

Supporting Information

Multi-functional groups decorated composite nanofiber separator with excellent chemical stability in ester-based electrolyte for enhancing the lithium-ion transport

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Table S1 Performance comparison between the separators in this work and those

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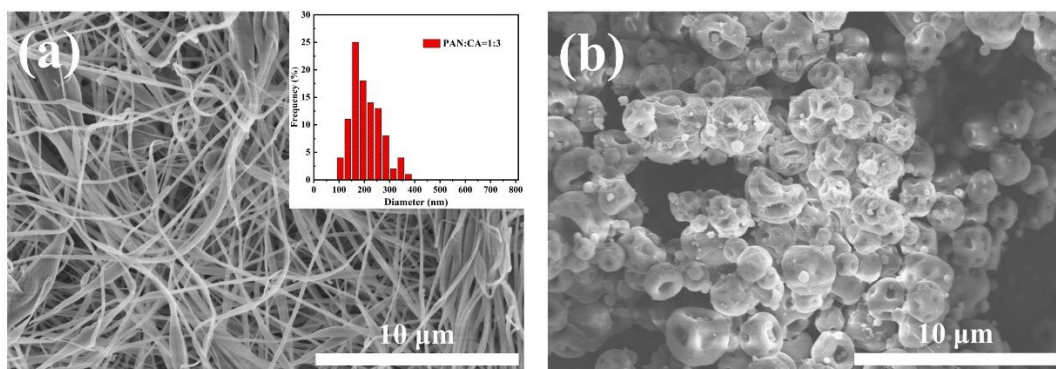


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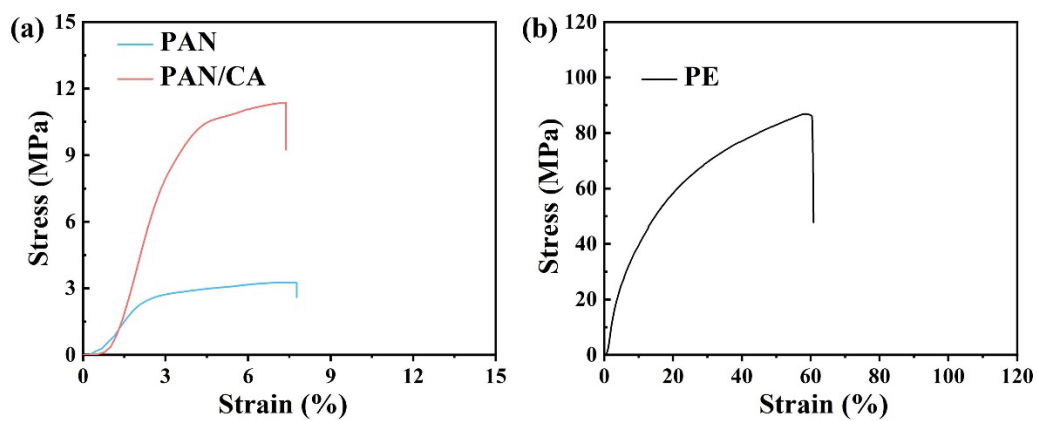


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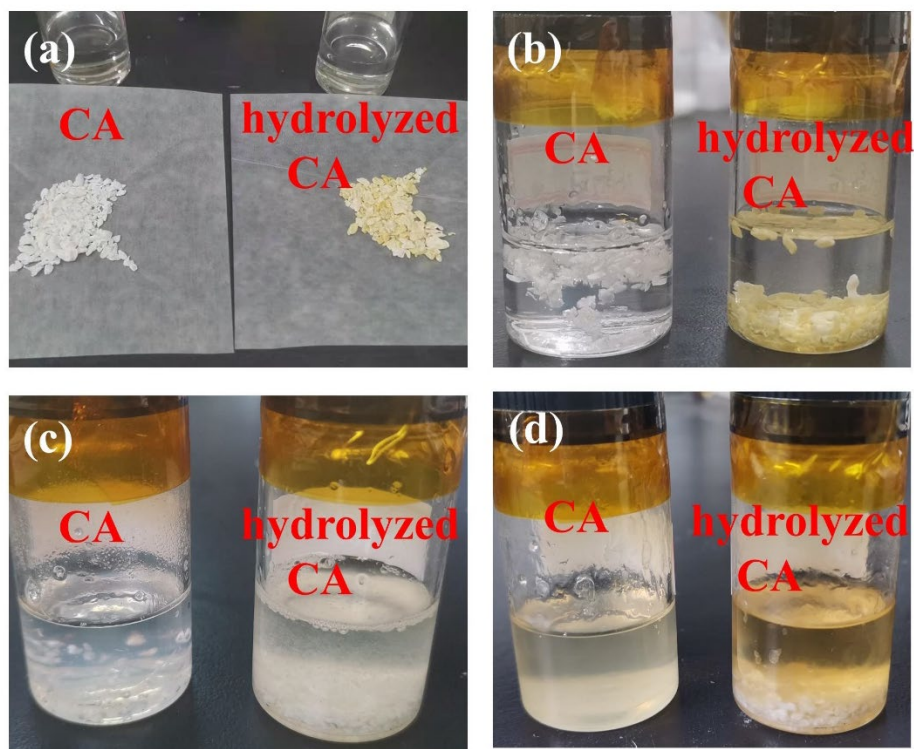


