Supporting Information

Highly Improved Aqueous Zn||$LiMn_2O_4$ Hybrid-ion Battery Using Poly(ethylene glycol) and Manganese Sulfate as Electrolyte Additives

Jingyi Kong[1], Hanling Guo[1], Yuan Li[1], Min Gong[1], Xiang Lin[1], Liang Zhang[1], Dongrui Wang*[1,2]

[1] Department of Chemistry and Chemical Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China
[2] Beijing Key Laboratory for Bioengineering and Sensing Technology, University of Science and Technology Beijing, Beijing 100083, China

*Corresponding author, wangdr@ustb.edu.cn

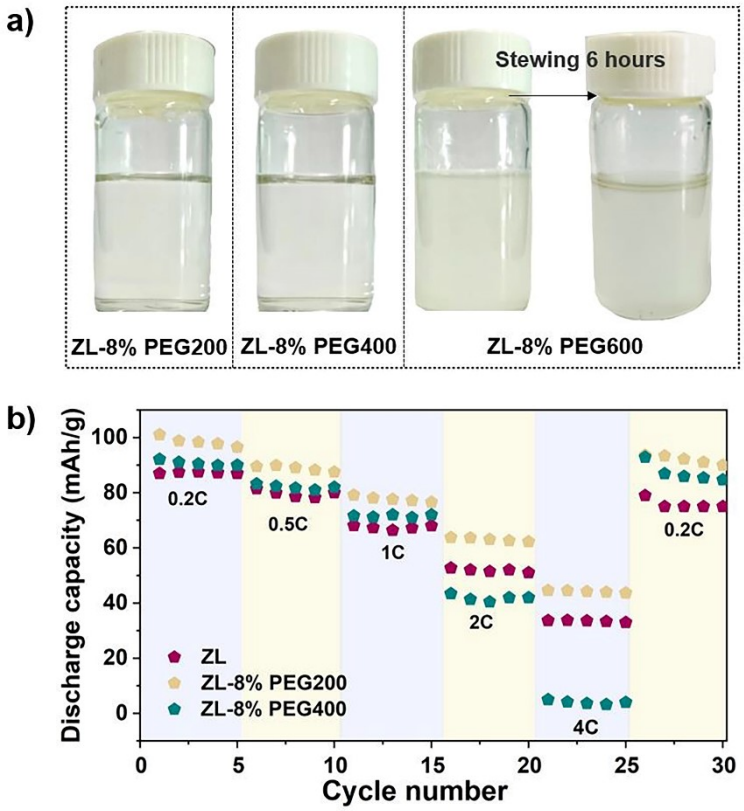

Figure S1. (a) Digital photographs of various electrolytes. (b) Rate performance of Zn||LMO cells using ZL, ZL-8% PEG200, and ZL-8% PEG400 as the electrolyte.

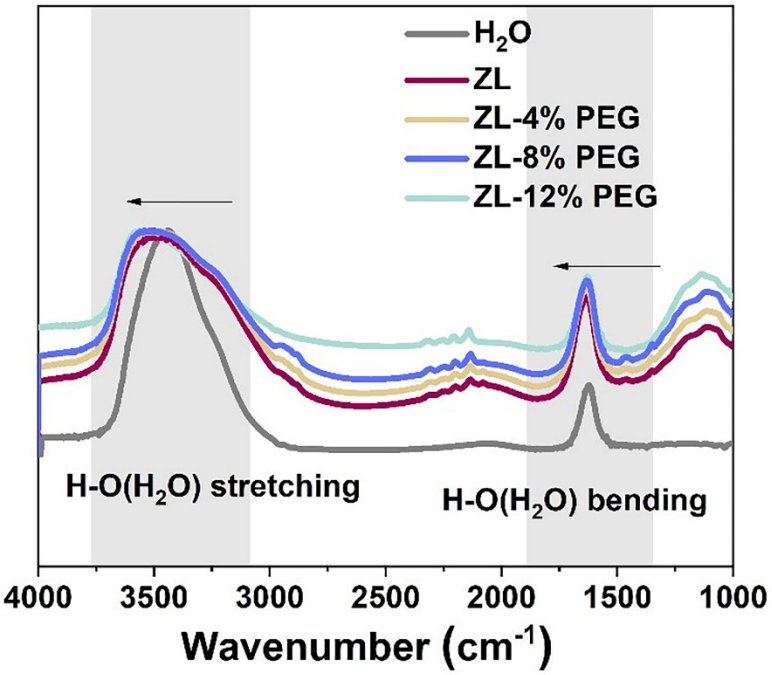

Figure S2. Normalized FTIR spectra of various electrolytes and H_2O.

