Supporting Information

Constructing compatible interface between $Li_7La_3Zr_2O_{12}$ solid electrolyte and $LiCoO_2$ cathode for stable cycling performances at 4.5 V

Yuwan Dong,[a] Panzhe Su,[a] Guanjie He,[b] Huiling Zhao[a] and Ying Bai*[a]*

[a] International Joint Research Laboratory of New Energy Materials and Devices of Henan Province, School of Physics & Electronics, Henan University, Kaifeng, 475004, P. R. China

[b] Materials Research Centre, UCL Department of Chemistry, Christopher Ingold Building, 20 Gordon Street, London, WC1H 0AJ, UK

*** Corresponding author.**

E-mail: zhao@henu.edu.cn (H. Zhao); ybai@henu.edu.cn (Y. Bai)

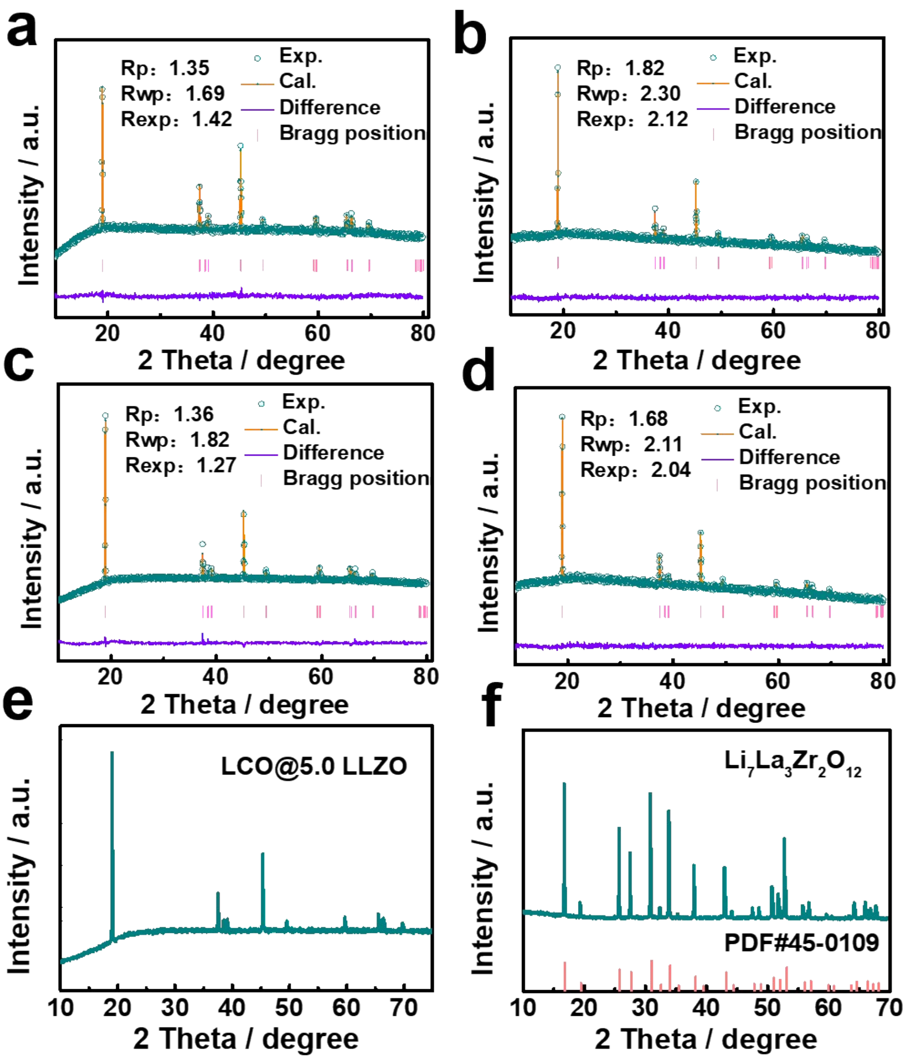

Fig. S1. (a-d) Rietveld refinement XRD spectra for the pristine LCO and LCO@LLZO samples. (e, f) XRD patterns of the LCO@5.0 LLZO and pure phase LLZO samples.