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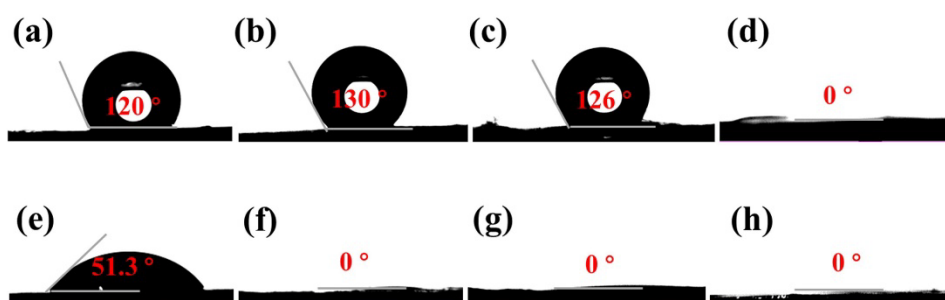


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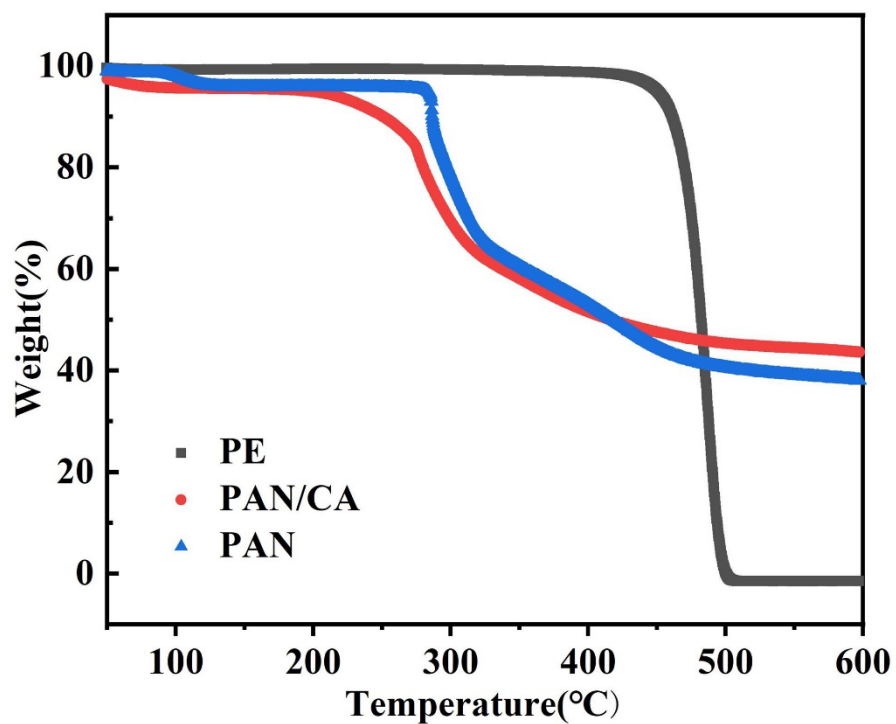


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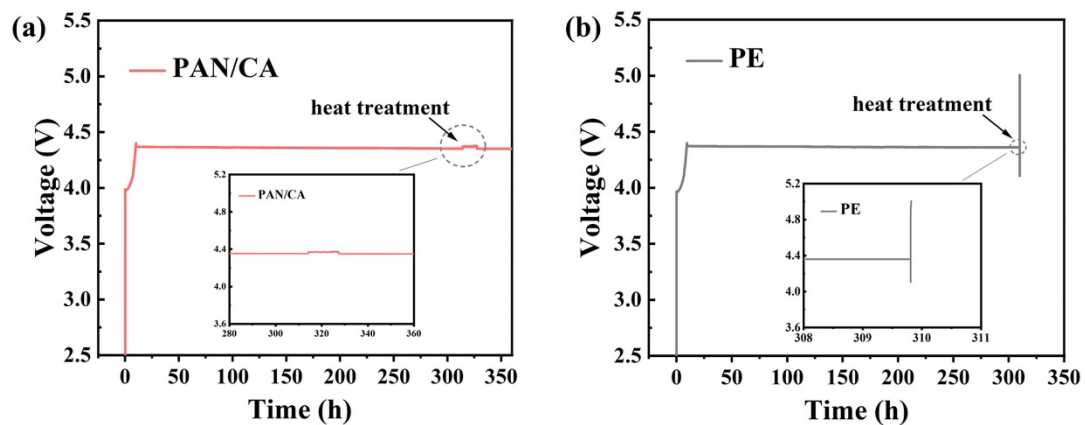