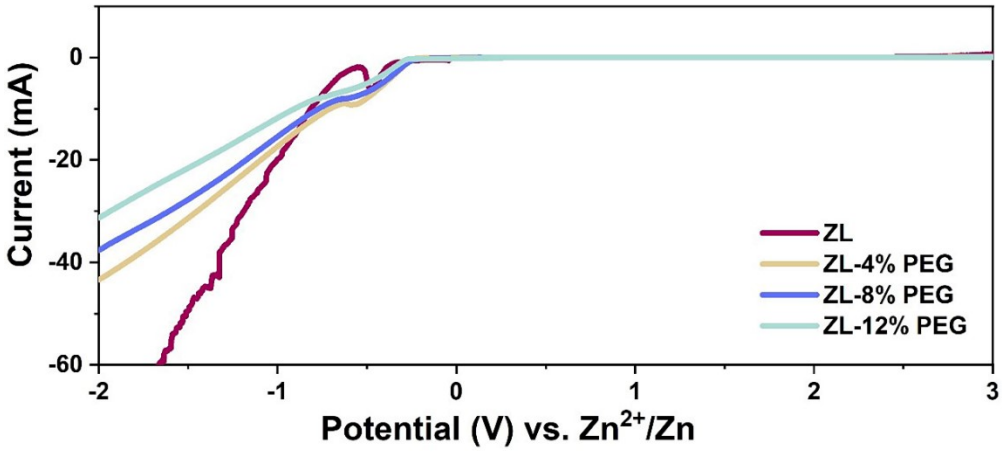

Figure S3. Linear sweep voltammetry (LSV) curves of Ti foils by using ZL electrolyte with/without the PEG additive at 10 mV/s.

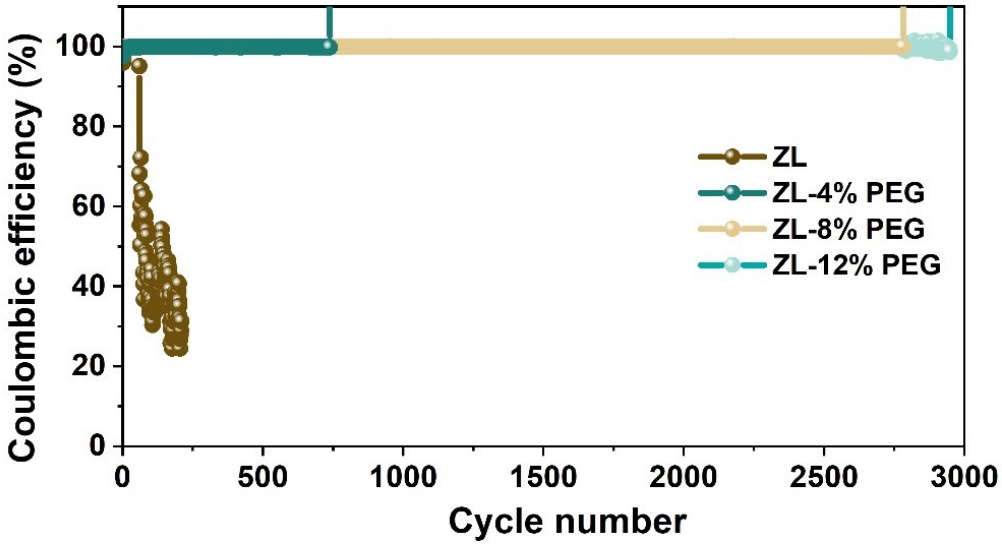

Figure S4. Coulombic efficiency of Cu||Zn asymmetric cells using various electrolytes cycled at 2 mA/cm^2 and 1 mAh/cm^2.

Table S1. A survey of cyclic performance of Zn||Zn symmetric cells containing PEG under galvanostatic plating/stripping.

