Supporting Information

Fluorine-rich deep eutectic electrolytes enabling robust interphases and nonflammability of high-voltage lithium metal batteries

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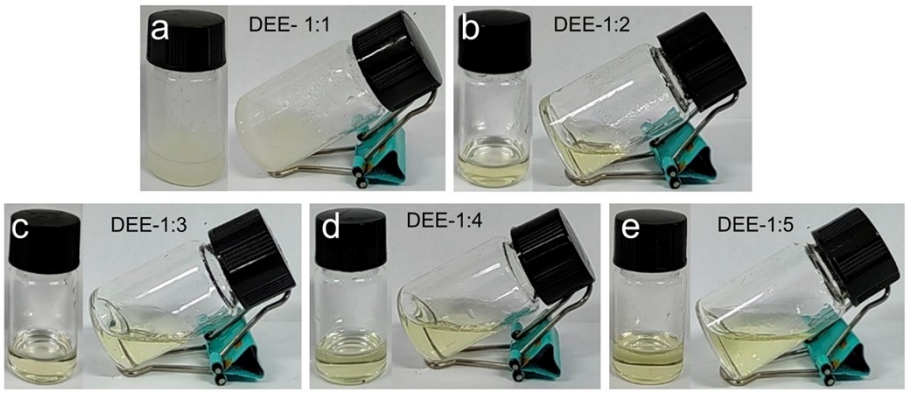

Fig. S1 DEEs formed by CTFP and LiTFSI at various molar ratios.

Fig. S2 Optical diagram of stability of DEE-1:4 solutions at room temperature.

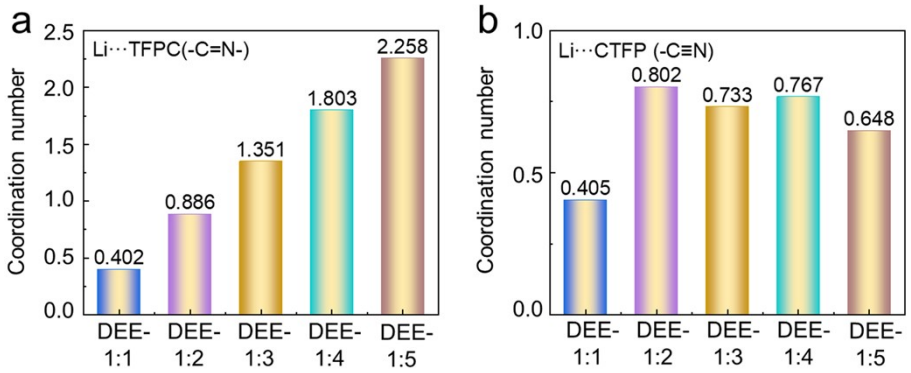

Fig. S3 Calculation of coordination number of DEEs at various molar ratios.

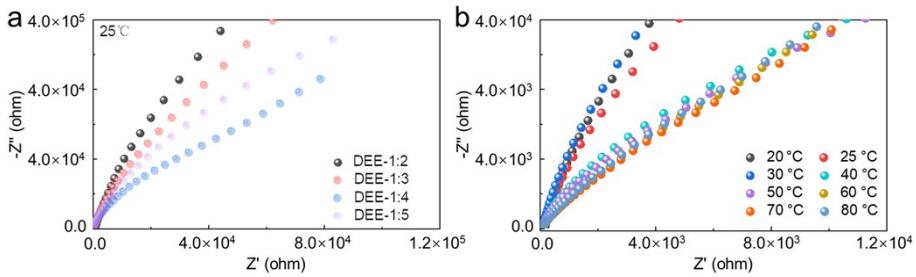

Fig. S4 (a) Impedance diagram of DEEs at various molar ratios at 25 °C. (b) Impedance diagram of the DEE-1:4 at 20 °C to 80 °C.