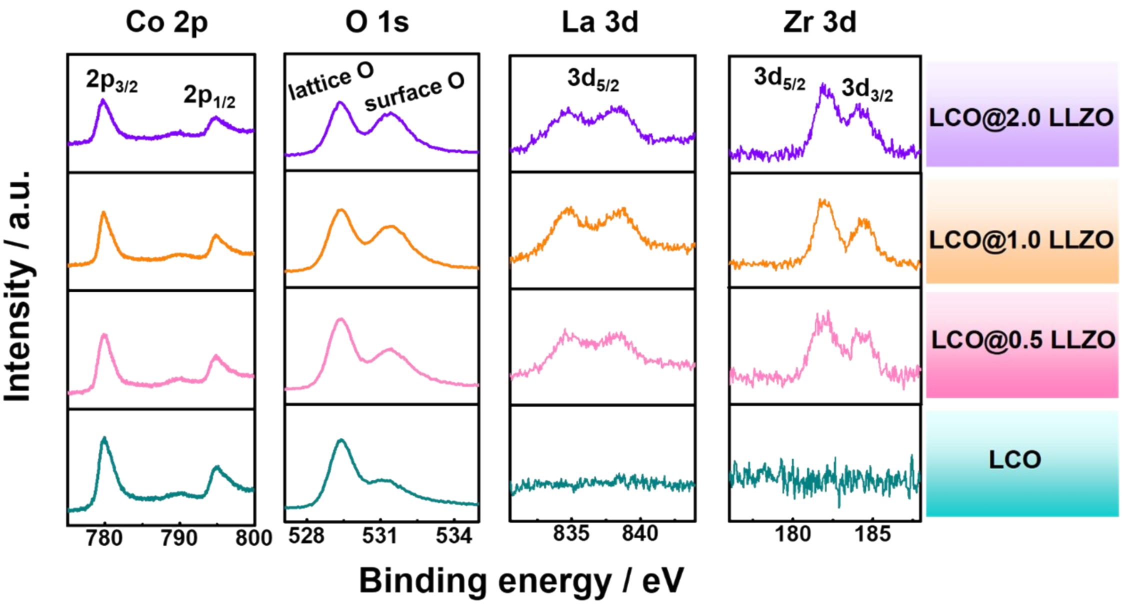

Fig. S2. XPS spectra of Co 2p, O 1s, La 3d and Zr 3d for the pristine and LCO@LLZO samples.