Electrodes	Electrolyte	Current density (mA/cm^2)	Plated Zn per cycle (mAh/cm^2)	Life cycle	Ref.
Zn||Zn	ZL-8% PEG-0.1 Mn	2	1	1000	This work
		1	1		
Zn||Zn	3 M LiCl+ 4 M $ZnCl_2$	-	-	-	**1**
Zn||Zn	1 M $ZnSO_4·7H_2O$ + 2 M Li_2SO_4 + 4% FS + 1% PEG200	-	-	-	**2**
Zn||Zn	1 m $Zn(ClO_4)_2$ + 10 m $LiClO_4$ + 10% PVA	-	-	-	**3**
Zn||Zn	2 M $ZnSO_4·7H_2O$ + 1 M Li_2SO_4 + 4% FS + 1% PEG300	-	-	-	**4**
Zn||Zn	1 M $ZnSO_4·7H_2O$ + 10 000 ppm PEG200 + 50 ppm BDA.	0.5	1	890	**5**
Zn||Zn	1 M $Zn(OTf)_2$ + 30% H_2O + 70% PEG	2	1	8000	**6**
		1	1	9000	
Zn||Zn	2 M $Zn(OTf)_2$ + 50% H_2O + 50% PEG	1	1	1000	**7**

ZL:1 m $ZnSO_4.7H_2O$ + 2 m Li_2SO_4;

Mn: $MnSO_4·H_2O$;

ppm: 1 ppm=1 mg/kg;

BDA: benzylidene acetone;

FS: Fumed silica with a particle size of ~7 nm;

PVA: Polyvinyl alcohol.

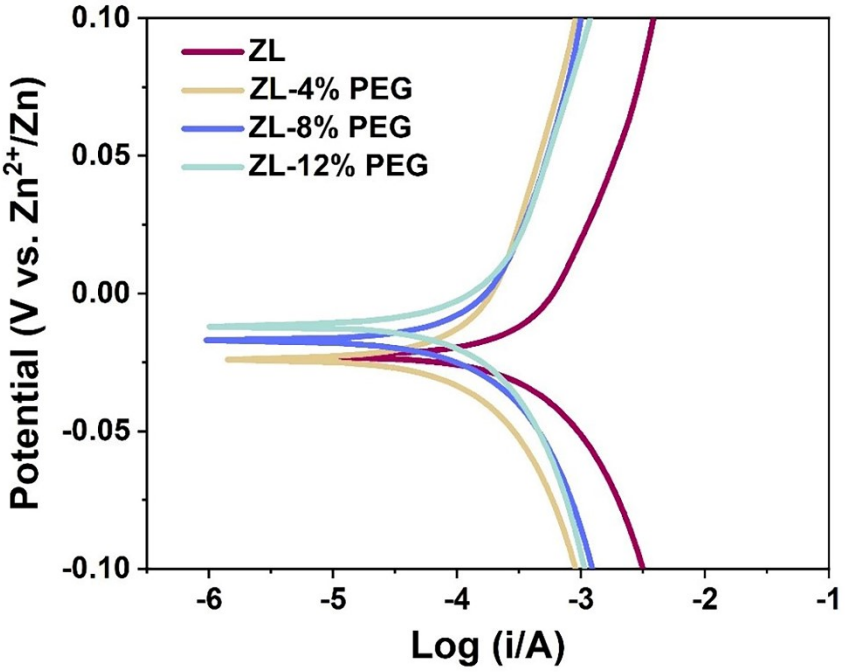

Figure S5. Tafel plots of Zn electrodes in various electrolytes at a scan rate of 10 mV/s.