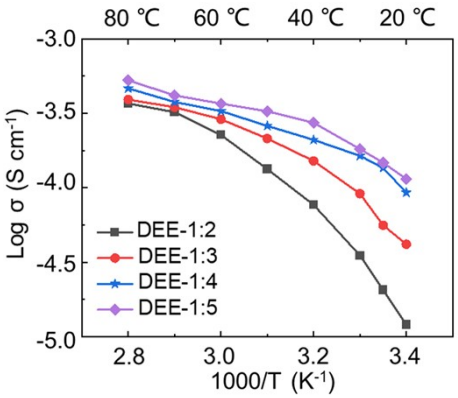

Fig. S5 Temperature dependence of ionic conductivity of DEEs at various molar ratios.

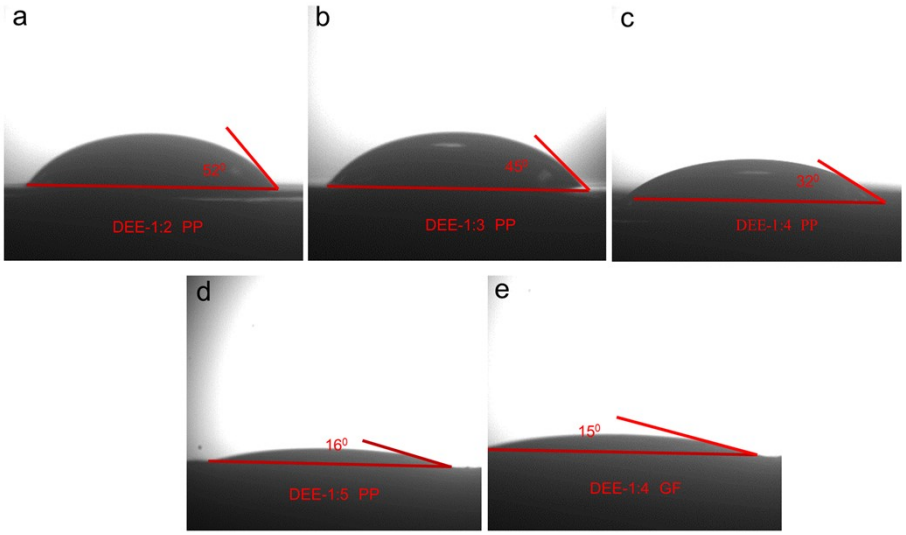

Fig. S6 (a-e) Contact angle test of DEEs at various molar ratios.

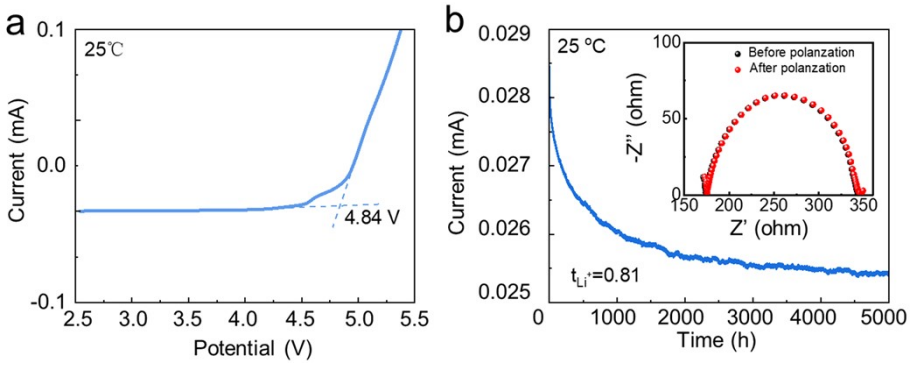

Fig. S7 (a) Electrochemical windows, and (b) Li^+ transference number of the DEE-1:4 at 25 °C.