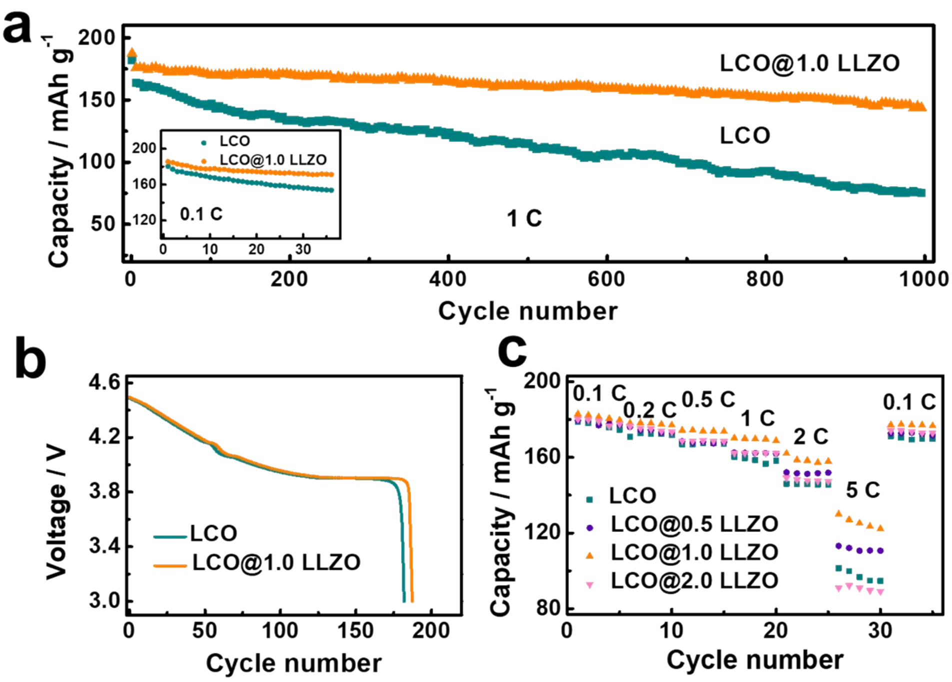

Fig. S3. (a) The long-term cycling performances under 1 C (inset with 0.1 C) and (b) initial discharge curves of the pristine and LCO@1.0 LLZO at high current rate of 1 C (1 C = 274 mA g^{-1}). (c) The rate performances of the pristine LCO and LLZO modified electrodes under different current rates.

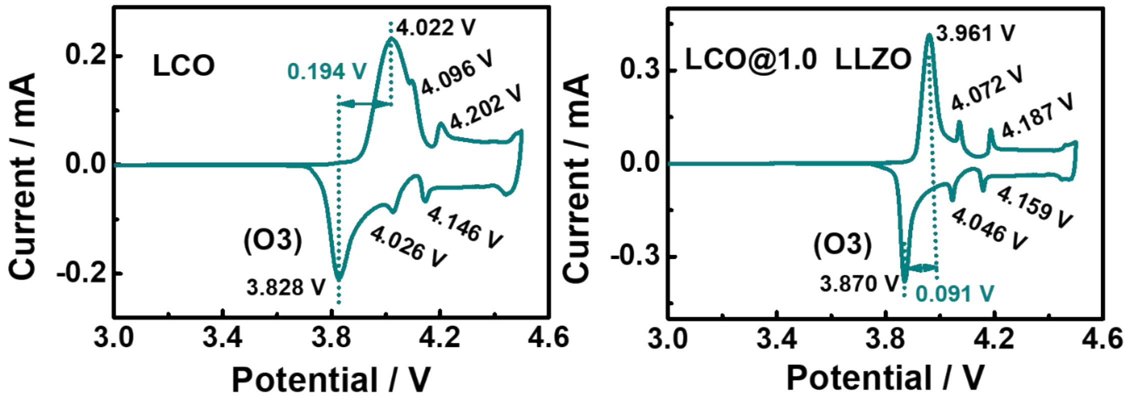

Fig. S4. CV curves of LCO and LCO@1.0 LLZO electrodes at a scan rate of 0.05 mV s^{-1} in the voltage range of 3.0 ~ 4.5 V.

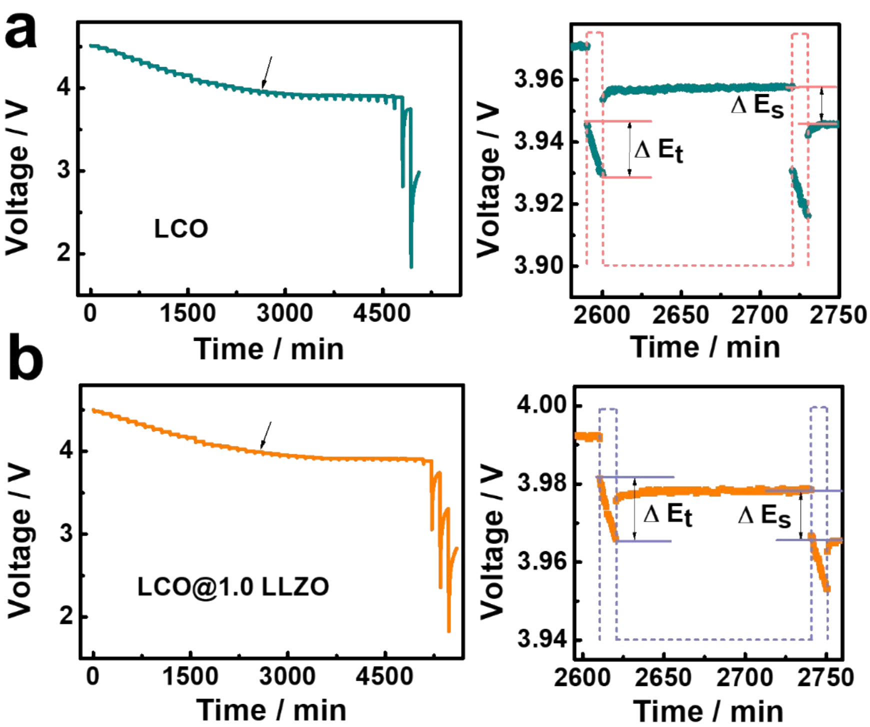

Fig. S5. GITT measurements for the Li/LCO cell (a) and LCO@1.0 LLZO cell (b) in the first cycle at high working-voltage of 4.5 V, and the corresponding zoomed curves marked by the arrows.

