Supporting Information

Composite solid polymer electrolyte incorporating MnO_2 nanosheets with reinforced mechanical properties and electrochemical stability for lithium metal battery

Yuhan Li,[a] Zongjie Sun,[a] Dongyu Liu,[b] Yiyang Gao,[a] Yuankun Wang,[a] Huaitian Bu,[c] Mingtao Li,[b] Yanfeng Zhang,[a] Guoxin Gao,[a] and Shujiang Ding[a]**

[a]Department of Applied Chemistry, School of Science, Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China.
*Email: gaoguoxin@mail.xjtu.edu.cn; dingsj@mail.xjtu.edu.cn

[b]International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Shaanxi 710049, China.

[c]Department of Materials and Nanotechnology, SINTEF Industry, Forskningsveien 1, 0373 Oslo, Norway.

Keywords: MnO_2 nanosheets; Polyethylene oxide; Composite polymer electrolyte; Solid Li metal battery; DFT calculations.

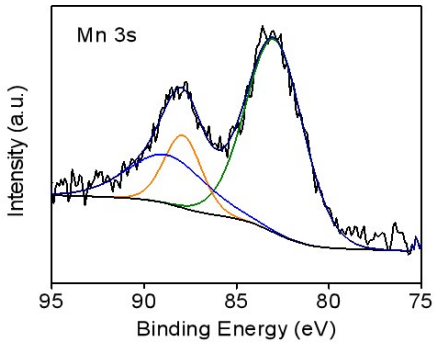

Figure S1. XPS spectra of MnO_2 nanosheets: MnO_2 3s spectrum.

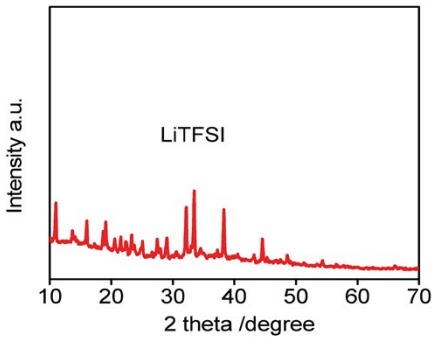

Figure S2. XRD of LiTFSI. The peaks at 11.04°, 16.03°, 19.09°, 20.55°, 21.54°, 23.32°, 25.07°, 27.4°, 29.03°, 32.20°, 33.48°, 38.30° and 44.54° perfectly match to (002), (011), (201), (111), (202), (013), (113), (212), (114), (015), (115), (116) and (125) crystal planes.

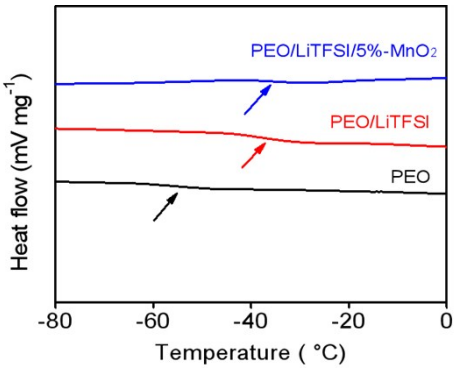

Figure S3. DSC spectrum of LiTFSI for detailed region.

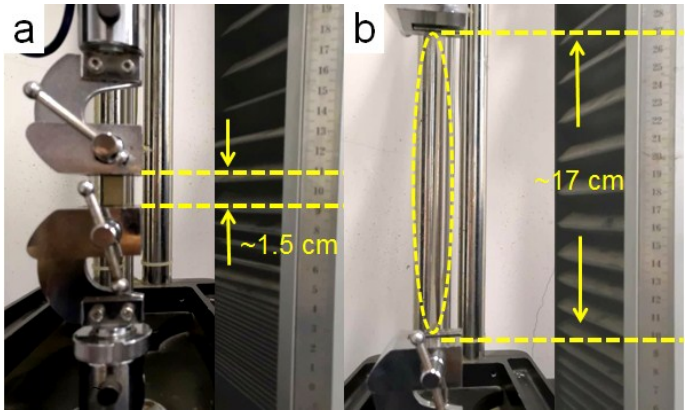

Figure S4. The digital photos of CPE containing 5 wt % MnO_2 nanosheets at the initial and final tension states.

