Supporting Information

Flexible interfacial modification layer towards enhanced performance in LATP-based all-solid-state batteries

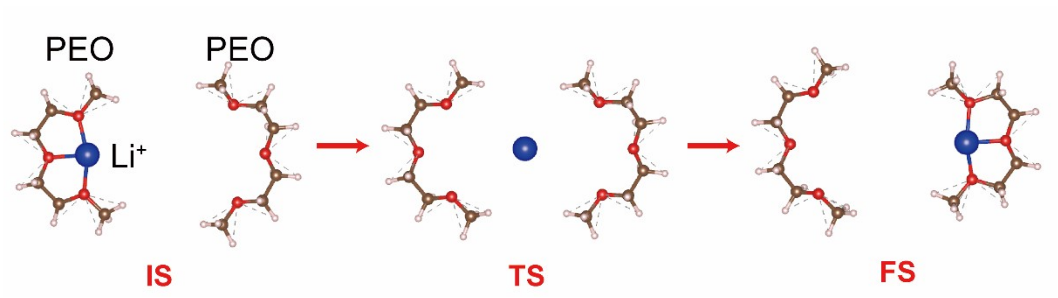

Figure S1. The Li^+ migration pathway in PEO system for the DFT calculation.

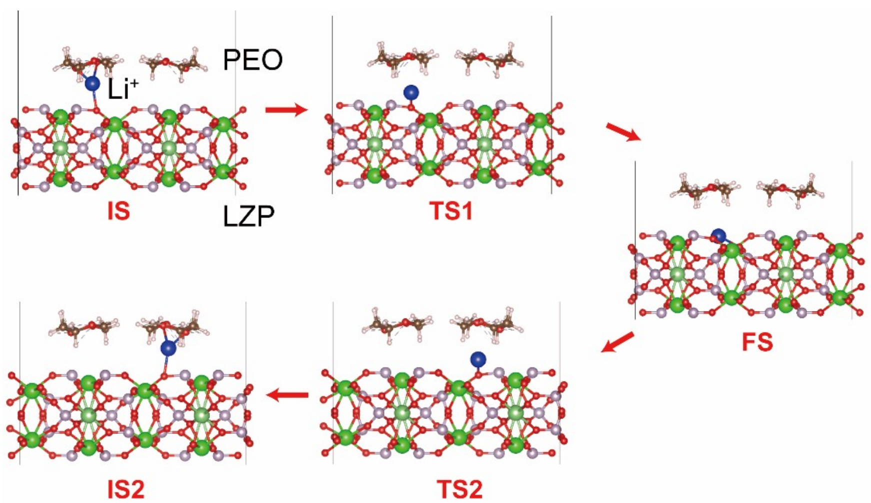

Figure S2. The Li^+ migration pathway in PEO_LZP system for the DFT calculation.