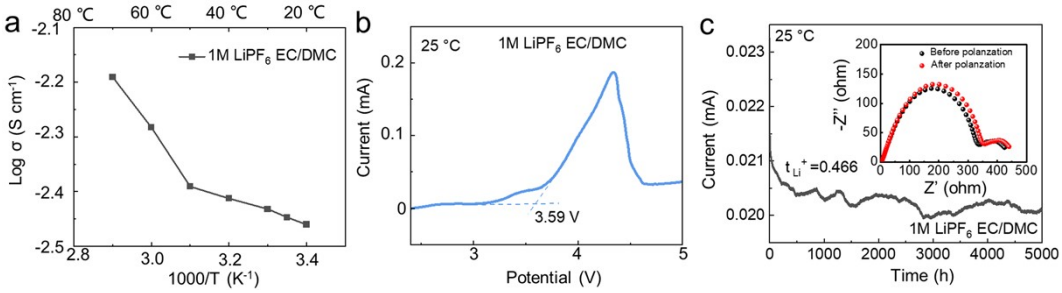

Fig. S8 (a) Temperature dependence of ionic conductivity of 1M $LiPF_6$ EC/DMC at various molar ratios. (b) Electrochemical windows, and (c) Li^+ transference number of the 1M $LiPF_6$ EC/DMC at 25 °C.

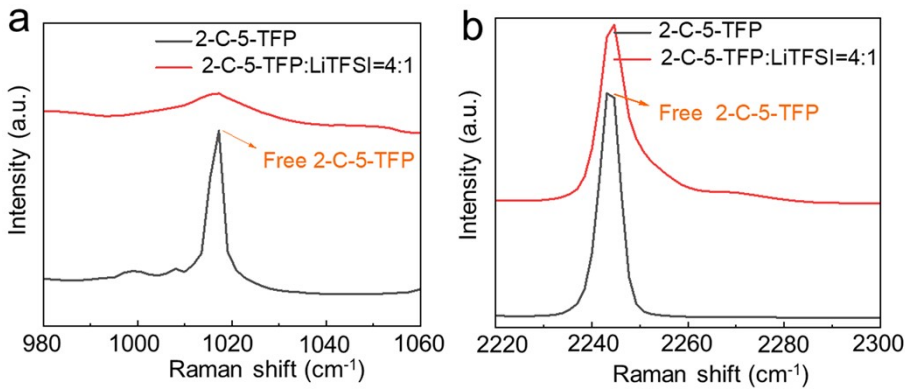

Fig. S9 (a-b) Raman spectra of pyridine-N and cyanide-N group of 2-C-5-TFP and corresponding DEEs.

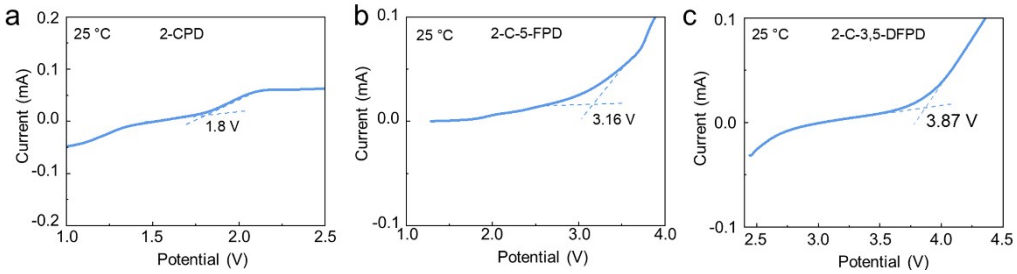

Fig. S10 (a-c) Electrochemical windows of the 2-CP, 2-C-5-FP, 2-C-3,5-DFP at 25 °C, respectively.