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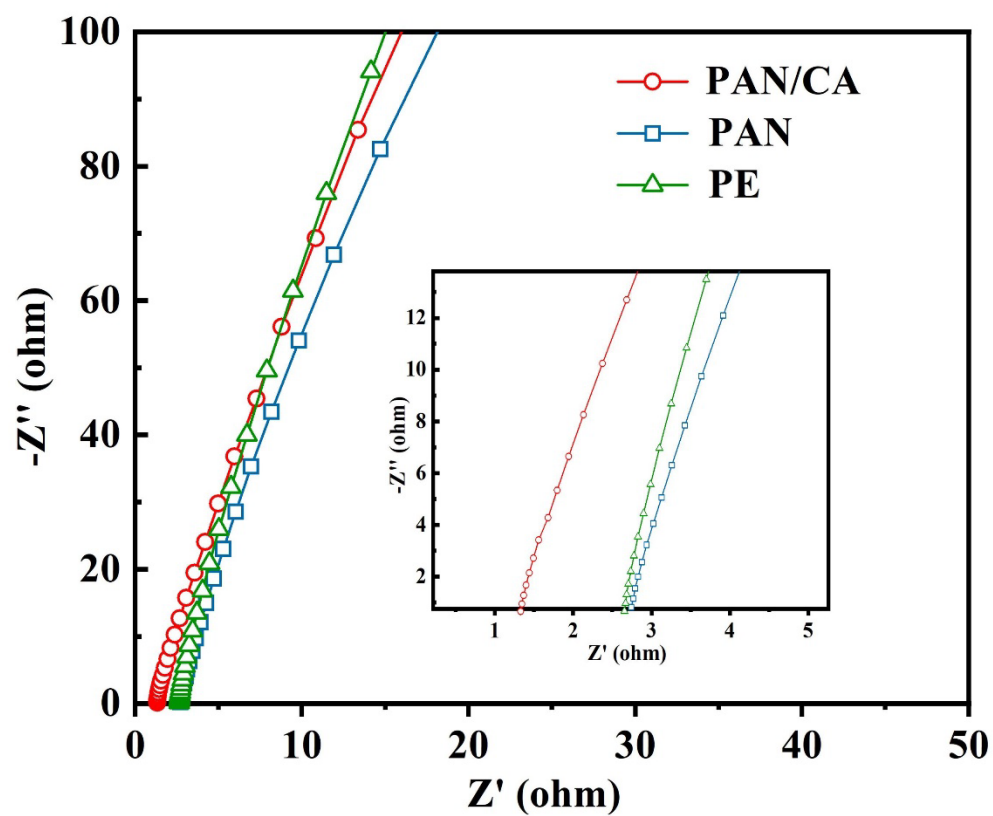


Figure S7. Nyquist plots of PAN/CA, PAN and PE separators assembled in SS symmetrical cells.