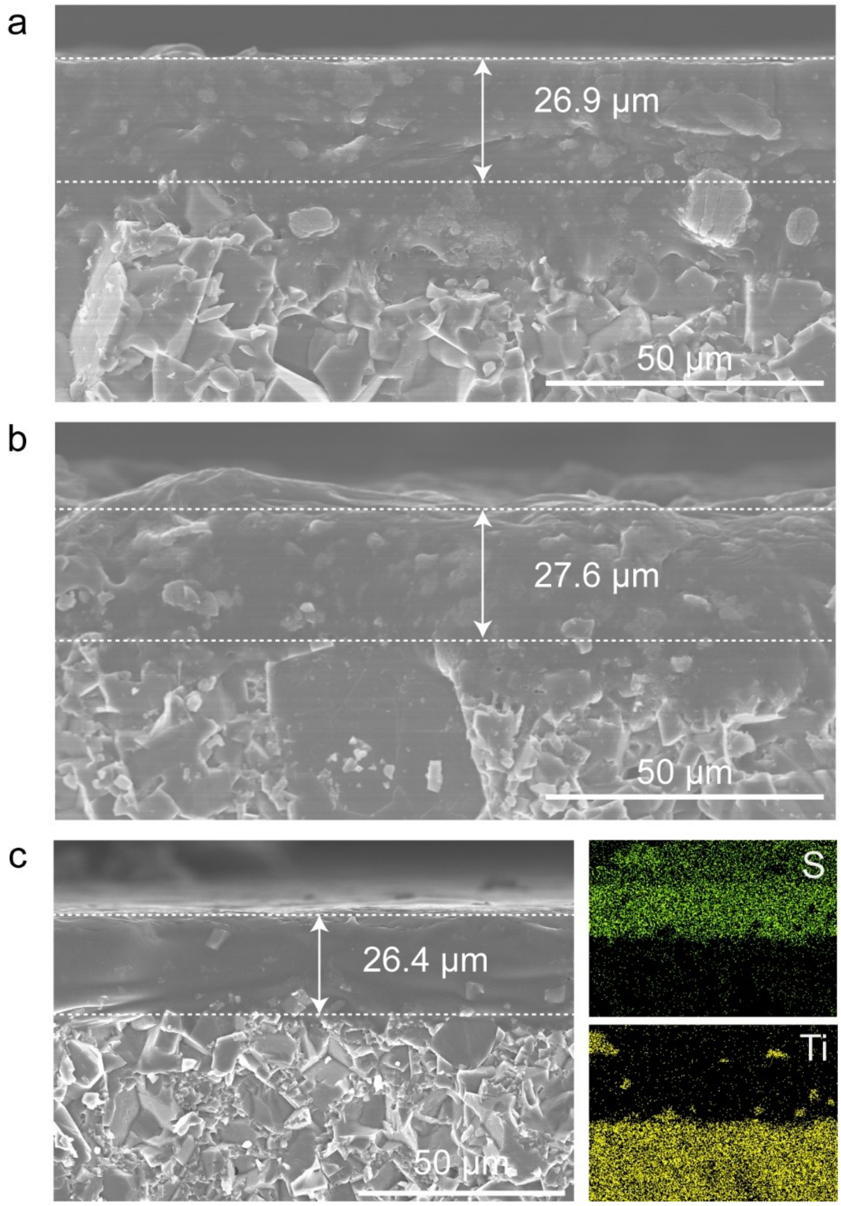

Figure S3. (a)-(b) The cross-section SEM image of the different PEO_LZP modified LATP pellets. (c) The cross-section SEM image of the PEO modified LATP pellet and corresponding EDS mapping.

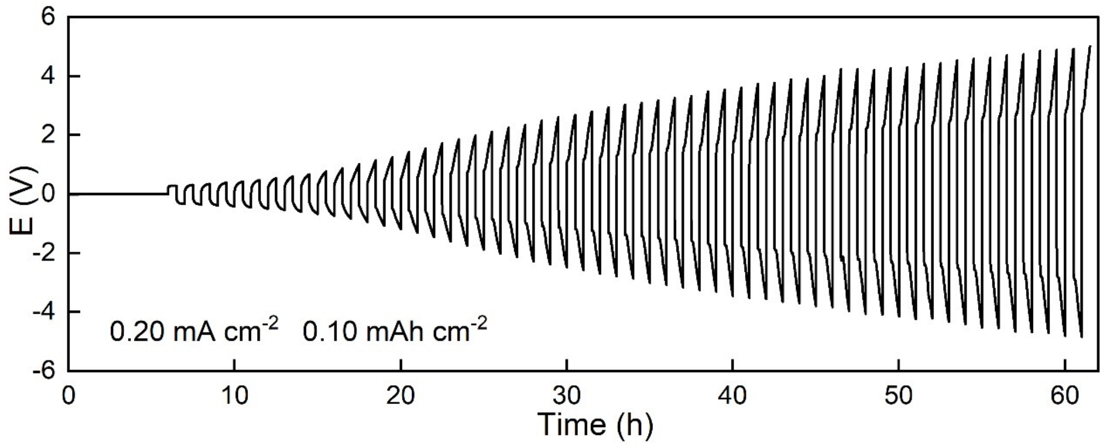

Figure S4. The plating/striping profile of the Li/LATP/Li symmetric cell at a current density of 0.20 mA cm^{-2}.