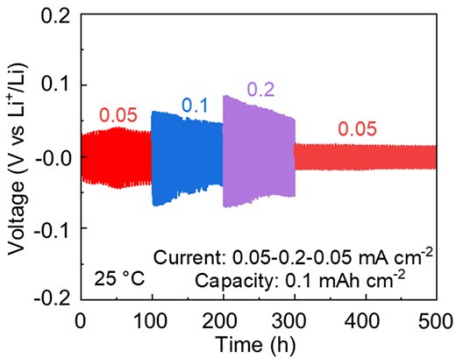

Fig. S11 Voltage profiles of the Li//1M $LiPF_6$ EC/DMC//Li cells at various current densities.

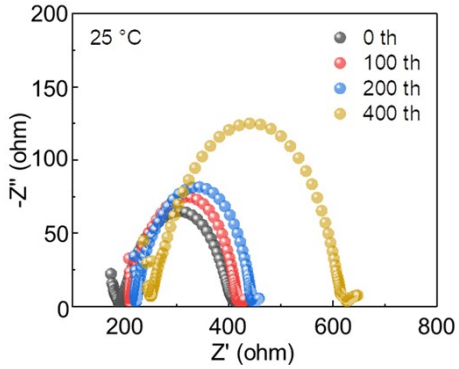

Fig. S12 EIS profiles of Li//DEE-1:4//Li cell at different cycles under a constant current density of 0.1 mA cm^{-2}.

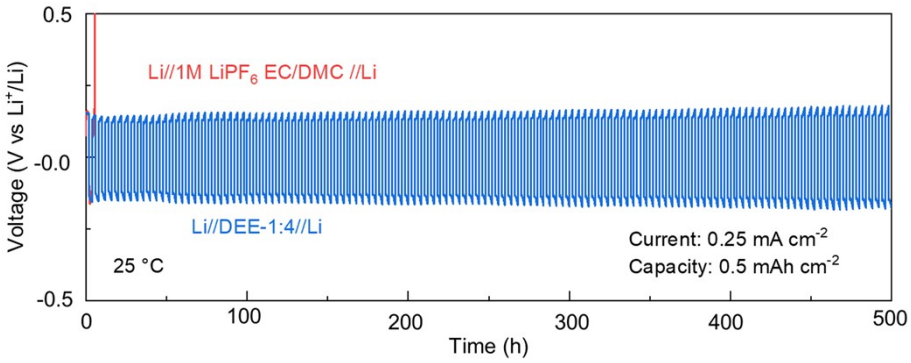

Fig. S13 Voltage profiles of the Li//DEE-1:4//Li cells and Li//1M $LiPF_6$ EC/DMC//Li cells with area capacity of 0.5 mAh cm^{-2}.

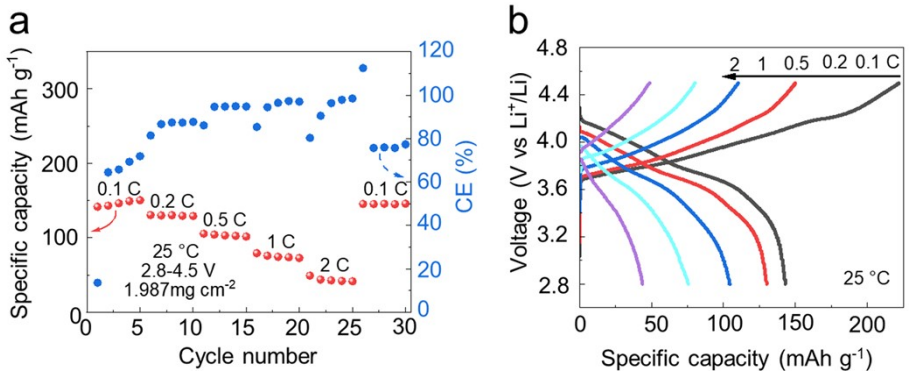

Fig. S14 (a) Rate performances and (b) Charge-discharge curves of Li//1M $LiPF_6$ EC/DMC//NCM811 cells at different C rates.