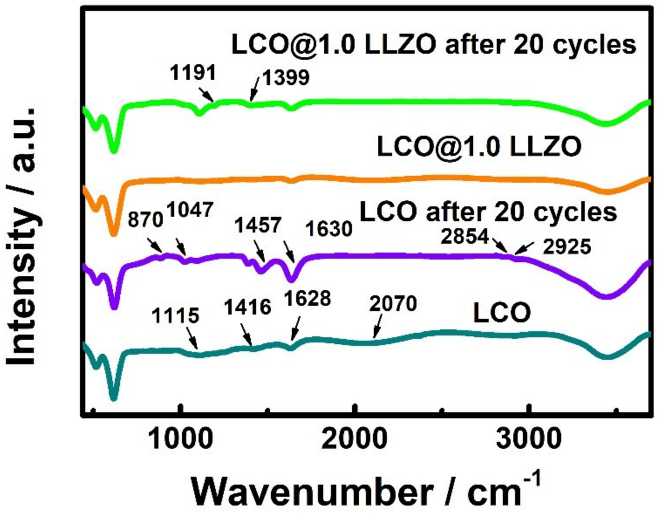

Fig. S6. FTIR spectra of the pristine and LCO@1.0 LLZO samples before and after cycling in the operating voltage of 3.0 ~ 4.5 V at room temperature.

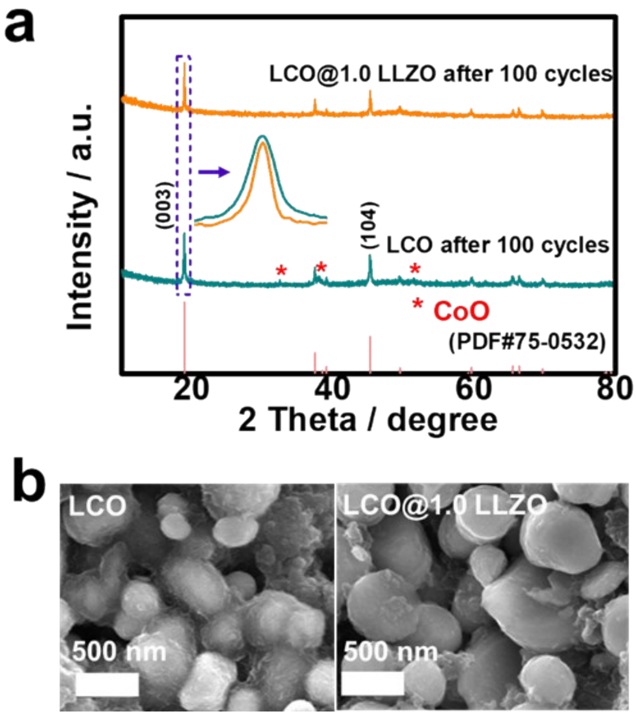

Fig. S7. XRD patterns (a) and SEM images (b) of the pristine and the LCO@1.0 LLZO electrodes after 100 cycles in the working voltage range of 3.0 ~ 4.5 V at the elevated temperature of 55 °C.

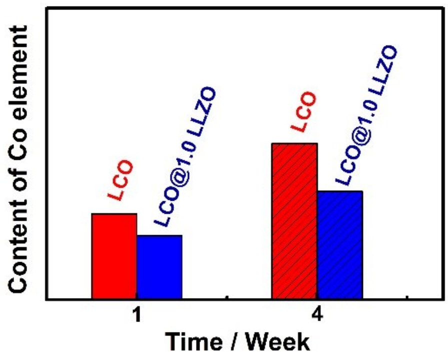

Fig. S8. The Co content histogram of the pristine and LCO@1.0 LLZO soaked electrolytes after 1 and 4 weeks.

