. Lv and Y. Huang, *Chem. Eng. Sci.*, 2023, **275**, 118705.
4. J. Zhang, N. Zhao, M. Zhang, Y. Li, P. K. Chu, X. Guo, Z. Di, X. Wang and H. Li, *Nano Energy*, 2016, **28**, 447-454.
5. Y. Lin, Y. Cheng, J. Li, J. D. Miller, J. Liu and X. Wang, *RSC Adv.*, 2017, **7**, 24856-24863.
6. D. Lin, W. Liu, Y. Liu, H. R. Lee, P. C. Hsu, K. Liu and Y. Cui, *Nano Lett*, 2016, **16**, 459-465.
7. Q. Wang, Z. Cui, Q. Zhou, X. Shangguan, X. Du, S. Dong, L. Qiao, S. Huang, X. Liu, K. Tang, X. Zhou and G. Cui, *Energy Storage Mater.*, 2020, **25**, 756-763.
8. Y. Cui, G. Yu, R. Liu, D. Miao and D. Wu, *Chin. J. Chem.*, 2023, **41**, 2848-2854.
9. L. Chen, Y. Li, S.-P. Li, L.-Z. Fan, C.-W. Nan and J. B. Goodenough, *Nano Energy*, 2018, **46**, 176-184.