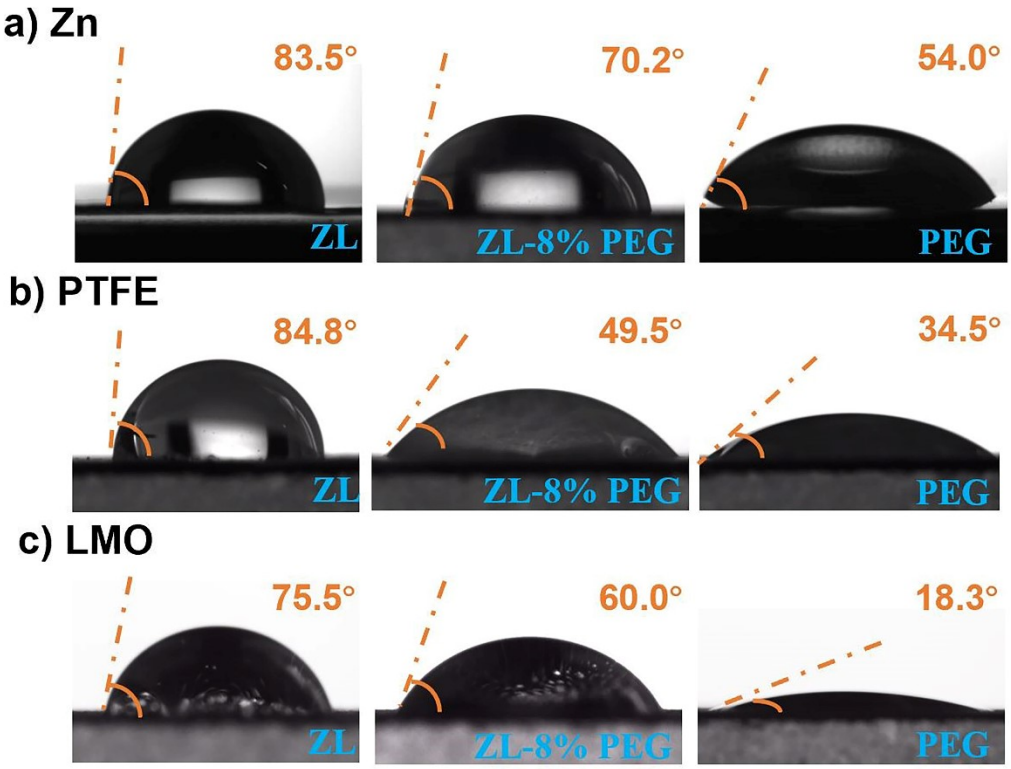

Figure S6. Contact angles of liquids on (a) Zn anodes, (b) PTFE separators, and (c) LMO cathodes.

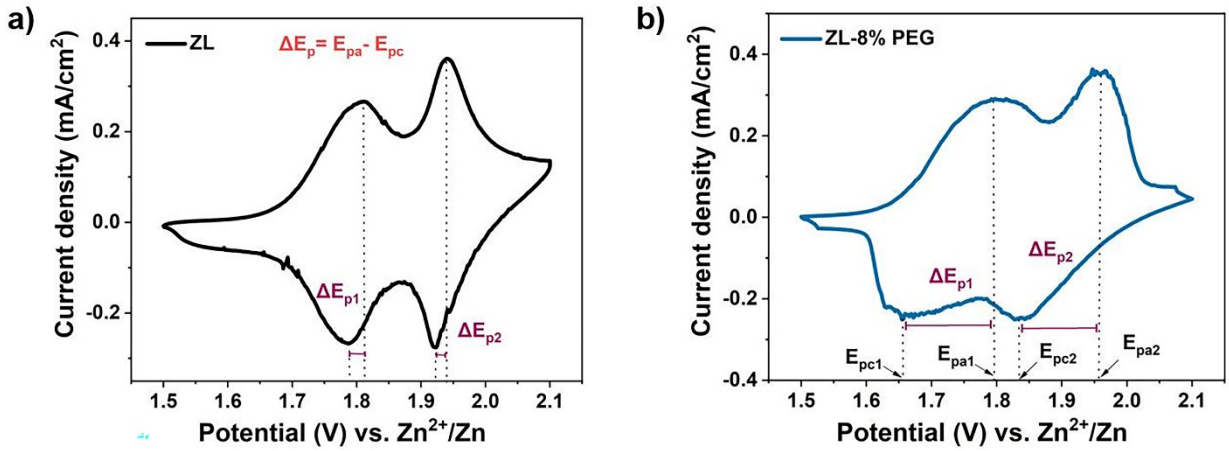

Figure S7. Cyclic voltammetry curves of LMO cathode in (a) ZL and (b) ZL-8% PEG at a scan rate of 0.1 mV/s.