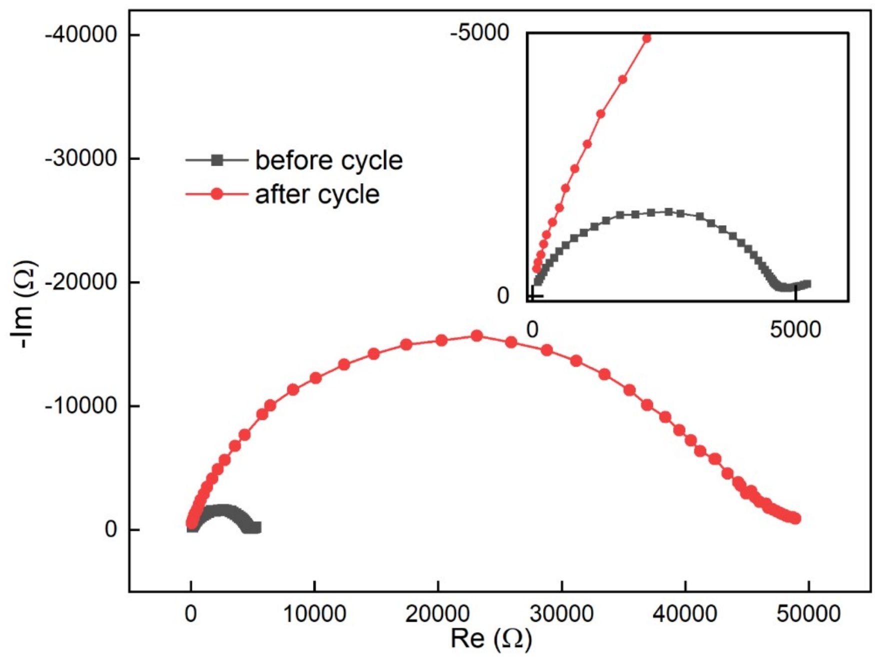

Figure S5. The Nyquist plot of the Li/LATP/Li symmetric cell before and after cycling.