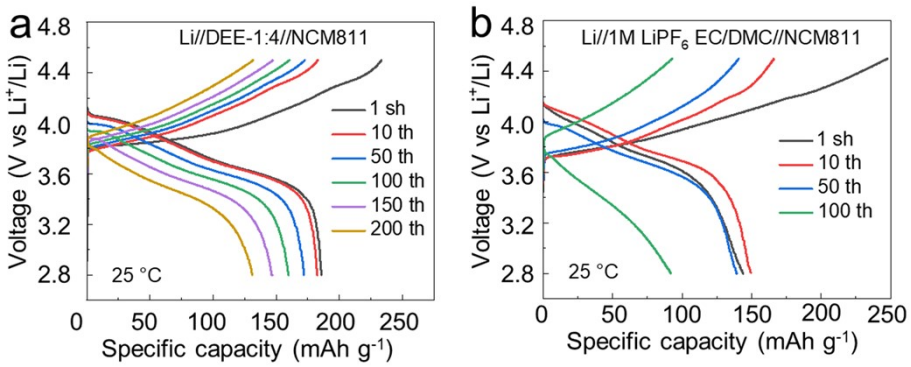

Fig. S15 (a-b) Charge-discharge curves of Li//DEE-1:4//NCM811 cells and Li//1M $LiPF_6$ EC/DMC//NCM811 cells with different number of cycles at 0.5 C.

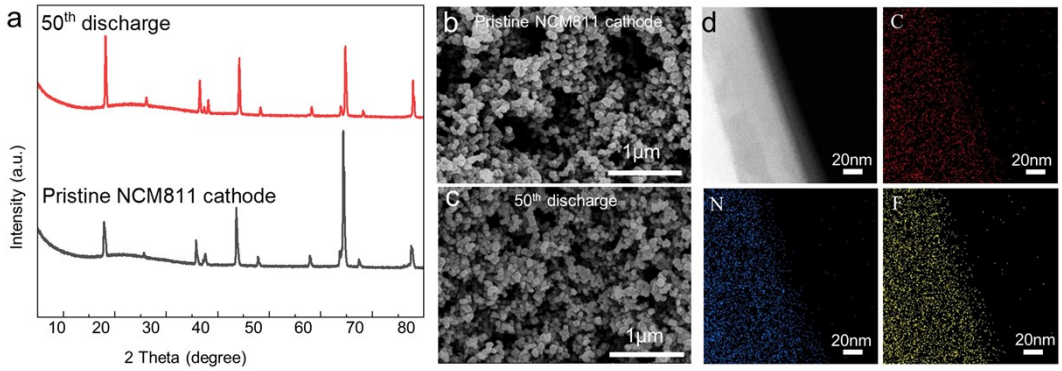

Fig. S16 (a-c) XRD curves and SEM images of NCM811 cathode before and after 50 cycles. (d) Element mapping distribution of CEI layer of NCM811 cathode after 50 cycles.