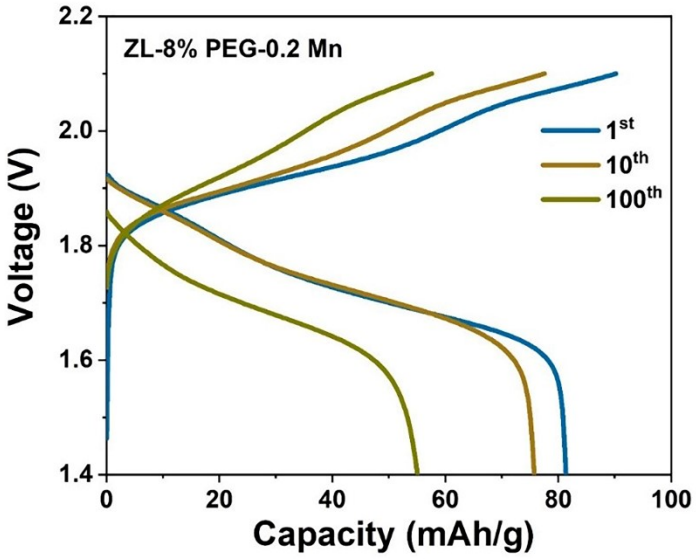

Figure S8. GCD profiles of Zn||LMO full cell under 1 C at 1st, 10th, 100th cycle in ZL-8% PEG-0.2 Mn.

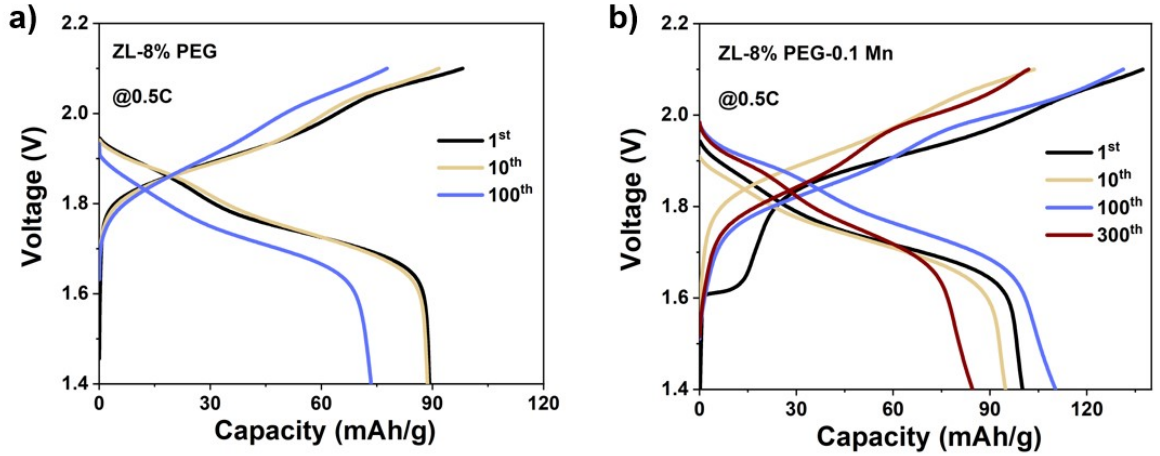

Figure S9. GCD profiles of Zn||LMO full cells under 0.5 C at different cycles using (a) ZL-8% PEG and (b) ZL-8% PEG-0.1 Mn as the electrolyte, respectively.

Table S2. Comparison of cyclic performance of Zn||LMO full cells under different charging/discharging rates.

Cathode/Total mass, mg/cm^2	**Anode**	**electrolyte**	**Voltage/V**	**Rate**	**Capacity retention (% @number of cycles)**	**Total lifespan/h**	**Ref.**
LMO/KB/PVDF 3.0	Zn foil	ZL-8% PEG-0.1 Mn	1.80	2 C	50% @500 cycles	250	This work
				0.5 C	85% @300 cycles	600	
LMO/AB/PVDF 2.4	Zn foil	3 M LiCl-4 M $ZnCl_2$	1.75[a]	4 C	90% @1000 cycles	250	**1**
LMO/KS-6/PVDF 5.3	Zn foil	1 M $ZnSO_4{\cdot}7H_2O$ -2 M Li_2SO_4 -4% FS-1% PEG200	1.80[a]	4 C	80.2%@1000 cycle	250	**2**
LMO/SP/PTFE 5~6	Zn foil	1 m $Zn(ClO_4)_2$-10 m $LiClO_4$-10% PVA	1.65[a]	1 C	75.0% @300 cycles	300	**3**
LMO/KS-6/PVDF 4~6	Zn foil	2 M $ZnSO_4{\cdot}7H_2O$ -1 M Li_2SO_4-4% FS-1% PEG300	1.80[a]	1 C	75.0% @300 cycles	300	**4**