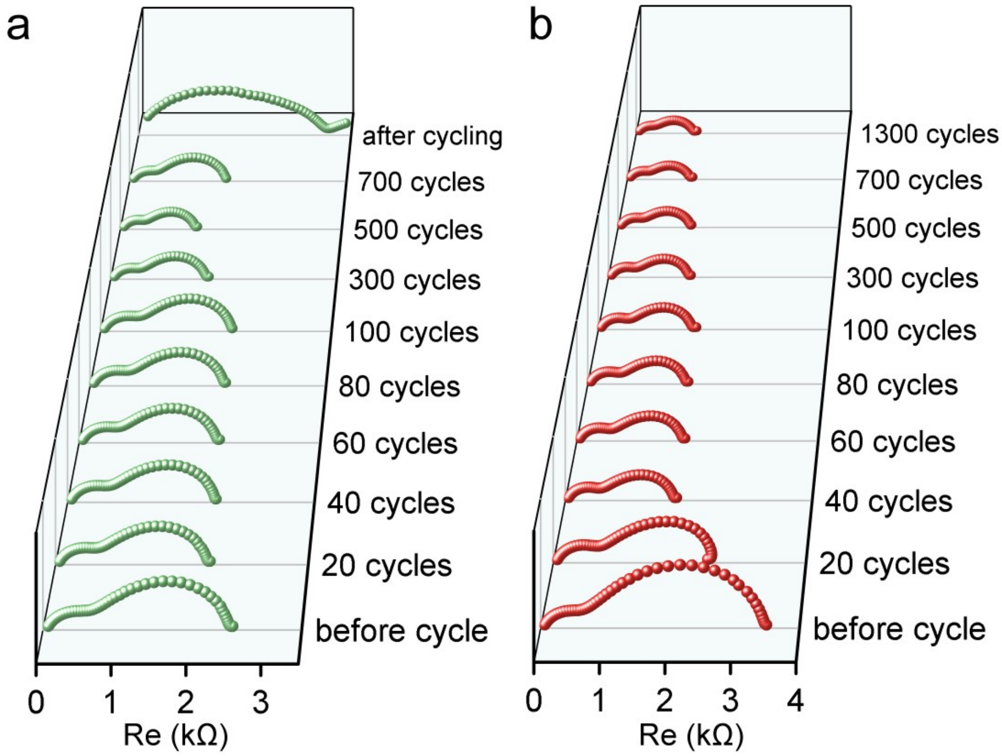

Figure S6. The impedance changes of the (a) PEO modified LATP and (b) PEO_LZP modified LATP during cycling at 0.20 mA cm^{-2}.

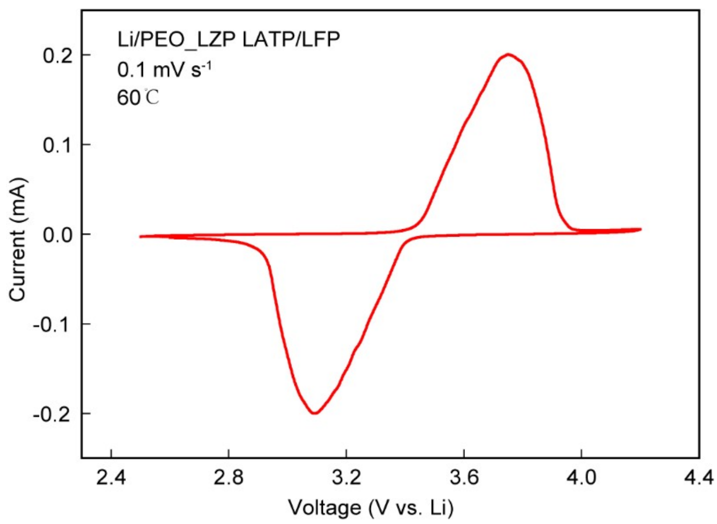

Figure S7. The CV curve of the Li/PEO_LZP LATP/LFP full cell.

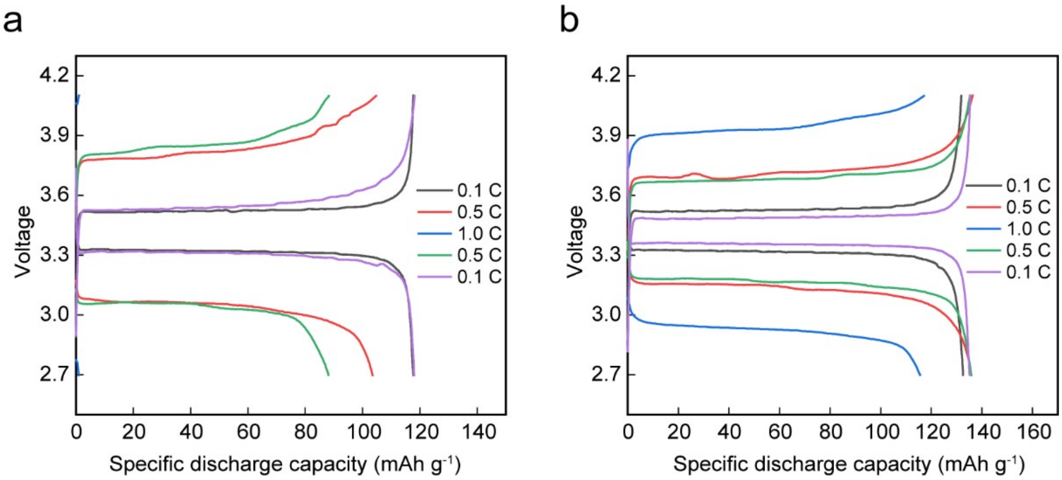

Figure S8. The charge/discharge profiles of the full cells assembled with the (a) PEO modified and (b) PEO_LZP modified LATP pellet at different rate.

