

Surface-modified BaTiO₃ as a functional filler in poly(ethylene oxide)-based solid polymer electrolytes for lithium-metal batteries

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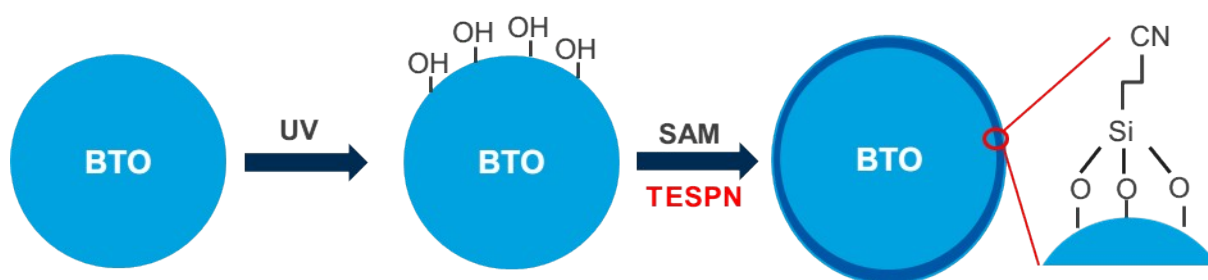


Figure S1. Schematic diagram of the coating process of BTO@TESPN.

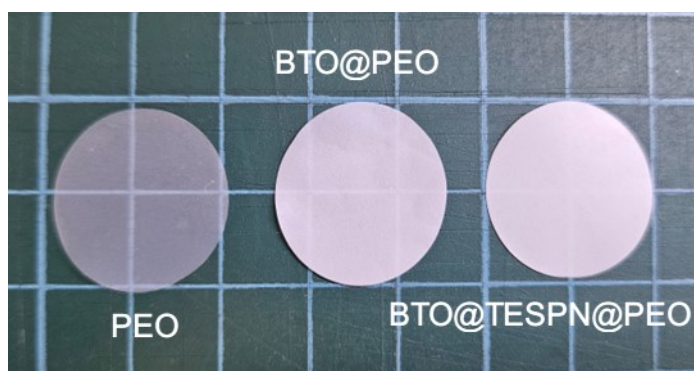


Figure S2. Optical photographs of PEO, BTO@PEO and BTO@TESPN@PEO electrolytes.

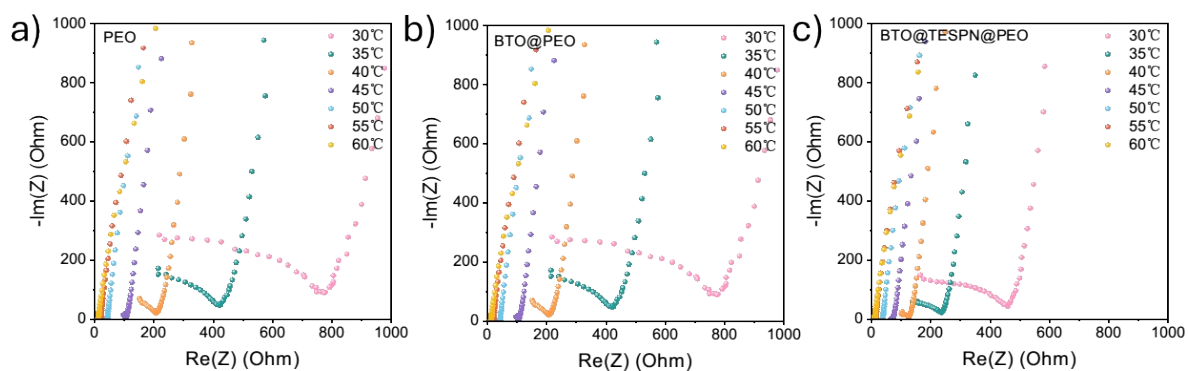


Figure S3. Electrochemical impedance plots of a) PEO, b) BTO@PEO, c) BTO@TESPN@PEO electrolytes in stainless steel-stainless steel symmetric cells at 30-60 °C.

