Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

High-Capacity Sulfide All-Solid-State Lithium battery with Conversion-type Iron Fluoride Cathode

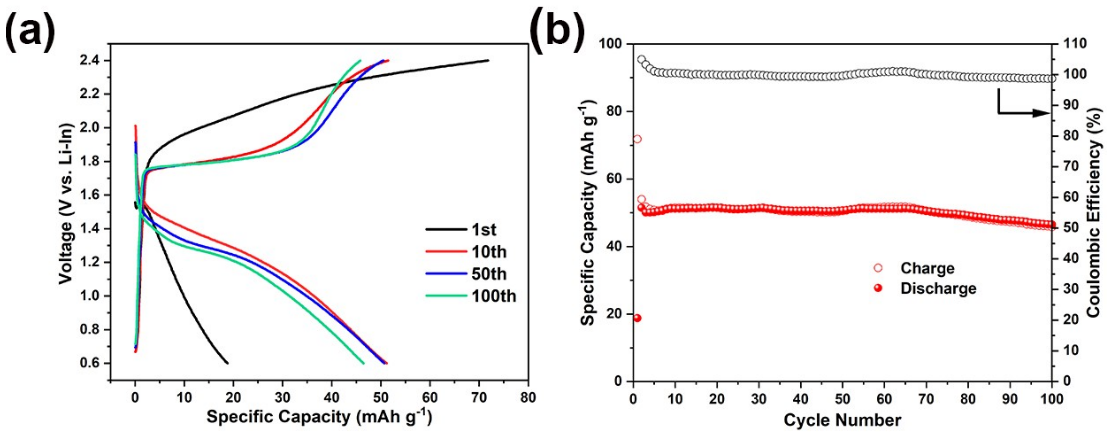

Figure S1 a) Discharge/charge curves of Li_6PS_5Cl/C at 50 mA g^{-1} in the voltage range of 0.6-2.4 V (vs. Li-In). b) Cycling performance of Li_6PS_5Cl/C at 50 mA g^{-1} in the voltage range of 0.6-2.4 V vs. Li-In. Cycling test at 30 °C. Cell construction: Li-In/Li_6PS_5Cl/Li_6PS_5Cl (76.9 wt%)-SP (23.1 wt%) cell.It could be seen that Li_6PS_5Cl/C electrodes exhibited a reversible capacity of only about 48 mAh g^{-1}.

Table S1. Summary of the specific capacity and the capacity retention after 50 cycles in previous literature and in this work.

No.	Cathode material	Classification	Voltage (V vs. Li^+/Li)	Current density	50^{th} (mAh/g)	50^{th} capacity retention	Ref.

1	HTB-FeF_3/rGO	Liquid lithium battery	1.0-4.5	50 mA/g	123	25.84%	[1]
2	C/FeOF/FeF_3 nanocomposite	Liquid lithium battery	1.5-4.5	20 mA/g	130	29.66%	[2]
3	FeF_3/porous carbon	Liquid lithium battery	1.5-4.5	20.8 mA/g	200	32.89%	[3]
4	7%MoO_3-encapsulated $FeF_3 \cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	20.7 mA/g	215.7	50.87%	[4]
5	FeF_3 nanowires	Liquid lithium battery	1.5-4.5	50 mA/g	223	41.07%	[5]
6	FeF_3-C@LiF additive	Liquid lithium battery	1.5-4.5	40 mA/g	229	57.25%	[6]
7	$Fe_{1-2x/3}Mn_xF_3 \cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.1 C	258.9	91.1%	[7]
8	Ni-Doped $FeF_3 \cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	40 mA/g	264	64.08%	[8]
9	FeF_3-rGO	Liquid lithium battery	1.5-4.5	71.2 mA/g	274	66.18%	[9]
10	FeF_3-graphitized-Carbon	Liquid lithium battery	1.5-4.5	71.2 mA/g	286	76.47%	[10]
11	Pre-lithiated FeF_3	Liquid lithium battery	1.2-4.5	25 mA/g	300	94.94%	[11]
12	Nanosized TiO_2-coated $FeF_3 \cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.1 C	323	49.39%	[12]
13	FeF_3/mesoporous carbon nanocomposites	Liquid lithium battery	1.1-4.5	142 mA/g	650	89.68%	[13]
14	HTB-FeF_3	Solid-state lithium battery	1.2-3.9	0.1 C	~ 332	51.47%	[14]
15	HTB-FeF_3	Solid-state lithium battery	1.2-4.0	0.1 C	~ 358	68.32%	[15]
16	HTB-FeF_3	Solid-state lithium battery	1.2-4.0	0.1 mA/cm^2	~ 378	75.6%	[16]
17	HTB-FeF_3	Solid-state lithium battery	1.2-4.0	0.1 mA/cm^2	~ 383	76.6%	[17]
18	HTB-FeF_3	Solid-state lithium battery	1.2-3.9	0.1 C	~ 400	57.14%	[18]
19	5%rGO-FeF_3	All-solid-state lithium battery	1.2-3.0	50 mA/g	742	119.12%	This work

Table S2. The performance of reversible specific capacity and cycle number of FeF_3 cathode in previous literature and in this work.