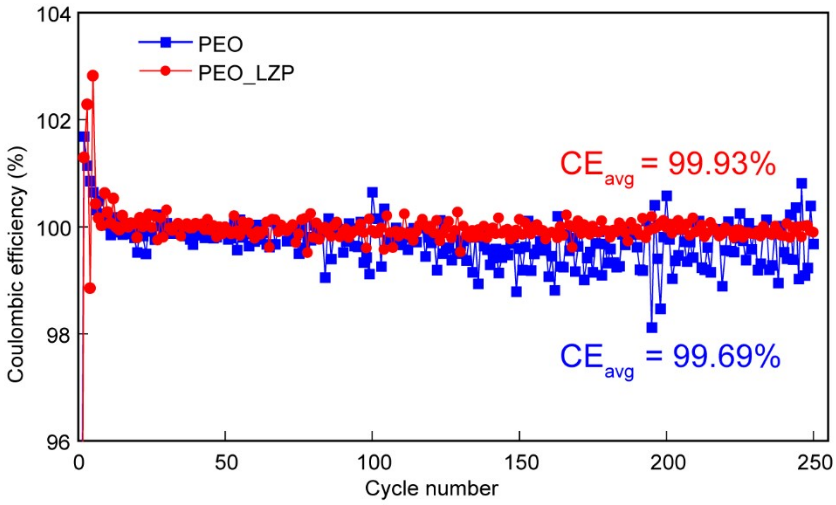

Figure S9. The coulombic efficiency of the full cells at 0.5 C.