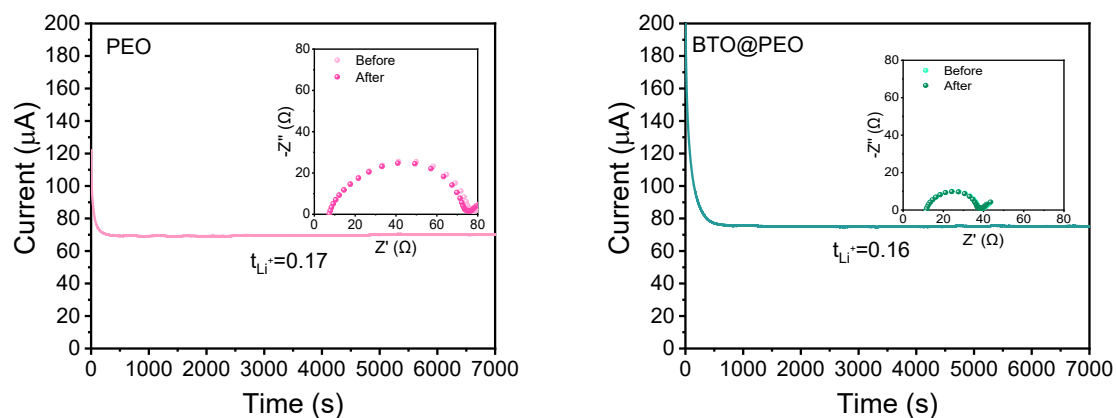


Figure S4. Li-transfer number of PEO and BTO@PEO SPE.

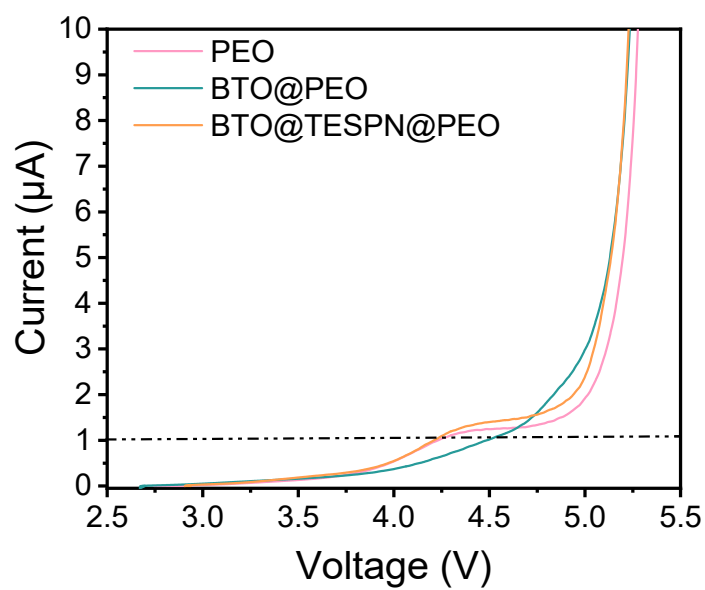


Figure S5. Linear sweep voltammetry plots of PEO, BTO@PEO and BTO@TESPN@PEO electrolytes at a scan rate of 0.1 mV s^{-1} at 60°C with stainless steel working electrode and Li counter electrode.

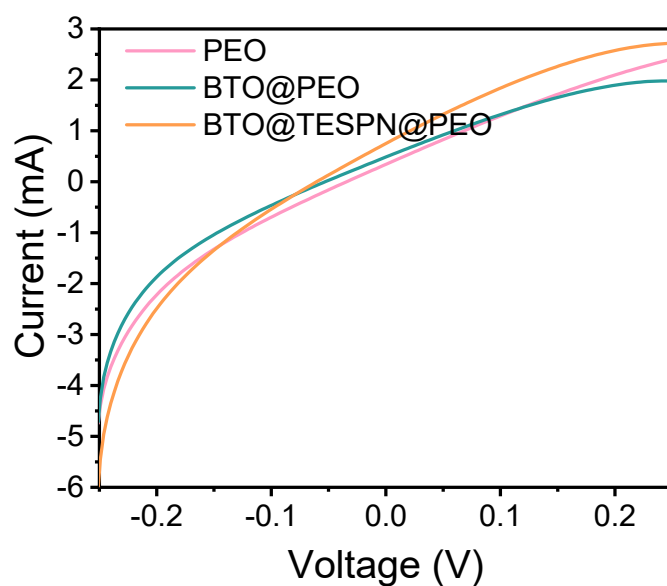


Figure S6. Linear sweep voltammograms of Li-Li symmetric cell with PEO, BTO@PEO and BTO@TESPN@PEO electrolytes from -0.25 V to 0.25 V with a scan rate of 1 mV s⁻¹.