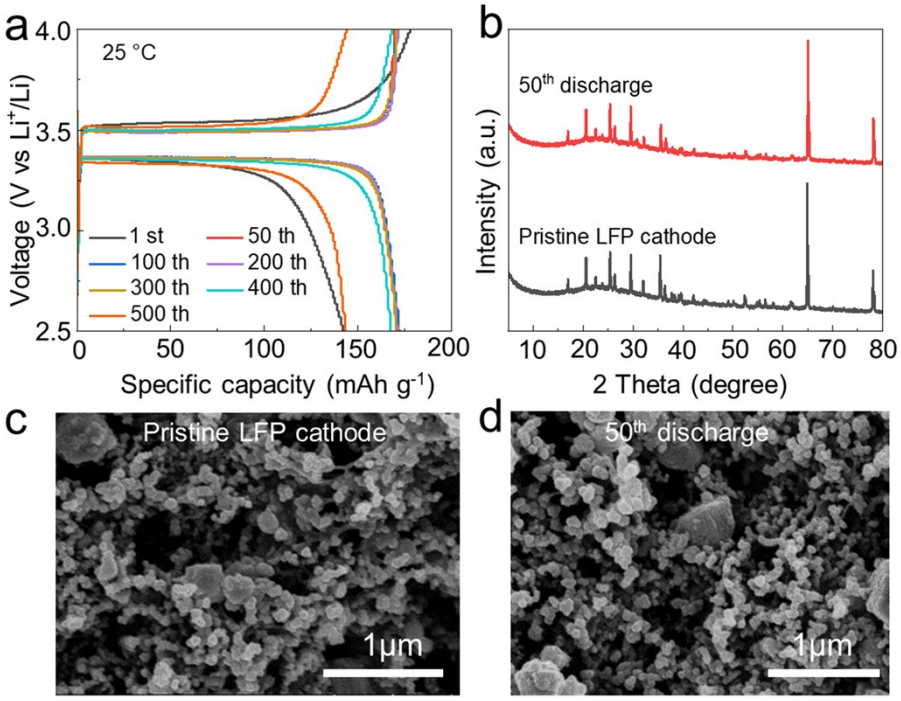

Fig. S17 (a) Charge-discharge curves of Li//DEE-1:4//LFP cell with different number of cycles at 0.5 C. (b-d) XRD curves and SEM images of LFP cathode before and after 50 cycles.

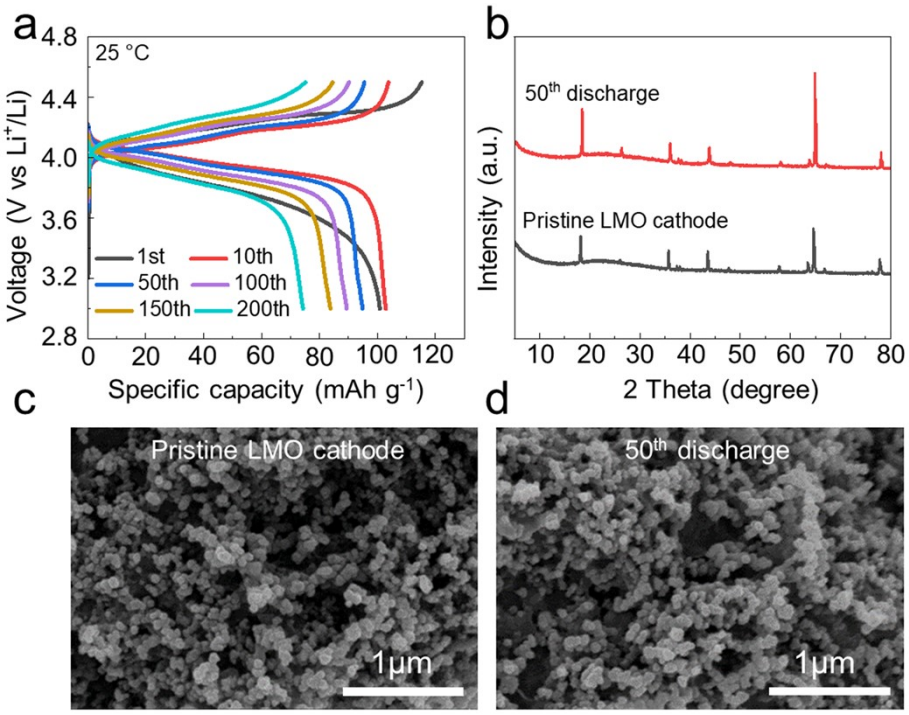

Fig. S18 (a) Charge-discharge curves of Li//DEE-1:4//LMO cell with different number of cycles at 0.5 C. (b-d) XRD curves and SEM images of LMO cathode before and after 50 cycles.

Table S1. Comparison of the Various performance of DEEs with other reported polymer electrolytes.