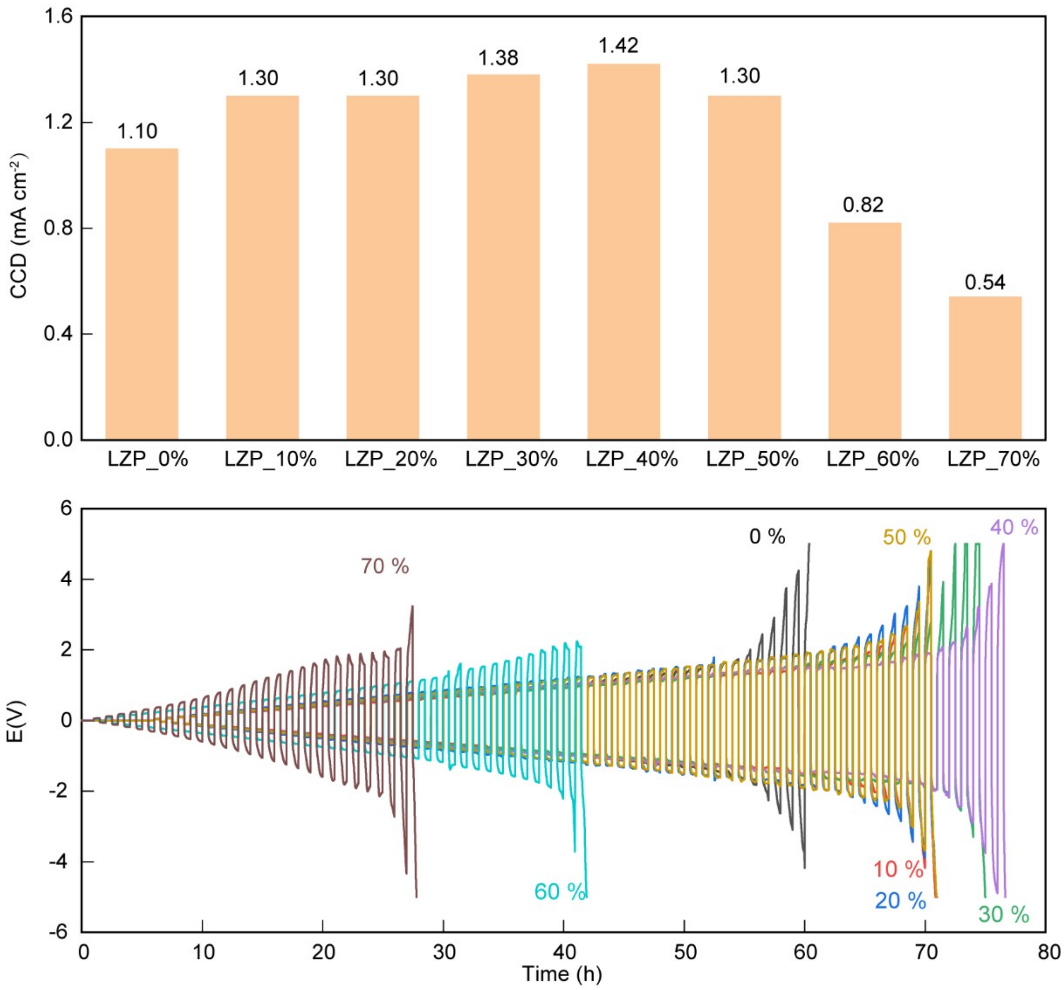

Figure S10. The CCD results of the PEO_LZP modified LATP with different LZP content when the addition of the modification solution was 30 μL.

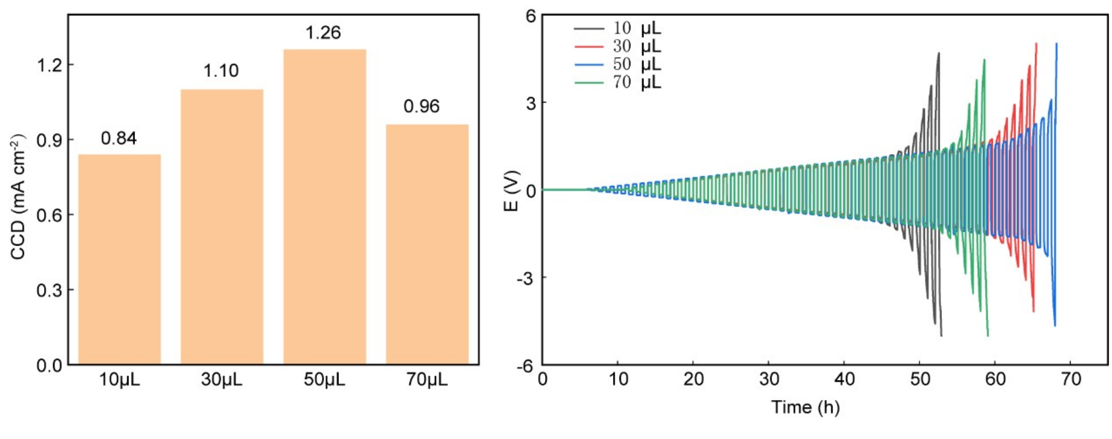

Figure S11. The CCD results of the PEO modified LATP with different addition of modification solution.

Table S1. Summary of various LATP/LAGP based high-performance electrolytes for all-Solid-State Lithium Batteries