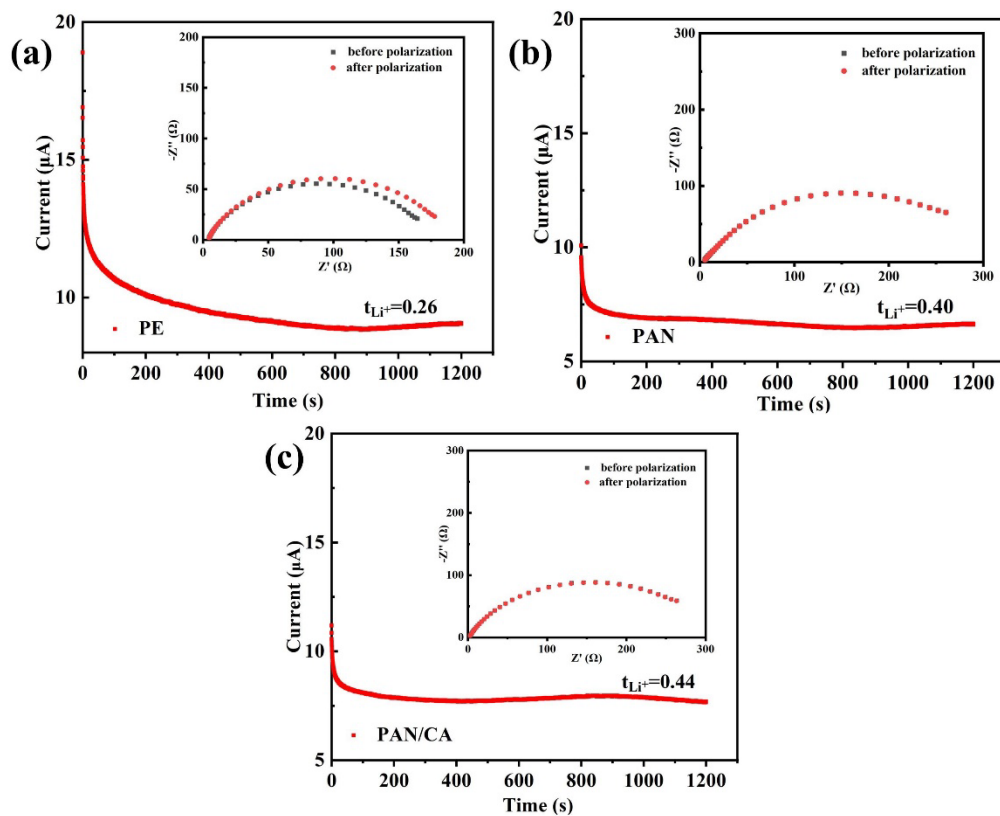


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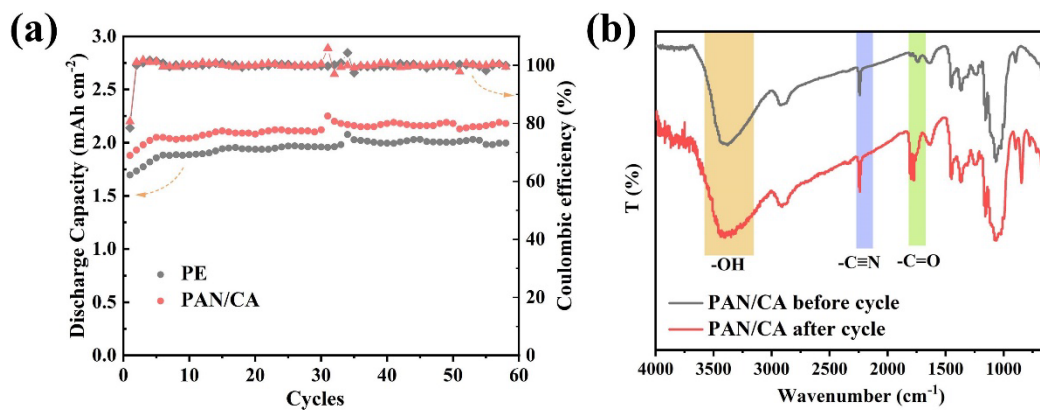


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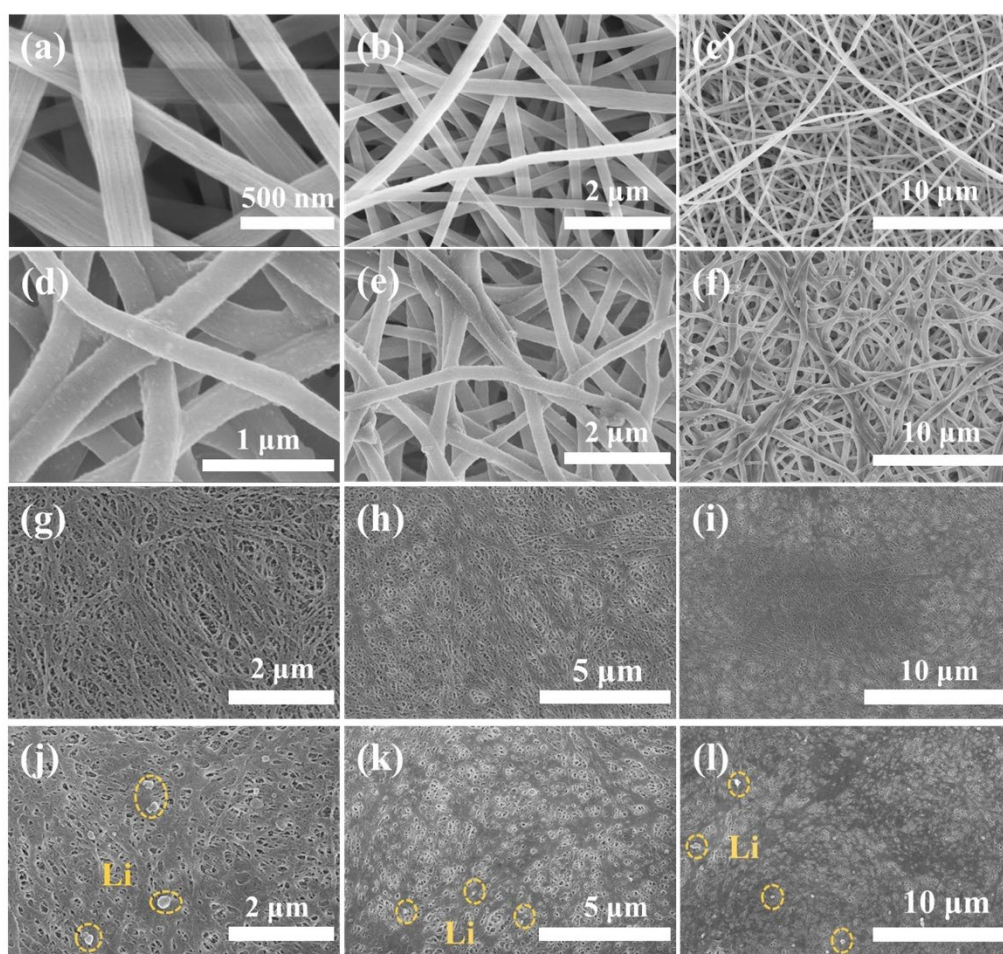