Electrolytes	Liquid /Gel	Cathode material	Operating voltage	Specific capacity (mAh g^{-1})	Cell cycle	Capacity retention ratio	Ref.
DpyDS	Liquid	$LiFePO_4$	3-3.5 V	130(0.1C)	5	100%(0.1C)	[1]
PVDF/DMIm	Gel	$LiFePO_4$	2.5-4 V	158(0.1C)	800	80%(2C)	[2]
SN/LiDFOB	Liquid	$LiCoO_2$	3-4.7 V	228(0.1C)	500	70%(1C)	[3]
TXE/SN	Liquid	$LiCoO_2$	3-4.3 V	152.9(0.5C)	200	90%(0.3C)	[4]
UPyMA–PETEA	Gel	$LiMn_2O_4$	3-4.4 V	117.2(0.1C)	200	86.1%(0.1C)	[5]
Urea	Liquid	$LiFePO_4$	2-3.8 V	161(0.1C)	1000	92.1%(1C)	[6]
PEO/DMMSA	Gel	$LiFePO_4$	2-3.8 V	168(0.2C)	30	100%(0.2C)	[7]
ETG	Gel	$LiFePO_4$	2.5–4.2V	158.8(0.1C)	100	81.4%(0.1C)	[8]
X-PPS-D4	Gel	$LiFePO_4$	2.5–3.8V	154(0.1C)	1000	86%(1C)	[9]
Urea/FEC	Liquid	$LiFePO_4$	2-3.8 V	140.7(50mA g^{-1})	200	94.3%(50mA g^{-1})	[10]
$LiNO_3$/NMAC	Liquid	NCM622	3-4.3 V	168(0.1C)	600	84%(0.5C)	[11]
PDOL	Gel	$LiFePO_4$	2.5–4V	139.6(0.1C)	200	90%(0.2C)	[12]
ASPE	Gel	$LiCoO_2$	3–4.6V	192.7(0.1C)	1000	84%(0.5C)	[13]
TFA/EC/FEC	Liquid	$LiFePO_4$	2.4-4.1V	148(0.1C)	70	67.6%(0.1C)	[14]
CNCE/SN	Gel	$LiCoO_2$	3-4.45V	162	200	85%(0.1C)	[15]
PEGMEA/SN	Gel	$LiFePO_4$	2.5-4.2V	163(0.1C)	1500	80.3%(0.5C)	[16]
SSH-PEPEA	Gel	$LiFePO_4$	2.5–4.2V	131.7(0.1C)	100	86.1%(0.1C)	[17]
LBS	Liquid	$LiFePO_4$	2.5-4.2V	122(3C)	500	90(2C)	[18]
CPE5	Gel	$LiFePO_4$	2.5-3.8V	155(0.2C)	400	95.3%(0.2C)	[19]
PDMS-SN	Liquid	NCM622	3-4.2V	167(100mA g^{-1})	100	87%(100mA g^{-1})	[20]
CTFP	Liquid	NCM811	2.8-4.5V	205.5(0.1C)	200	70.6%(0.5C)	This work

References

1 J. H. Song, Y. B. Si, W. Guo, D. H. Wang and Y. Z. Fu, *Angew. Chem.-Int. Edit.*, 2021, **60**, 9881-9885.

2 X. P. Pei, Y. J. Li, T. Ou, X. C. Liang, Y. Yang, E. N. Jia, Y. Tan and S. J. Guo, *Angew. Chem.-Int. Edit.*, 2022, **61**, e202205075.

3 Z. L. Hu, F. Xian, Z. Y. Guo, C. L. Lu, X. F. Du, X. Y. Cheng, S. Zhang, S. M. Dong, G. L. Cui and L. Q. Chen, *Chem. Mat.*, 2020, **32**, 3405-3413.

4 J. N. Zhang, H. Wu, X. F. Du, H. Zhang, L. Huang, F. Sun, T. T. Liu, S. W. Tian, L. X. Zhou, S. J. Hu, Z. X. Yuan, B. T. Zhang, J. J. Zhang and G. L. Cui, *Adv. Energy Mater.*, 2023, **13**, 2202529.