No.	Electrolyte	Modification layer	Symmetric cell: Current density/Cycle number		Full cell: With liquid electrolyte/C rate/Cycle number/Capacity retention				mechanism	Ref.
1	LATP	PEO/PAN	0.2	1000	Y	0.5	120	89	Antioxidative PAN and PEO that inhibits reduction reaction	1
2	LAGP	Graphite/PEO	0.1	1000	N	0.1	100	/	Graphite can serve as redox reaction sites and second current collector and PEO that inhibits reduction reaction	2
3	LATP	PVDF-HFP	0.16	400	Y	1.0	300	97.2	Endowing the interface with improved contact, favorable Li^+ diffusion and inhibiting interfacial reactions	3
4	LATP	PEO	0.10	200	N	0.3	100	/	As a interfacial adhesive with perfect compatibility	4
5	LATP	PEO	0.05	400	N	0.05	45	93.3	Avoiding side reactions and ensuring intimate contact with high viscosity	5
6	LAGP	MOF/PEO	0.15	400	N	0.1	60	79.7	Preventing the redox reaction, providing intimate contact and Li^+ transport pathways	6
7	LATP	BN/PEO	0.3	500	Y	0.5	500	99.9	Facilitating ion transport and reducing interfacial impedance	7
8	LAGP	GPE	0.5	400	N	0.3	300	93.4	Improving the compatibility and charge transfer kinetics at the interface, avoiding the danger of thermal runaway	8
9	LATP	SnO_2	1.0	1000	Y	0.1	200	90.17	Achieving intimate	9

									contact and in-situ forming SEI that regulates uniform lithium deposition	
10	LAGP	LiPON/Li	0.1	150	Y	1	100	88.2	Providing good contact and chemical stability that blocks the reduction of Ge^{4+}	10
11	LAGP	Al	0.1	1200	Y	0.1	160	/	Inducing the uniform distribution of electric field and accelerating the diffusion of Li atoms	11
12	LATP	Al/LiF	0.1	900	Y	0.5	350	83.2	Promoting the interfacial stability by the increased barrier width and homogenized electric field	12
13	LATP	BTO/PVDF-TrFE-CTFE	0.2	2000	N	0.5	250	78.6	Reducing the interfacial impendence and inducing the uniform Li deposition	13
14	LAGP	C_3N_4	0.3	3000	Y	0.1	300	82.8	Inhibiting side reactions and guiding uniform Li deposition	14
15	LAGP	ZnF_2	0.1	1000	Y	0.1	40	/	Inhibiting side reactions and dendrite Li, enabling the uniform Li^+ flux distribution	15
16	LATP	Al/PEO	0.2	5000	Y	0.5	500	88.9	Homogenizing the electric field distribution and interphases growth, protecting LATP from electron attack	16
17	LATP	BN/CMC	0.2	1200	Y	0.5	500	92.0	Reducing interfacial resistance, motivating Li^+ migration and improving interfacial compatibility	17
18	LATP	MoS_2/PEO	0.2	800	Y	1.0	400	86.2	Promoting interfacial ion transport and improving interfacial contact	18

19	LATP	$SnCl_4$	0.2	4000	Y	0.5	420	90.4	Improving interfacial contact, avoiding side reactions and guiding uniform Li deposition	19
20	LATP	g-C_3N_4/PEO	0.1	670	N	0.1	100	86	Suppressing the side reaction and accelerating interfacial Li^+ conduction	20
21	LATP	CuF_2	0.2	2200	Y	0.5	540	80.3	Improving interfacial contact, avoiding side reactions and guiding uniform Li deposition	21
22	LATP	MOF/PEO	0.2	1600	Y	0.2	200	99.3	Ensuring intimate contact and promoting uniform Li^+ flow	22
23	LATP	PEO/LZP	0.2 0.5	5000 600	N	0.5	250	No degradation	Improving interfacial contact, increasing Young's modulus and promoting interfacial Li^+ conduction	This work

Reference

1. J.-Y. Liang, X.-X. Zeng, X.-D. Zhang, T.-T. Zuo, M. Yan, Y.-X. Yin, J.-L. Shi, X.-W. Wu, Y.-G. Guo and L.-J. Wan, *J. Am. Chem. Soc.*, 2019, **141**, 9165-9169.
2. W. Li, Q. Wang, J. Jin, Y. Li, M. Wu and Z. Wen, *Energy Stor. Mater.*, 2019, **23**, 299-305.
3. L. Pan, S. Sun, G. Yu, X. X. Liu, S. Feng, W. Zhang, M. Turgunov, Y. Wang and Z. Sun, *Chem. Eng. J.*, 2022, **449**, 137682.
4. Z. Yang, H. Yuan, C. Zhou, Y. Wu, W. Tang, S. Sang and H. Liu, *Chem. Eng. J.*, 2020, **392**, 123650.
5. Y. Jin, C. Liu, X. Zong, D. Li, M. Fu, S. Tan, Y. Xiong and J. Wei, *J. Power Sources*, 2020, **460**, 228125.
6. R. Zhao, L. Gao, M. Song, Y. Ye, Z. Liang, J. Bian, J. Zhu, S. Li, R. Zou and Y. Zhao, *ACS Energy Lett.*, 2021, **6**, 3141-3150.