[a] Estimated value

ZL:1 m $ZnSO_4.7H_2O$ + 2 m Li_2SO_4

LMO: $LiMn_2O_4$

KB: Ketjenblack
AB: Acetyleneblack
PVDF: polyvinylidene fluoride
KS-6: A high-purity natural graphite
PG: Porous graphene
FS: Fumed silica with a particle size of ~7 nm

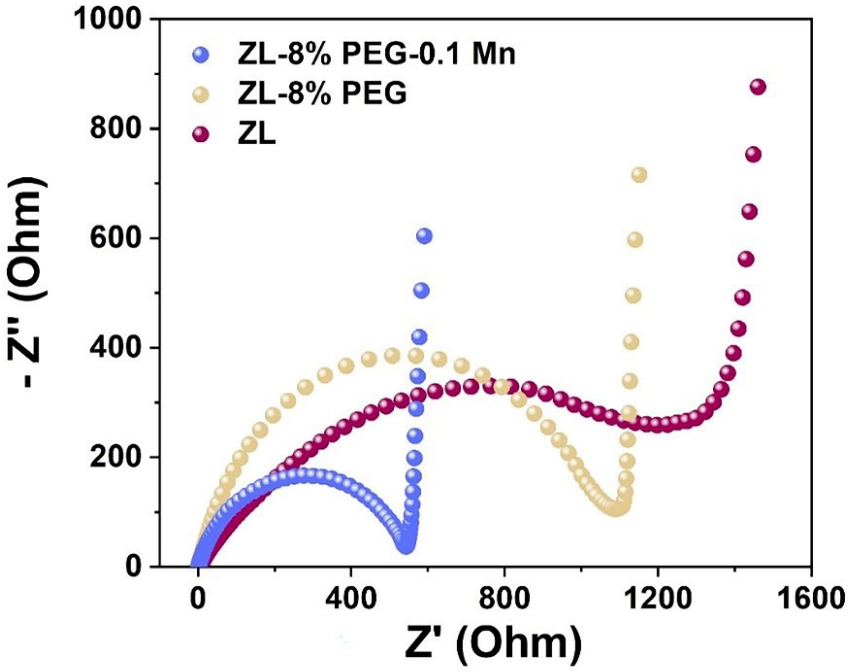

Figure S10. Nyquist plots of pristine Zn||LMO cells in ZL, ZL-8% PEG and ZL-8% PEG-0.1 Mn electrolytes, respectively.