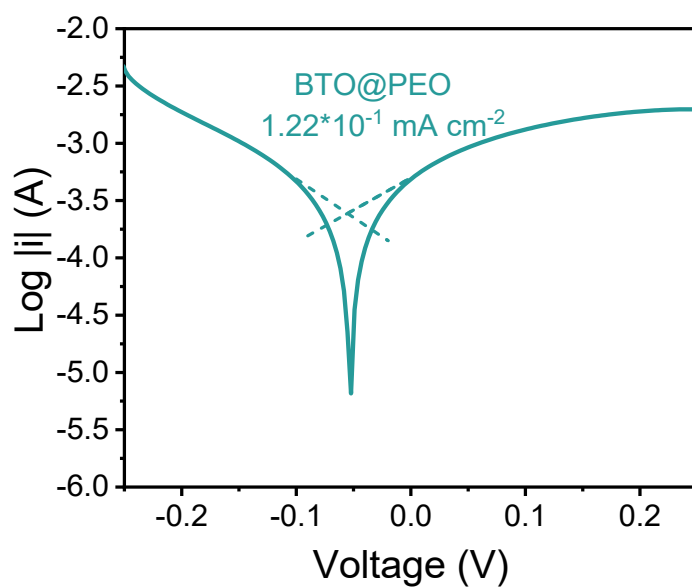


Figure S7. Tafel plots and exchange current density of BTO@PEO obtained from the linear sweep voltammetry tests in the range of -0.25 V to 0.25 V

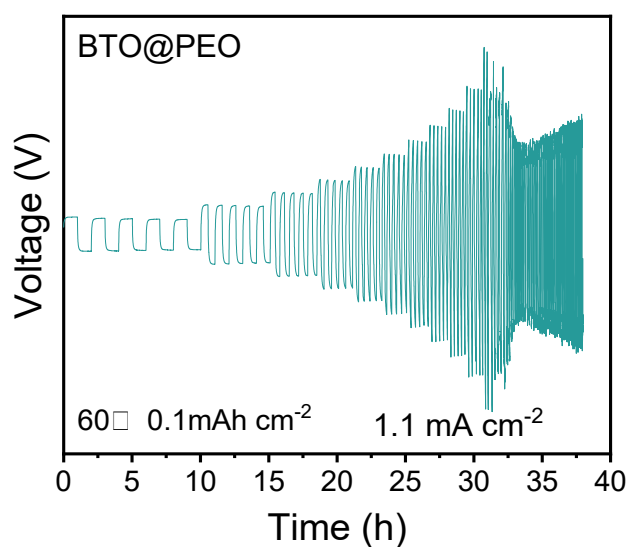


Figure S8. Critical current density of symmetric cells with BTO@PEO electrolytes from a rate-performance test with a capacity of 0.1 mAh cm^{-2} per half cycle.