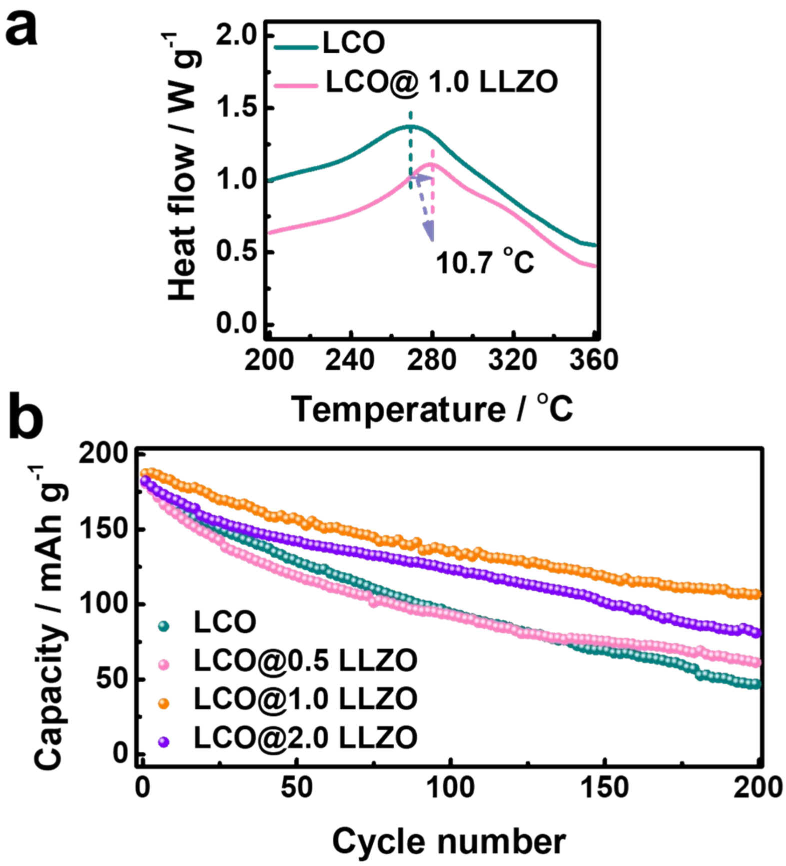

Fig. S9. (a) DSC profiles of the pristine and LCO@1.0 LLZO samples after 30 cycles (at the high fully charging-state of 4.5 V). (b) Cycle performances of all the as-prepared samples at the current density of 0.1 C and the elevated temperature of 55 °C.

Table S1. Refinement parameters for the XRD spectra of all as-prepared samples.

Sample	*a (Å)*	*c (Å)*	*c/a*	*I(003)/I(104)*
LCO	2.816	14.054	4.99	1.386
LCO@0.5 LLZO	2.816	14.054	4.99	1.758
LCO@1.0 LLZO	2.816	14.055	4.99	1.862
LCO@2.0 LLZO	2.816	14.054	4.99	1.895

Table S2. Comparison of the capacity retentions of surface-modified LCO electrodes at the high cutoff voltage of 4.5 V.

Material	Current density	Capacity retention	Ref.
LCO@ZrO_xF_y	1 C	200 cycles-56.4 %	1
LCO@MgF	0.2 C	50 cycles- over 80 %	2
LCO@Al_2O_3	1 C	1000 cycles- 72.5 %	3
LCO@ZrO_2	0.5 C	30 cycles- 85 %	4
LCO@LATP	1 C	700 cycles- over 60 %	5
LCO@LaF_3	0.1 C	50 cycles- 90.9 %	6
LCO@Al_2O_3	0.1 C	50 cycles- 91.8 %	7
LCO@$MgAl_2O_4$	0.5 C	70 cycles- 96.8 %	8
LCO@Al_2O_3	1/9 C	50 cycles- 88.4 %	9
Al_2O_3 ALD on LCO	0.2 C	50 cycles- 79.8 %	10
This work	1 C	1000 cycles- 76.8 %	

Table S3. EIS fitting values of the pristine and LCO@1.0 LLZO electrodes.

