

Enabling Non-flammable Li-metal Batteries via Electrolyte Functionalization and Interface Engineering

Jing Yu,^{†a} Yu-Qi Lyu,^{†a} Jiapeng Liu,^a Mohammed B. Effat,^a Stephen C.T. Kwok,^{ab}

Junxiong Wu,^a Francesco Ciucci,^{*abc}

[a] J. Yu, Dr. Y. Q. Lyu, J. Liu, M. B. Effat, J. Wu, Dr. S. C.T. Kwok, Prof. F. Ciucci

Department of Mechanical and Aerospace Engineering

The Hong Kong University of Science and Technology

Hong Kong, China SAR

E-mail: *francesco.ciucci@ust.hk* (Francesco Ciucci)

[b] Dr. S.C.T. Kwok, Prof. F. Ciucci

Guangzhou HKUST Fok Ying Tung Research Institute, China

[c] Prof. F. Ciucci

Department of Chemical and Biological Engineering

The Hong Kong University of Science and Technology

Hong Kong, China SAR

[†]: These authors contributed equally to this work.

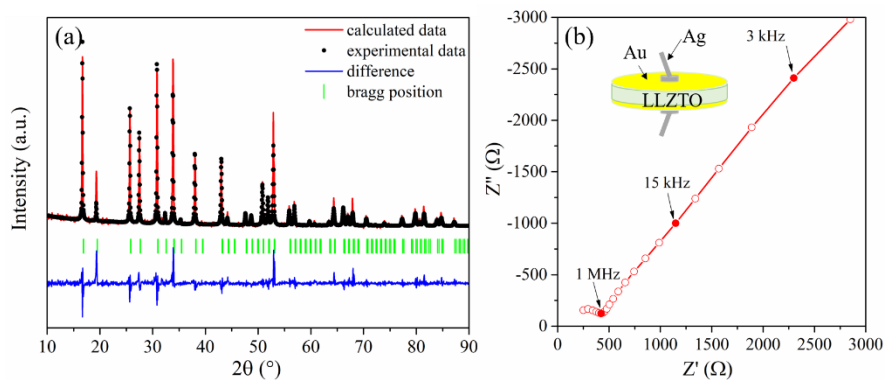


Fig. S1. (a) A Rietveld refined XRD pattern of the LLZTO pellet. (b) A typical EIS of a Au|LLZTO|Au cell.

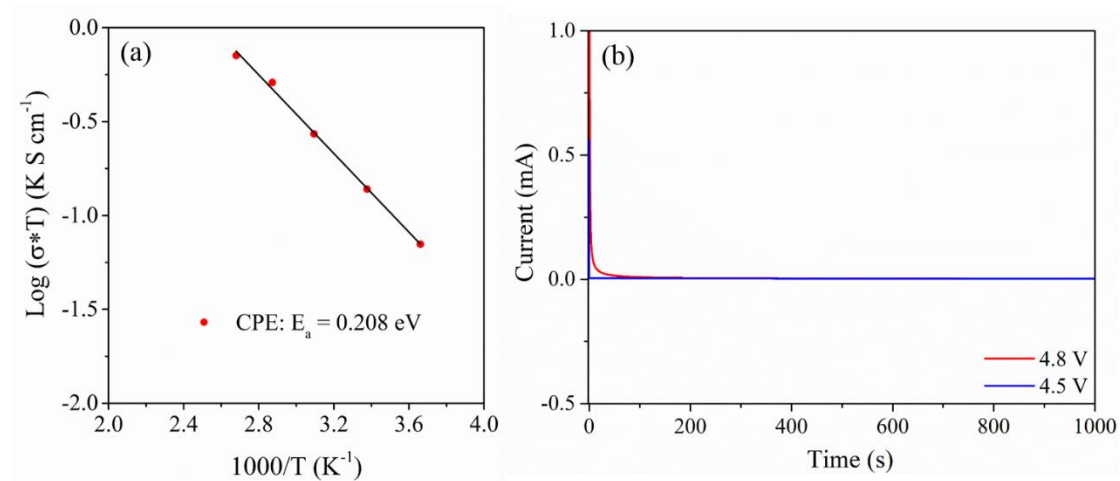


Fig. S2. (a) The Arrhenius plot of CPE. (b) Chronoamperometric measurements on a Li|CPE|SS cell.

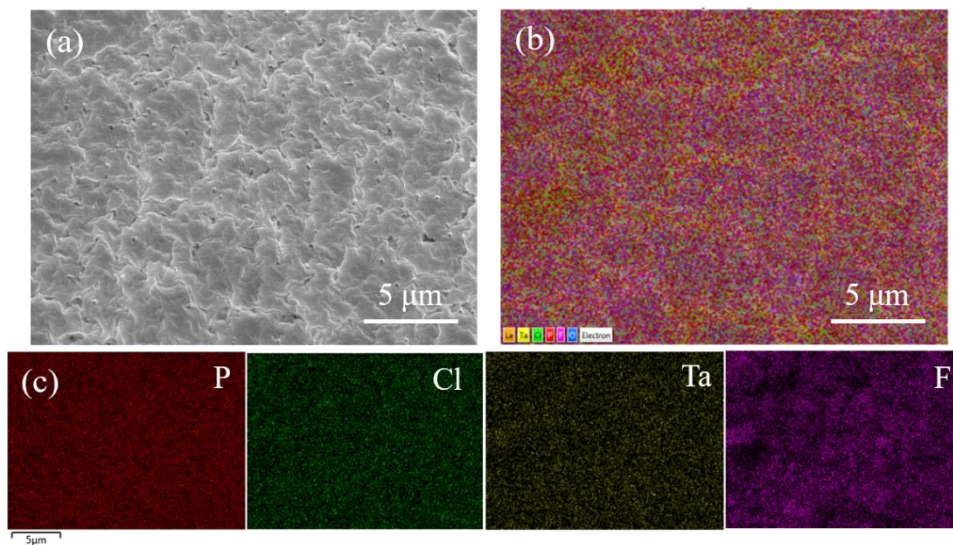


Fig. S3. (a) A typical SEM image and (b & c) the corresponding EDS mappings of the CPE membrane.