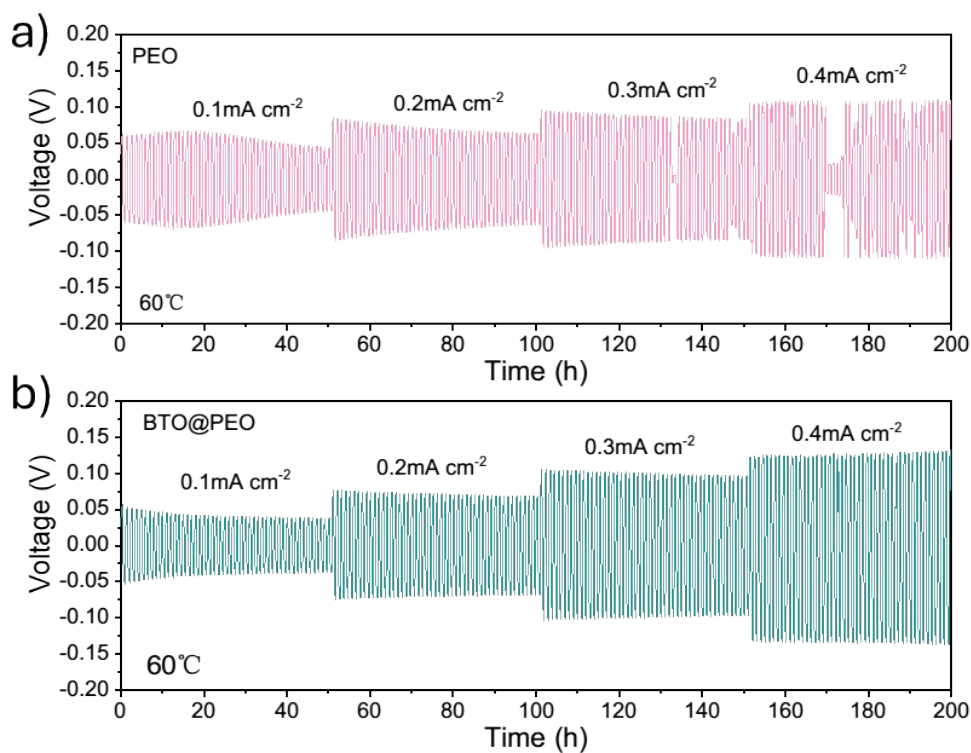


Figure S9. Galvanostatic cycling of Li-Li symmetric cell with a) PEO, b) BTO@PEO from 0.1 to 0.4 mA cm^{-2} with a capacity limit of 0.05 to 0.2 mAh cm^{-2} (half hour charge/half hour discharge).

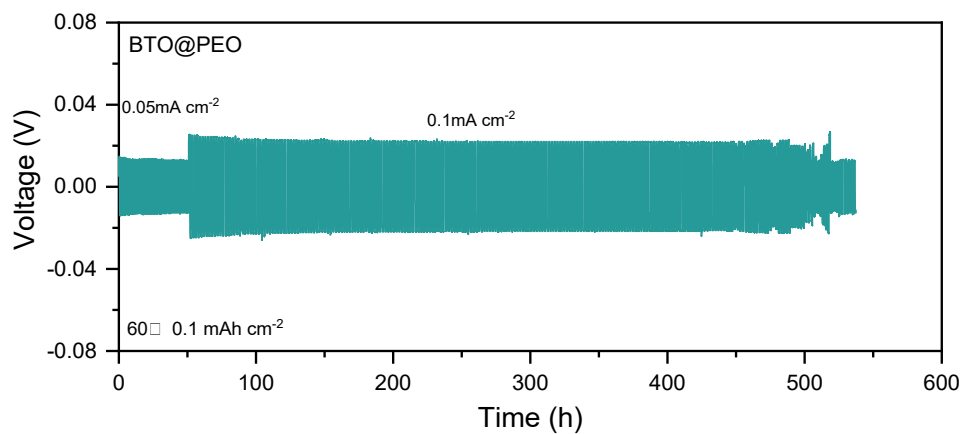


Figure S10. Galvanostatic cycling of Li-Li symmetric cell with BTO@PEO electrolytes with 0.1 mA cm⁻².

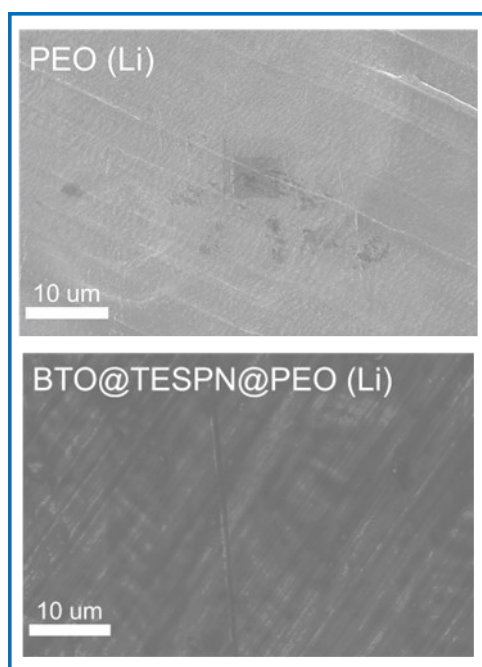


Figure S11. SEM images of Li anode after 10 cycles at 0.1 mA cm⁻²/0.1 mAh cm⁻² with PEO and BTO@TESPN@PEO electrolytes.