7. Q. Cheng, A. Li, N. Li, S. Li, A. Zangiabadi, T.-D. Li, W. Huang, A. C. Li, T. Jin, Q. Song, W. Xu, N. Ni, H. Zhai, M. Dontigny, K. Zaghib, X. Chuan, D. Su, K. Yan and Y. Yang, *Joule*, 2019, **3**, 1510-1522.
8. W. Lei, C. Zhang, R. Qiao, M. Ravivarma, H. Chen, F. B. Ajdari, M. Salavati-Niasari and J. Song, *ACS Appl. Energy Mater.*, 2023, **6**, 4363-4371.
9. L. Wang, L. Wang, Q. Shi, C. Zhong, D. Gong, X. Wang, C. Zhan and G. Liu, *J. Energy Chem.*, 2023, **80**, 89-98.
10. S. Lee, S. Jung, S. Yang, J.-H. Lee, H. Shin, J. Kim and S. Park, *Appl. Surf. Sci.*, 2022, **586**, 152790.
11. S. Zhang, Q. Sun, G. Hou, J. Cheng, L. Dai, J. Li and L. Ci, *Nano Res.*, 2023, **16**, 6825-6832.
12. L. Luo, F. Zheng, H. Gao, C. Lan, Z. Sun, W. Huang, X. Han, Z. Zhang, P. Su and P. Wang, *Nano Res.*, 2023, **16**, 1634-1641.
13. T. Gu, L. Chen, Y. Huang, J. Ma, P. Shi, J. Biao, M. Liu, W. Lv and Y. He, *Energy & Environ. Mater.*, 2023, **6**, e12531.
14. C. Cui, C. Zeng, G. Huang, X. Feng, Y. Zhang, T. Zhai and H. Li, *Adv. Energy Mater.*, 2022, **12**, 2202250.
15. J. Yu, Q. Liu, X. Hu, S. Wang, J. Wu, B. Liang, C. Han, F. Kang and B. Li, *Energy Stor. Mater.*, 2022, **46**, 68-75.
16. L. Luo, Z. Sun, H. Gao, C. Lan, X. Huang, X. Han, P. Su, Z. Zhang, C. Li and W. Huang, *Adv. Energy Mater.*, 2023, **13**, 2203517.
17. L. Zhu, Y. Wang, Y. Wu, W. Feng, Z. Liu, W. Tang, X. Wang and Y. Xia, *Adv. Funct. Mater.*, 2022, **32**, 2201136.
18. Q. Xia, S. Yuan, Q. Zhang, C. Huang, J. Liu and H. Jin, *Adv. Sci.*, 2024, **11**, 2401453.
19. D. Ding, H. Tao, X. Fan, X. Yang and L. Z. Fan, *Adv. Funct. Mater.*, 2024, **34**, 2401457.
20. J. Chen, G. Liu, P. Zhai, Y. Wan and X. Guo, *ACS Appl. Mater. Interfaces*, 2024, **16**, 33388-33395.
21. D. Ding, H. Ma, H. Tao, X. Yang and L.-Z. Fan, *Chem. Sci.*, 2024, **15**, 3730-3740.

22. H. Bao, D. Chen, J. Cao, P. Jiang, K. Li, R. Liu, Y. Zhao, Y. Zheng, B. Liao and Y. Zhang, *J. Energy Chem.*, 2024, **95**, 511-518.