Fig. S4. Flammability of the CPE membrane with the DMF solvent.

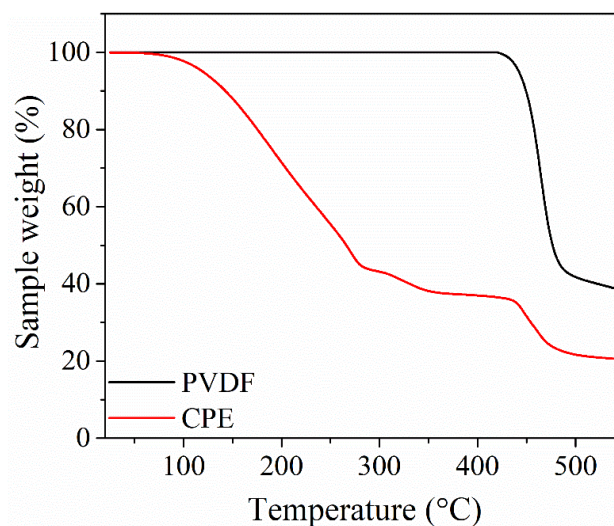


Fig. S5. TGA of PVDF and the CPE membrane.

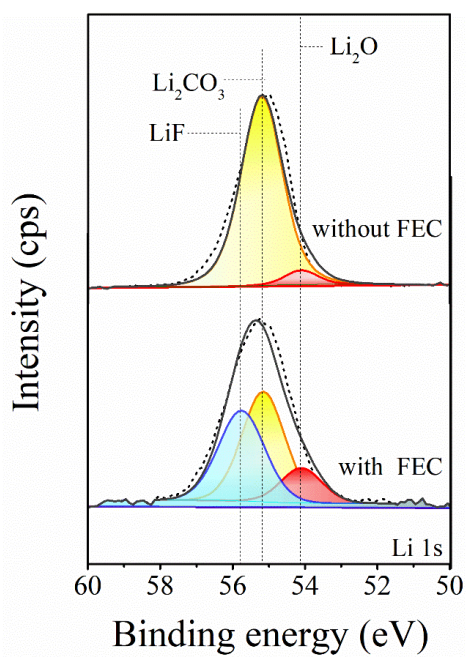


Fig. S6. XPS of the surface of the Li metal with and without FEC.

Table S1. Comparison of the electrochemical performance of Li/LFP cells with various polymer electrolytes.

Electrolyte	Operating potential (V)	C-Rate	Discharge capacity (mAh g ⁻¹)	Cycling Temperature (°C)	Cycle number (Capacity retention)	Ref.
Nanocomposite solid polymer electrolyte with LiFSI	2.5-3.7	0.1 C	160	70	50 (97.5%)	1
2D boron nitride nanoflakes in gel polymer electrolyte	2.5-4.2	1 C	135	RT	300 (88%)	2
PEO based CPE	2.5-4.2	1 C	116	RT	500 (70%)	3
PVDF based CPE	3.0-4.2	0.4 C	150	RT	120 (98%)	4
PVDF based hybrid electrolyte	3.0-3.8	0.5 C	113	RT	180 (92.5%)	5
Deep eutectic solvent-silica CPE	2.5-4.2	0.1 C	112	RT	100 (/)	6
PEO/ Y-type oligomer/Al ₂ O ₃ /Li TFSI hybrid electrolyte	2.0-4.2	0.2 C	142	30	150 (/)	7
This work	2.5-4.2	0.2 C	157	RT	500 (96.8%)	
This work	2.5-4.2	1 C	144	RT	300 (99.3%)	

References

1. X. Judez, M. Piszcz, E. Coya, C. Li, I. Aldalur, U. Oteo, Y. Zhang, W. Zhang, L. M. Rodriguez-Martinez, H. Zhang and M. Armand, *Solid State Ionics*, 2018, **318**, 95-101.
2. J. Shim, H. J. Kim, B. G. Kim, Y. S. Kim, D.-G. Kim and J.-C. Lee, *Energy Environ. Sci.*, 2017, **10**, 1911-1916.
3. C. Fu, S. Lou, Y. Cao, Y. Ma, C. Du, P. Zuo, X. Cheng, W. Tang, Y. Wu and Y. Gao, *Electrochim. Acta*, 2018, **283**, 1261-1268.
4. X. Zhang, T. Liu, S. F. Zhang, X. Huang, B. Q. Xu, Y. H. Lin, B. Xu, L. L. Li, C. W. Nan and Y. Shen, *J. Am. Chem. Soc.*, 2017, **139**, 13779-13785.
5. W. Zhang, J. Nie, F. Li, Z. L. Wang and C. Sun, *Nano Energy*, 2018, **45**, 413-419.
6. B. Joos, T. Vranken, W. Marchal, M. Safari, M. K. Van Bael and A. T. Hardy, *Chem. Mater.*, 2018, **30**, 655-662.
7. R. Tan, R. Gao, Y. Zhao, M. Zhang, J. Xu, J. Yang and F. Pan, *ACS Appl. Mater. Interfaces*, 2016, **8**, 31273-31280.