Table S1. Comparison of capacity of PEO-based electrolyte

Electrolyte compositions	Li ⁺ :EO	Specific capacity (mAh g ⁻¹)	Cycle number	Capacity retention	Working temperature (°C)	Current density
PEO+LLZO+SCN ^[1]	1:18	130.2	500	80%	60	1.0 C
PEO+SN+LiAlO ₂ ^[2]	1:10	141.3	25	84.9%	60	1.0 C
PEO+LLZTO+SN ^[3]	1:18	151.1	200	98%	60	0.5 C
PEO+LLZTO@PDA ^[4]	1:8	142.6	50	99%	50	0.2 C
PEO+PI ^[5]	1:15	138	300	96%	60	0.5 C
PEO+MOF ^[6]	1:18	151	100	95%	60	0.5 C
PEO+aligned LAGP ^[7]	1:8	148.7	300	93.3%	60	0.3 C
PEO+LLZO ^[8]	1:16	162.7	120	91.7%	60	0.1 C
PEO+KPF ₆ ^[9]	1:16	142.1	200	91.3%	60	0.5 C
PEO+H ₂ TPP(PEG) ₄ ^[10]	-	158.2	120	97.1%	60	0.2 C
PEO+LS-AFE ^[11]	1:16	112.4	150	96.7%	60	2.0 C
PEO+SBA-LiIL ^[12]	1:16	150.3	90	88.4%	60	0.07 C
PEO+HPEA ^[13]	1:26	155.4	110	90.8%	50	0.1 C
PEO+BTO@TESPN (our work)	1:20	155.4	700	93.0%	60	0.5 C

References

- [1] F. Chen, W. Zha, D. Yang, S. Cao, Q. Shen, L. Zhang, D. R. Sadoway, *J. Electrochem. Soc.* **2018**, *165*, A3558.
- [2] N. Zhang, J. He, W. Han, Y. Wang, *J. Mater. Sci.* **2019**, *54*, 9603.
- [3] W. Zha, F. Chen, D. Yang, Q. Shen, L. Zhang, *J. Power Sources* **2018**, *397*, 87.
- [4] Z. Huang, W. Pang, P. Liang, Z. Jin, N. Grundish, Y. Li, C.-A. Wang, *J. Mater. Chem. A* **2019**, *7*, 16425.
- [5] J. Wan, J. Xie, X. Kong, Z. Liu, K. Liu, F. Shi, A. Pei, H. Chen, W. Chen, J. Chen, X. Zhang, L. Zong, J. Wang, L.-Q. Chen, J. Qin, Y. Cui, *Nat. Nanotechnol.* **2019**, *14*, 705.
- [6] J.-F. Wu, X. Guo, *J. Mater. Chem. A* **2019**, *7*, 2653.
- [7] X. Wang, H. Zhai, B. Qie, Q. Cheng, A. Li, J. Borovilas, B. Xu, C. Shi, T. Jin, X. Liao, Y. Li, X. He, S. Du, Y. Fu, M. Dontigny, K. Zaghib, Y. Yang, *Nano Energy* **2019**, *60*, 205.
- [8] Z. Wan, D. Lei, W. Yang, C. Liu, K. Shi, X. Hao, L. Shen, W. Lv, B. Li, Q.-H. Yang, F. Kang, Y.-B. He, *Adv. Funct. Mater.* **2019**, *29*, 1805301.
- [9] J. Li, J. Liang, Z. Ren, C. Shi, Y. Li, L. Zhang, Q. Zhang, C. He, X. Ren, *Electrochimica Acta* **2022**, *429*, 141061.
- [10] Q. Zeng, P. Chen, Z. Li, X. Wen, W. Wen, Y. Liu, H. Zhao, S. Zhang, H. Zhou, L. Zhang, *ACS Appl. Mater. Interfaces* **2021**, *13*, 48569.
- [11] Z. Shi, W. Guo, L. Zhou, Q. Xu, Y. Min, *J. Mater. Chem. A* **2021**, *9*, 21057.
- [12] X. Shen, R. Li, H. Ma, L. Peng, B. Huang, P. Zhang, J. Zhao, *Solid State Ion.* **2020**, *354*, 115412.
- [13] P. Chen, X. Liu, S. Wang, Q. Zeng, Z. Wang, Z. Li, L. Zhang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 43146.