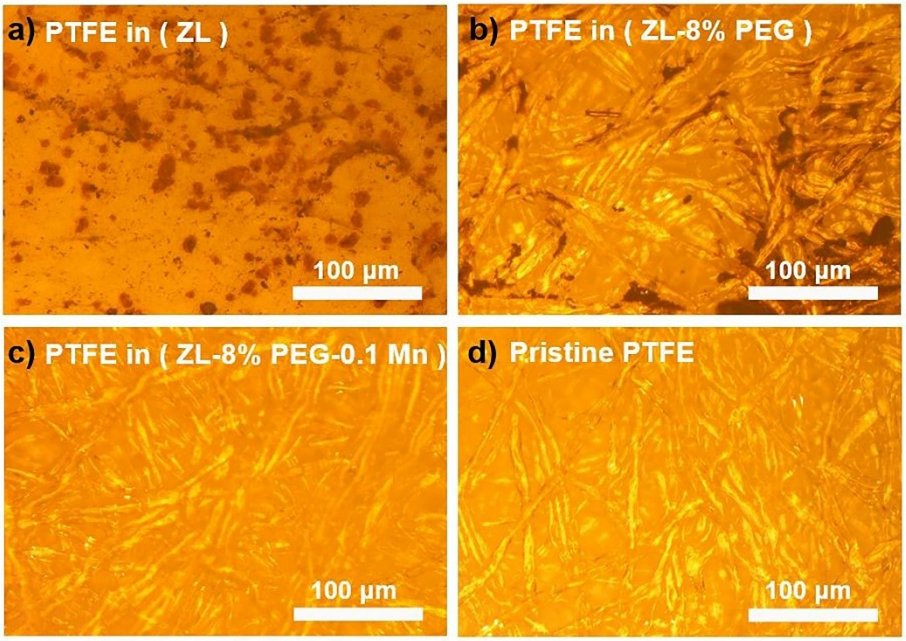

Figure S11. Optical microscope images of surfaces of PTFE separators in Zn||LMO full cells with different electrolytes (a-c) after 100 cycles of GCD tests under 2C. (d) The surface of a fresh PTFE

separator.

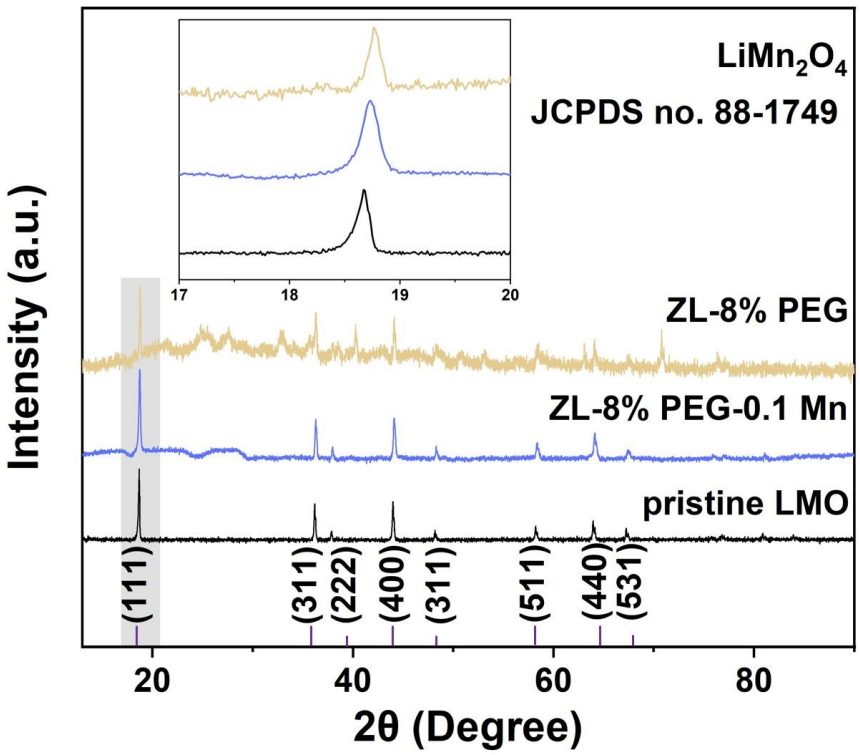

Figure S12. Ex-situ XRD patterns of LMO before and after 100 cycles of GCD tests in Zn||LMO full cells using ZL-8% PEG and ZL-8% PEG-0.1 Mn electrolytes.