Resistance	electrode	*1st*	*10th*	*30th*
R_{sf} (Ω)	LCO	174.9	280.2	469.6
	LCO@1.0 LLZO	197.8	284.5	481.8
R_{ct} (Ω)	LCO	261.1	634.1	2135.0
	LCO@1.0 LLZO	182.9	325.5	549.3

Table S4. New peaks appeared and their corresponding identifications in the FTIR spectra of the pristine and LCO@1.0 LLZO electrodes after 20 cycles.

Peak position (cm^{-1})	Assignment
870, 1416	CO_3^{2-} bend, Li_2CO_3[11]
1047, 1115	C-O st, $ROCO_2Li$[12]
1191	R-F[13]
1399, 1457	C-O st, Li_2CO_3[12]
1628, 1630	C=O asym st, RCOOLi[12]
2070	CH_2 bend, $ROCO_2Li/(CH_2OCO_2Li)_2$[14]
2854, 2925	C-H, $ROCO_2Li$[15,16]

Table S5. The Co element concentrations of the pristine and LCO@1.0 LLZO samples immersed in the electrolytes with different soakage time.

Sample	Week 1	Week 4
LCO	294.79 μg L^{-1}	535.72 μg L^{-1}
LCO@1.0 LLZO at 4.5 V	220.26 μg L^{-1}	371.33 μg L^{-1}

Supplementary References

1. Z. Wang, Z. Wang, H. Guo,W. Peng, X. Li, J. Wang, *Mater. Lett.,* 2014, **123**, 93–96.

2. Y. Bai, K, Jiang, S. Sun, Q. Wu, X. Lu, N. Wan, *Electrochim. Acta,* 2014, **134**, 347-354.

3. A. Zhou, Q. Liu, Y. Wang, W. Wang, X. Yao, W. Hu, L. Zhang, X. Yu, J. Li, H. Li, *J. Mater. Chem. A,* 2017, **5**, 24361-24370.

4. B. J. Hwanga, C. Y. Chena, M. Y. Chenga, R. Santhanama, K. Ragavendrana, *J. Power Sources,* 2010, **195**, 4255–4265.

5. J. H. Shim, J. M. Han, J. H. Lee, S. Lee, *ACS Appl. Mater. Interfaces,* 2016, **8**, 12205−12210.

6. Z. Yanga, Q. Qiaoa, W. Yang, *Electrochim. Acta,* 2011, **56**, 4791–4796.

7. W. Zhang, Z. Chi, W. Mao, R. Lv, A. Cao, and L. Wan, *Angew. Chem. Int. Ed.,* 2014, **53**, 12776 –12780.

8. D. D. Liang, H. F. Xiang, X. Liang, S. Cheng and C. H. Chen, *RSC Adv.,* 2017, 7, 6809.

9. B. Han, T. Paulauskas, B. Key, C. Peebles, J. S. Park, R. F. Klie,T. Vaughey, and F. Dogan, *ACS Appl. Mater. Interfaces,* 2017, **9**, 14769−14778.

10. H. M. Cheng, F. M. Wang, J. P. Chu, R. Santhanam, J. Rick, and S. C. Lo, *J. Phys. Chem. C,* 2012, **116**, 7629−7637.

11. A. A. Shaltout, M. A. Allam and M. A. Moharram, *Spectrochim. Acta A*, 2011, **83**, 56-60.

12. K. I. Morigaki and A. Ohta, *J. Power Sources*, 1998, **76**, 159-166.

13. D. Ostrovskii, F. Ronci, B. Scrosati and P. Jacobsson, *J. Power Sources,* 2001, **103**, 10-17.

14. M. M. Mady and M. A. Allam, *Phys. Medica*, 2012, **28**, 48-53.

15. E. Markevich, G. Salitra, F. Chesneau, M. Schmidt and D. Aurbach, *ACS Energy Lett.*, 2017, **2**, 1321-1326.

16. M. Si, D. Wang, R. Zhao, D. Pan, C. Zhang, C. Yu, X. Lu, H. Zhao and Y. Bai, *Adv. Sci.*, 2019, **7**, 1902538.