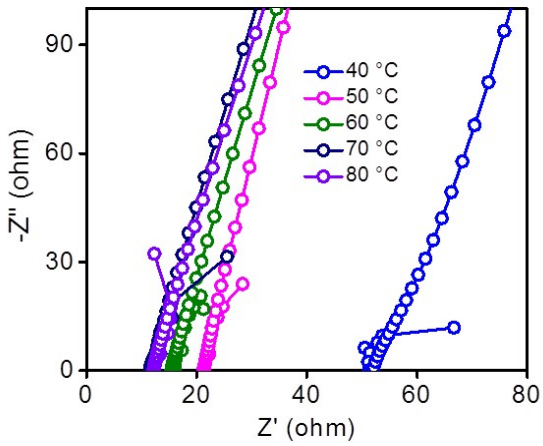

Figure S5. EIS plots of PEO/LiTFSI/MnO_2 CSPE composite electrolyte at different temperatures.

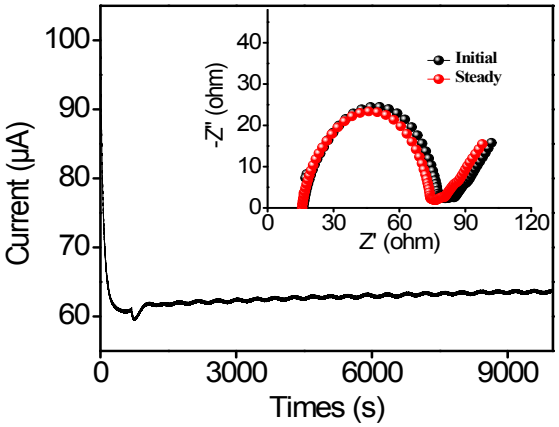

Figure S6. (a) i-t curve for PEO/LiTFSI SPE at 60 °C with polarization voltage of 10 mV. (b) The A. C impedance plots before and after the polarization.

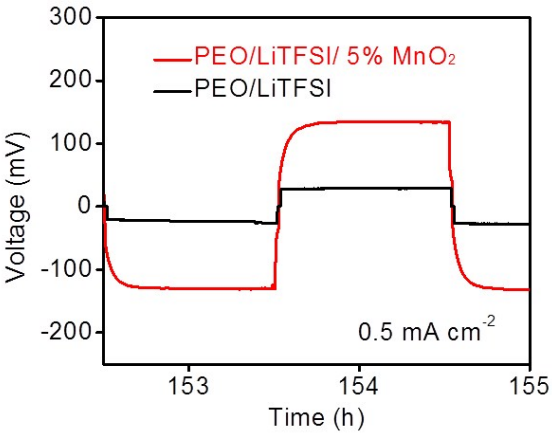

Figure S7. The magnified region of voltage profiles for selected cycles at 0.5 mA cm^{-2}.

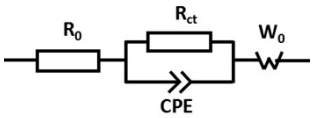

Figure S8. The equivalent circuit of Li/PEO/LiTFSI SPE/$LiFePO_4$ and Li/PEO/LiTFSI/MnO_2 CSPE/$LiFePO_4$ cell at 60 °C.

Table S1. Mechanical data of PEO/LiTFSI SPE with different contents of MnO_2 nanosheets at room temperature.