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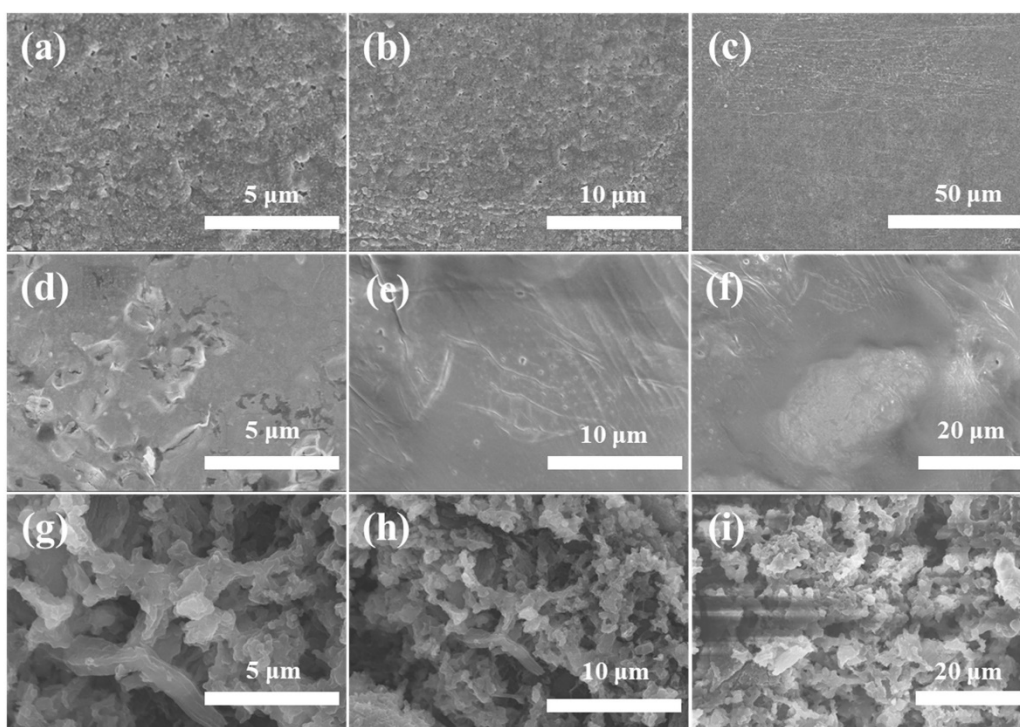


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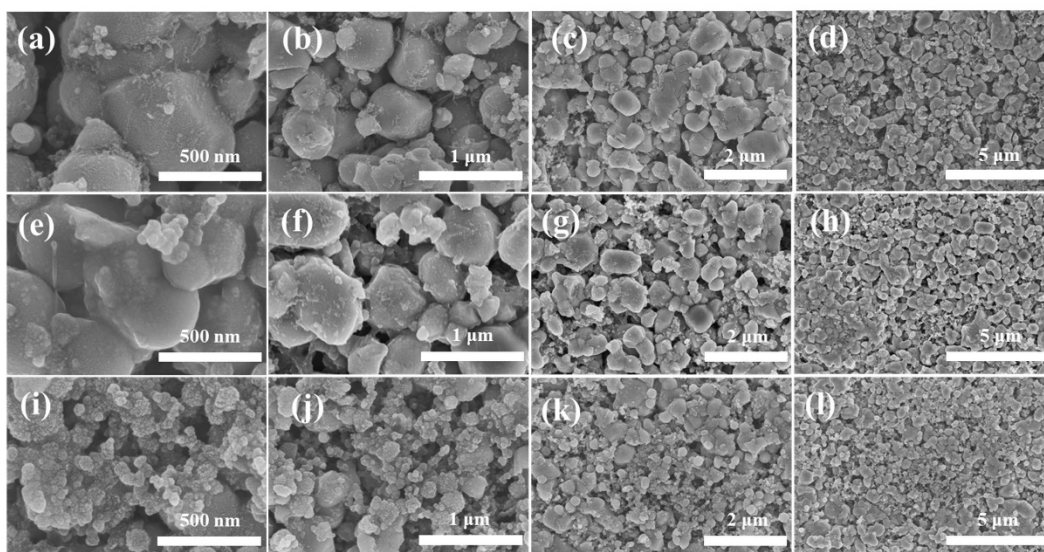