5 P. Jaumaux, Q. Liu, D. Zhou, X. F. Xu, T. Y. Wang, Y. Z. Wang, F. Y. Kang, B. H. Li and G. X. Wang, *Angew. Chem.-Int. Edit.*, 2020, **59**, 9134-9142.

6 W. T. Li, W. Liu, B. D. Huang, Z. W. Cai, H. Zhong, F. Guo and Y. H. Mai, *J. Mater. Chem. A*, 2022, **10**, 15449-15459.

7 P. P. Dong, X. H. Zhang, K. S. Han, Y. H. Cha and M. K. Song, *J. Energy Chem.*, 2022, **70**, 363-372.

8 Z. X. Li, S. Z. Zhang, Z. Jiang, D. Cai, C. D. Gu and J. P. Tu, *Mater. Chem. Phys.*, 2021, **267**, 124701.

9 Y. X. Jiang, Y. D. Song, X. Chen, H. J. Wang, L. J. Deng and G. Yang, *Energy Storage Mater.*, 2022, **52**, 514-523.

10 W. T. Li, W. Liu, Z. W. Cai, B. D. Huang, H. Zhong and Y. H. Mai, *J. Energy Storage*, 2023, **68**, 107766.

11 Y. H. Liang, W. B. Wu, D. P. Li, H. Wu, C. C. Gao, Z. J. Chen, L. J. Ci and J. H. Zhang, *Adv. Energy Mater.*, 2022, **12**, 2202493.

12 Y. Q. Wang, R. Xu, B. W. Xiao, D. Lv, Y. Peng, Y. Zheng, Y. H. Shen, J. C. Chai, X. H. Lei, S. Y. Luo, X. Y. Wang, X. M. Liang, J. W. Feng and Z. H. Liu, *Mater. Today Phys.*, 2022, **22**, 100620.

13 H. C. Wang, J. Song, K. Zhang, Q. Fang, Y. X. Zuo, T. H. Yang, Y. L. Yang, C. Gao, X. F. Wang, Q. Q. Pang and D. G. Xia, *Energy Environ. Sci.*, 2022, **15**, 5149-

5158.

14 L. Mezzomo, N. Pianta, I. Ostroman, N. Aloni, D. Golodnitsky, E. Peled, P. Mustarelli and R. Ruffo, *J. Power Sources*, 2023, **561**, 232746.

15 H. Zhang, L. X. Zhou, X. F. Du, J. J. Zhang, S. W. Tian, T. T. Liu, J. N. Zhang, S. J. Hu, W. L. Song, X. H. Zhou and G. L. Cui, *Carbon Energy*, 2022, **4**, 1093-1106.

16 D. C. Zhang, Y. X. Liu, Z. Y. Sun, Z. B. Liu, X. J. Xu, L. Xi, S. M. Ji, M. Zhu and J. Liu, *Angew. Chem.-Int. Edit.*, 2023, **11,** e202310006.

17 Q. Q. Li, Z. J. Zhang, Y. Li, H. Li, Z. Y. Liu, X. J. Liu and Q. Xu, *ACS Appl. Mater. Interfaces*, 2022, **14,** 49700-49708.

18 W. B. Wu, Y. H. Liang, D. P. Li, Y. Y. Bo, D. Wu, L. J. Ci, M. Y. Li and J. H. Zhang, *ACS Nano*, 2022, **16**, 14558-14568.

19 Y. C. Huang, Y. L. Chu, C. C. Chang, L. Y. Liu, H. S. Teng, B. H. Chen and J. S. Jan, *J. Electroanal. Chem.*, 2023, **940**, 117455.

20 W. P. Li, P. Wen, Y. Ren, W. Xie, J. Lin, M. Chen, Y. Yang and X. R. Lin, *ACS Energy Lett.*, 2023, **8**, 5128-5135.