	PEO/LiTFSI	PEO/LiTFSI/ 1% MnO_2	PEO/LiTFSI/ 3% MnO_2	PEO/LiTFSI/ 5% MnO_2	PEO/LiTFSI/ 7% MnO_2
tensile strength	0.56 MPa	0.88 MPa	1.14 MPa	1.27 MPa	0.77 MPa
elongation-at-break value	858 %	1804 %	861 %	1045 %	911 %

Table S2. The ionic conductivity of PEO/LiTFSI SPE with different contents of MnO_2 nanosheets at different temperature.

$\sigma \times 10^{-4}$ S cm^{-1}	PEO/LiTFSI	PEO/LiTFSI/1% MnO_2	PEO/LiTFSI/3% MnO_2	PEO/LiTFSI/5% MnO_2	PEO/LiTFSI/7% MnO_2
25 °C	0.055	0.084	0.083	0.08	0.177
30 °C	0.138	0.227	0.240	0.195	0.320
40 °C	0.430	0.72	0.588	0.623	0.920
50 °C	1.04	1.75	1.28	1.52	1.60
60 °C	1.37	2.06	1.47	2.10	1.82
70 °C	1.51	2.89	1.72	2.78	2.63
80 °C	1.49	2.71	1.78	2.66	2.90

Table S3. The ionic conductivity of PEO/LiTFSI SPE with different contents of MnO_2 nanosheets at different temperature.

	PEO	LiTFSI	PEO/LiTFSI	PEO/LiTFSI/MnO2
-CH_2- wagging absorptions in trans planar structure	1346		1354	1352
-CH_2- twist in helical structure	1279		1281	1281
-CH_2- twist in trans planar structure	1236		1240	1234
Asymmetric -SO_2- stretching		1325	1327	1336
Symmetric stretching of -CF_3		1244	1228	---
Asymmetric stretching of -CF_3		1198	1190	1190

Table S4. The corresponding simulated impedance parameters in an equivalent circuit.

Battery sample	Before cycle		After 5 cycles	
	R_0 (Ω)	R_{ct} (Ω)	R_0 (Ω)	R_{ct} (Ω)
PEO/LiTFSI/5% MnO_2	20.33	167.5	29.64	132.9
PEO/LiTFSI	23.49	2441	21.11	1372

Table S5. Comparison of electrochemical cycle performance of Li/PEO/LiTFSI/MnO_2 CSPE/$LiFePO_4$ with other reported PEO-based electrolyte.

Electrolyte	Cycle number	Discharge capacity (cathode material: $LiFePO_4$)	Temperature	Reference
PEO/LiTFSI/MnO_2 CSPE	300	143.5 mAh g^{-1}/ 0.5 C	60 °C	This work
$Li_7La_3Zr_2O_{12}$ Nanowire/PEO composite electrolyte	70	158.8 mAh g^{-1}/ 0.5 C	60 °C	Adv. Funct. Mater. **2019**, 29, 1805301
PEO/LLZO composite electrolyte	200	127 mAh g^{-1}/ 0.2 C	55 °C	Nano Energy **2018**, 46, 176
Pyrrolidone-PEO solid electrolyte	--	--	--	*Electrochimica Acta* **2019**, *293*, 25.
PEG-based polymer electrolyte	20	140 mAh g^{-1}/ 0.2 C	30 °C	*Adv. Mater. Interfaces* **2018**, 1801445
PEG-to-PVP triblock gel polymer electrolytes	30	135 mAh g^{-1}/ 0.1 C	60 °C	*Polym. Chem.* **2018**, *9, 5190*
Carbon quantum dots-PEO solid electrolyte	100	100 mAh g^{-1}/ 1 C	60 °C	Adv. Sci. **2018**, 1700996
Ionic liquid-PEO solid electrolyte	50	140 mAh g^{-1}/ 0.1 C	60 °C	*J. Hydrogen Energy* **2017**, *42*, 7212.
PIL-IL-SiO_2 nanoplates PEO polymer electrolyte	30	145.5 mAh g^{-1}/ 0.1 C	60 °C	*Nano Energy*, **2017**, *33*, 110.