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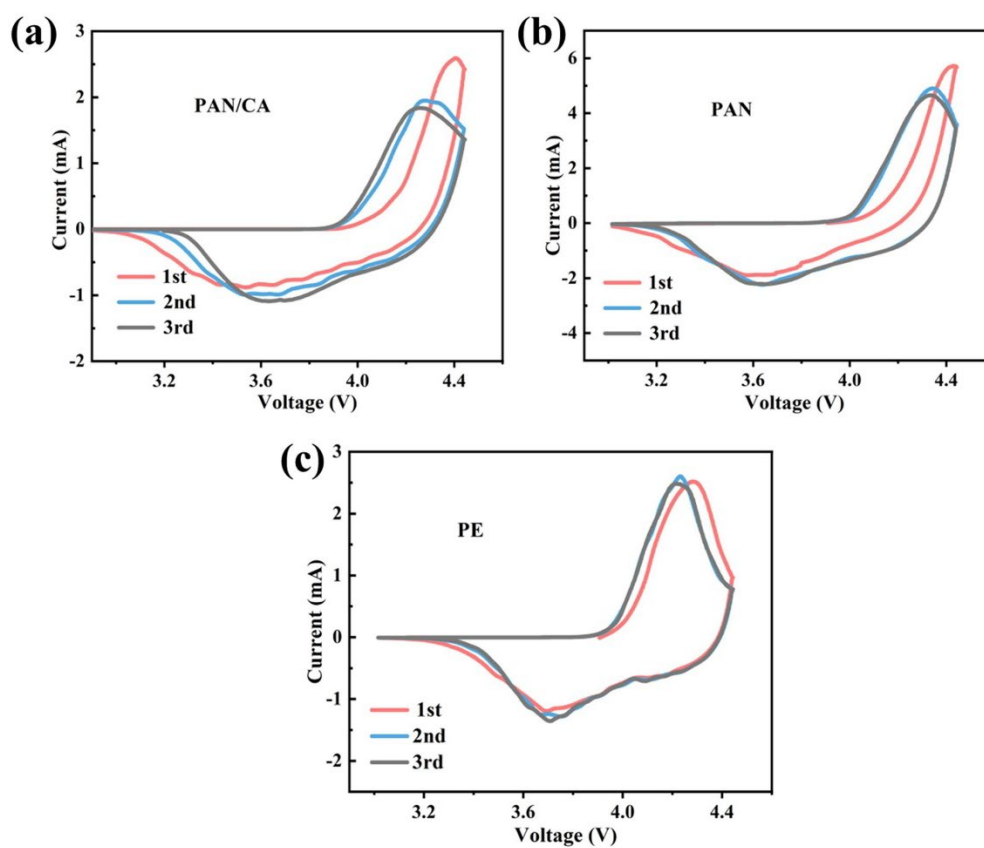


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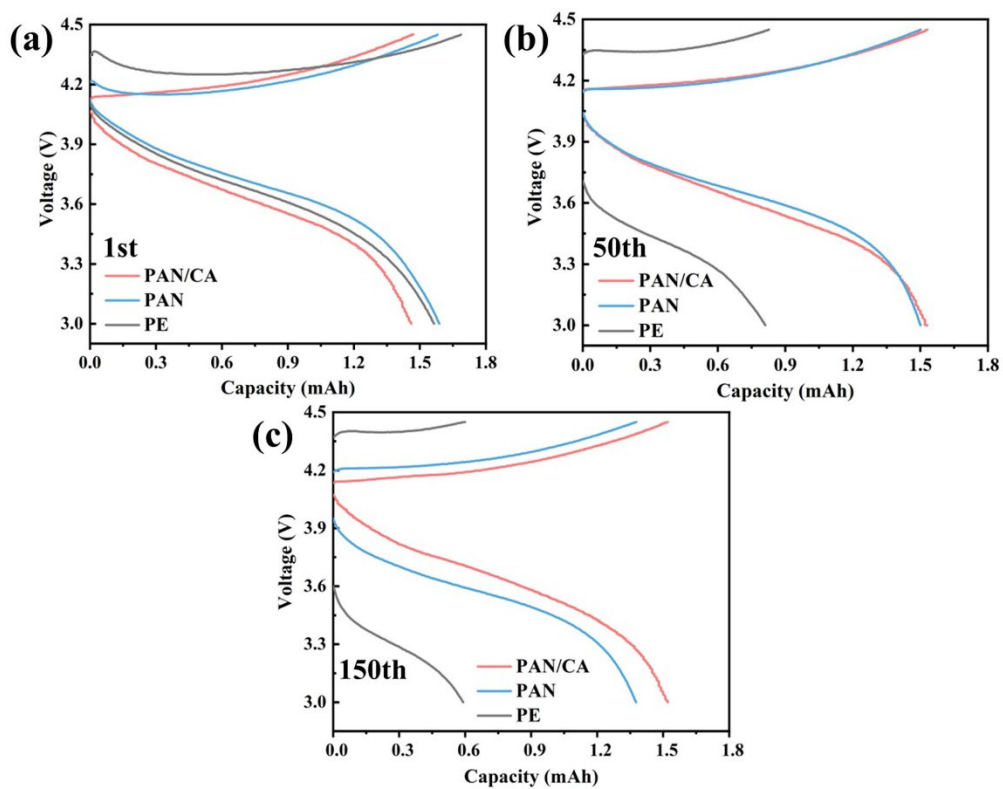


Figure S14. Discharge capacity -Voltage curves with different separators under different cycles: (a) 1st cycle; (b) 50th cycle; (c) 150th cycle.