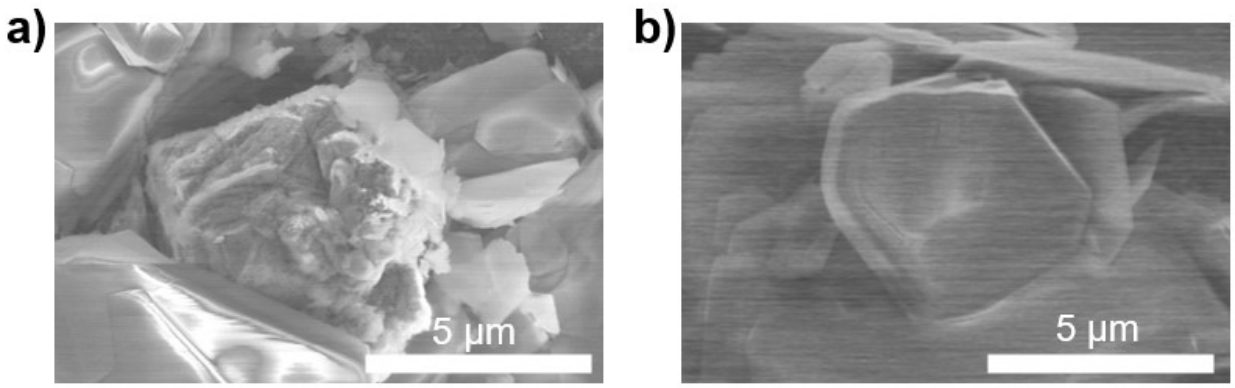

Figure S13. Typical SEM images of LMO after 100 cycles of GCD tests in Zn||LMO full cells using (a) ZL-8% PEG and (b) ZL-8% PEG-0.1 Mn electrolytes.

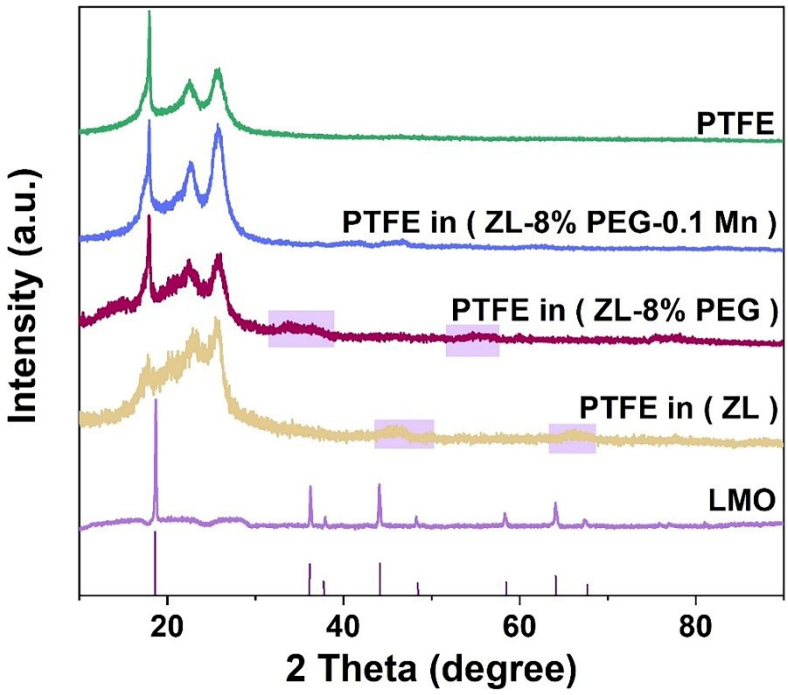

Figure S14. XRD patterns of PTFE separators in Zn||LMO full cells using various electrolytes after 100 cycles GCD tests. XRD patterns of pristine PTFE separator and LMO powders are also listed as comparison.

References

1. J. Yan, J. Wang, H. Liu, Z. Bakenov, D. Gosselink and P. Chen, *J. Power Sources.*, 2012, **216**, 222-226.
2. W. Xiong, T. K. A. Hoang, D. Yang, Y. Liu, M. Ahmed, J. Xu, X. Qiu and P. Chen, *J. Energy Storage.*, 2019, **26**, 100920.
3. S. Chen, R. Lan, J. Humphreys and S. Tao, *ACS Appl. Energy Mater.*, 2020, **3**, 2526-2536.
4. A. Mitha, H. Mi, W. Dong, I. S. Cho, J. Ly, S. Yoo, S. Bang, T. K. A. Hoang and P. Chen, *J. Electroanal. Chem.*, 2019, **836**, 1-6.
5. G. Lin, X. Zhou, L. Liu, D. Huang, H. Li, X. Cui and J. Liu, *RSC Adv*, 2022, **12**, 25054-25059.
6. Y. Wu, Z. Zhu, D. Shen, L. Chen, T. Song, T. Kang, Z. Tong, Y. Tang, H. Wang and C.S. Lee, *Energy Storage Mater.*, 2022, **45**, 1084-1091.
7. J. Zhou, H. Yuan, J. Li, W. Wei, Y. Li, J. Wang, L. Cheng, D. Zhang, Y. Ding, D. Chen and H. Wang, *Chem. Eng. J.*, 2022, **442**, 136218.