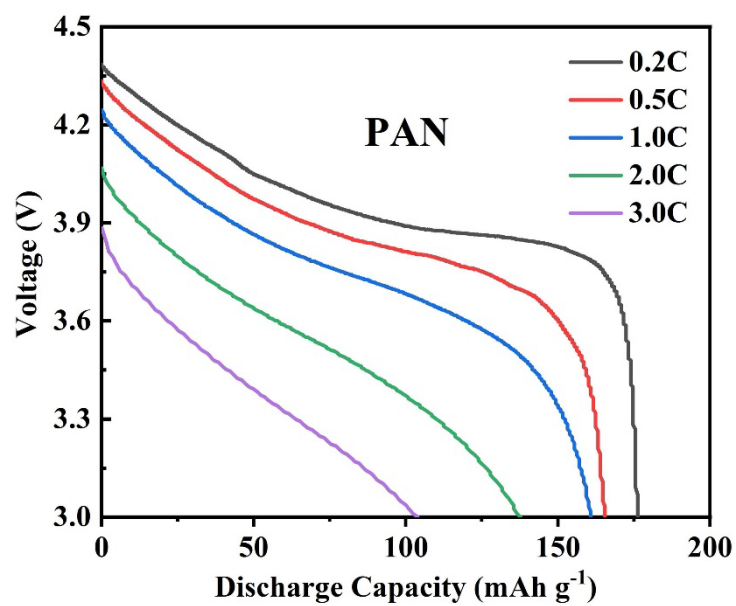


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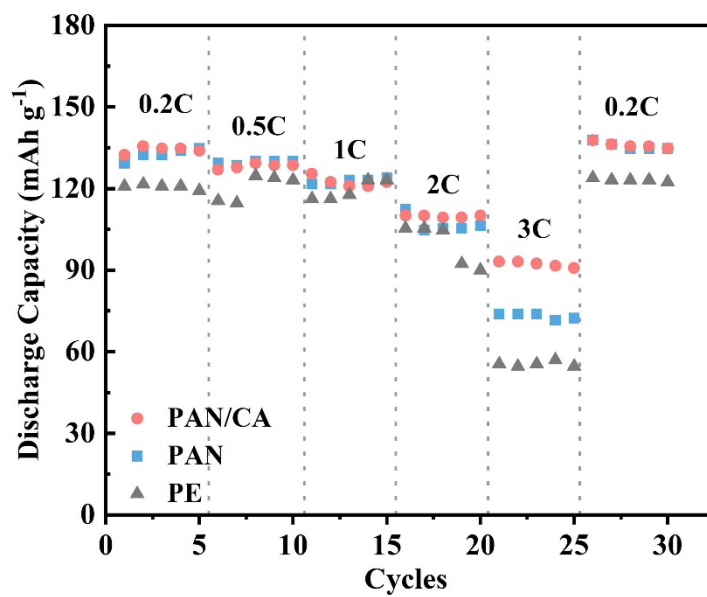


Figure S16. Rate performance of LiFePO₄/Li cells assembled with PAN/CA composite nanofiber separator, PAN nanofiber separator and PE separator.

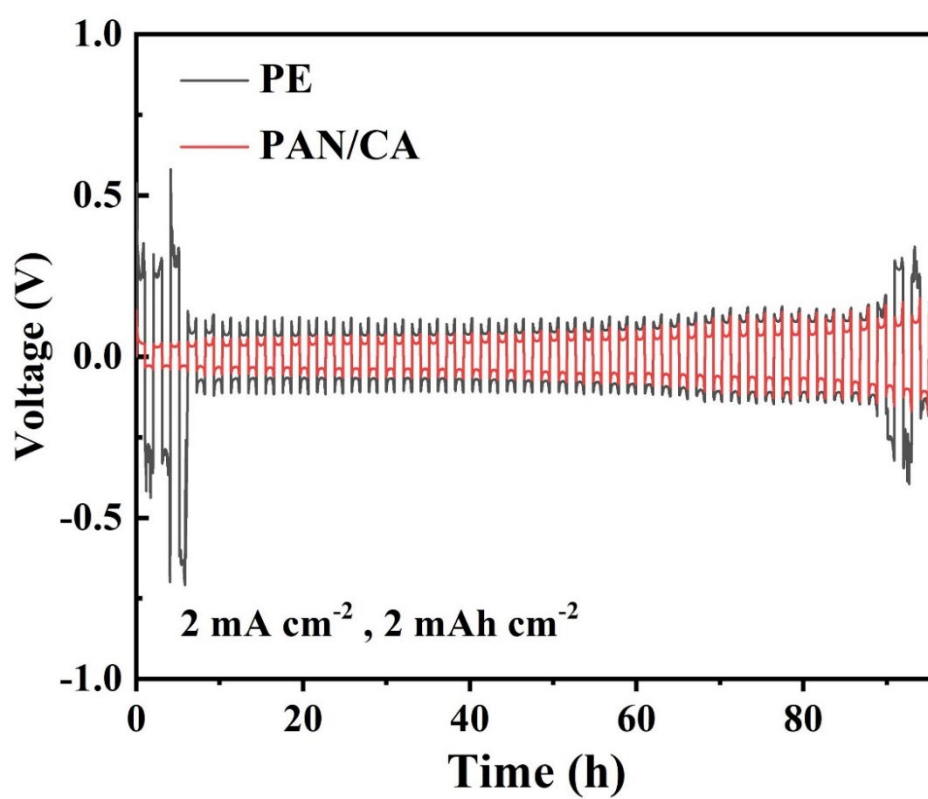


Figure S17. Charge-discharge voltage-time profiles of Li-symmetrical cells assembled with PAN/CA nanofiber separator and PE separator at current density of 2 mA cm^{-2} with an areal capacity of 2 mAh cm^{-2} .

Table S1. Performance comparison between the separators in this work and those reported in the Literature.

| separator | condition | σ (ms cm ⁻¹) | capacity | ref. |
|--|--|---------------------------------|--|------------------|
| PVDF-HFP/LAGP nanofiber separator | LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂ with 6.0 mg cm ⁻² | from 0.70 to 3.18 | 144.7 mAh g ⁻¹ (84.5%) after 500 cycles; 0.2C | 1 |
| CCN separator | LiFePO ₄ | from 0.31 to 0.45 | 99.4 mAh g ⁻¹ (64.1%) after 300 cycles; 1C | 2 |
| PI/SiO ₂ nanofiber separator | LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂ | from 0.52 to 1.55 | 149.6 mAh g ⁻¹ (88%) after 100 cycles; 1C | 3 |
| PAN nanofiber separator | LiMn ₂ O ₄ with 16.6 mg cm ⁻² | from 0.59 to 1.06 | 89.5 mAh g ⁻¹ (99.4%) after 100 cycles; 0.5C | 4 |
| SiO ₂ /PAN cross-linked separator | LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂ with 2.0 mAh cm ⁻² | from 0.46 to 2.10 | 162.1 mAh g ⁻¹ (94.0%) after 200 cycles; 0.5C | 5 |
| PI-COOH separator | LiCoO ₂ with 11.9 mg cm ⁻² | from 2.11 to 2.50 | 103.7 mAh g ⁻¹ (98.8%) after 100 cycles; 0.5C | 6 |
| Co-SIM-1/PAN separator | LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂ | from 0.90 to 1.62 | 135.2 mAh g ⁻¹ (81.3%) after 250 cycles; 5C | 7 |
| PAN/CA nanofiber separator | LiCoO₂ with 11.5 mg cm⁻² | from 0.306 to 1.15 | 131.3 mAh g⁻¹ (97.5%) after 300 cycles; 1C | This work |

Table S2. Physical properties of PAN/CA nanofiber separator, PAN nanofiber separator and PE separator.

| Separator | PAN/CA | PAN | PE |
|-----------------------------|--------|-------|-------|
| Porosity (%) | 61.47 | 82.54 | 33.51 |
| Thickness (μm) | 24 | 48 | 16 |
| Tensile strength (Mpa) | 11.36 | 3.26 | 86.35 |
| Electrolyte uptake (%) | 604.3 | 707.7 | 121.4 |

Reference

- 1 T. Liang, W. Liang, J. Cao, D. Wu, Enhanced Performance of High Energy Density Lithium Metal Battery with PVDF-HFP/LAGP Composite Separator, *ACS Applied Energy Materials*, 2021, **4**, 2578-2585.
- 2 T.W. Zhang, J.L. Chen, T. Tian, B. Shen, Y.D. Peng, Y.H. Song, B. Jiang, L.L. Lu, H.B. Yao, S.H. Yu, Sustainable Separators for High-Performance Lithium Ion Batteries Enabled by Chemical Modifications, *Adv. Funct. Mater*, 2019, **29**, 1902023.
- 3 D. Wu, N. Dong, R. Wang, S. Qi, B. Liu, D. Wu, In situ construction of High-safety and Non-flammable polyimide “Ceramic” Lithium-ion battery separator via SiO₂ Nano-Encapsulation, *Chem. Eng. J*, 2021, **420**, 129992.
- 4 X. Ma, P. Kolla, R. Yang, Z. Wang, Y. Zhao, A.L. Smirnova, H. Fong, Electrospun polyacrylonitrile nanofibrous membranes with varied fiber diameters and different membrane porosities as lithium-ion battery separators, *Electrochim. Acta*, 2017, **236**, 417-423.
- 5 S. Park, Y. Jung, W. Shin, K.H. Ahn, C.H. Lee, D. Kim, Cross-linked fibrous composite separator for high performance lithium-ion batteries with enhanced safety, *J. Membrane Sci*, 2017, **527**, 129-136.
- 6 C. Lin, H. Zhang, Y. Song, Y. Zhang, J. Yuan, B. Zhu, Carboxylated polyimide separator with excellent lithium ion transport properties for a high-power density lithium-ion battery, *J. Mater Chem A*, 2018, **6**, 991-998.
- 7 L. Yang, J. Cao, B. Cai, T. Liang, D. Wu, Electrospun MOF/PAN composite separator with superior electrochemical performances for high energy density lithium batteries,

Electrochim. Acta, 2021, **382**, 138346.