No.	Cathode material	Classification	Voltage (V vs. Li^+/Li)	Current density (1 C=500	Reversible specific capacity	Cycle number	Ref.

				mA/g) [a]	(mAh/g)		
1	HTB-FeF_3/rGO	Liquid lithium battery	1.3-4.3	0.024 C	150	100	[19]
2	β-$FeF_3\cdot 3H_2O$	Liquid lithium battery	1.5-4.5	0.04 C	100	5	[20]
3	HTB-FeF_3	Liquid lithium battery	1.3-4.5	0.04 C	200	100	[21]
4	C/FeOF/FeF_3 nanocomposite	Liquid lithium battery	1.5-4.5	0.04 C	130	53	[2]
5	FeF_3-N-doped porous hollow carbon nanofiber	Liquid lithium battery	1.5-4.5	0.04 C	277	20	[22]
6	Nanosized $FeF_3\cdot 0.33H_2O$	Liquid lithium battery	1.6-4.5	0.04 C	199.5	160	[23]
7	Fe/LiF/C	Liquid lithium battery	1.3-4.3	0.0416 C	92	10	[24]
8	FeF_3-rGO	Liquid lithium battery	1.5-4.5	0.0416 C	183	100	[25]
9	FeF_3/C nanocomposites	Liquid lithium battery	1.5-4.5	0.0416 C	200	50	[3]
10	$Fe_{(1-x)}Ti_xF_3$	Liquid lithium battery	1.0-4.5	0.0474 C	400	14	[26]
11	$Fe_{1-x}Ti_xF_3\cdot 0.33H_2O$/C	Liquid lithium battery	1.0-4.5	0.0474 C	162.66	40	[27]
12	7%MoO_3-encapsulated $FeF_3\cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.0474 C	215.7	50	[4]
13	$FeF_3\cdot 0.33H_2O$ hierarchical nanoparticle	Liquid lithium battery	1.5-4.2	0.0474 C	236.6	100	[28]
14	$FeF_3\cdot 0.33H_2O$	Liquid lithium battery	1.0-4.5	0.0474 C	166.5	35	[29]
15	Pre-lithiated FeF_3	Liquid lithium battery	1.2-4.5	0.05 C	300	50	[11]
16	FeF_3-C@LiF additive	Liquid lithium battery	1.5-4.5	0.08 C	229	50	[6]
17	Ni-Doped $FeF_3\cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.08 C	264	50	[8]
18	FeF_3 nanowires	Liquid lithium battery	1.5-4.5	0.1 C	223	50	[5]
19	Highly amorphized FeF_3	Liquid lithium battery	1.3-4.5	0.1 C	200	60	[30]
20	$FeF_3\cdot 0.33H_2O$ hollow porous microspheres	Liquid lithium battery	1.3-4.5	0.1 C	350	10	[31]

21	FeF_3 nanoflowers@CNT	Liquid lithium battery	1.5-4.5	0.1 C	360	10	[32]
22	FeF_3	Liquid lithium battery	1.0-4.5	0.1 C	320	5	[33]
23	$Fe_{1-2x/3}Mn_xF_3\cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.1 C	258.9	50	[7]
24	$Fe_{1-x}Mn_xF_3\cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.1 C	180	100	[34]
25	Nanosized TiO_2-coated $FeF_3\cdot 0.33H_2O$	Liquid lithium battery	1.5-4.5	0.1 C	323	50	[12]
26	$FeF_3\cdot 0.33H_2O$- rGO	Liquid lithium battery	1.0-4.0	0.1 C	165	30	[35]
27	FeF_3/C nanocomposite	Liquid lithium battery	1.0-4.0	0.1 C	161.58	40	[36]
28	HTB-FeF_3/rGO	Liquid lithium battery	1.0-4.5	0.1 C	123	50	[1]
29	FeF_3@GO	Liquid lithium battery	1.5-4.5	0.14 C	410	30	[37]
30	The hollow yolk-like spheres iron fluoride	Liquid lithium battery	1.5-4.2	0.1424 C	164	40	[38]
31	FeF_3@GO	Liquid lithium battery	1.5-4.5	0.1424 C	274	50	[9]
32	FeF_3-graphitized-Carbon	Liquid lithium battery	1.5-4.5	0.1424 C	286	50	[10]
33	FeF_3-CNT	Liquid lithium battery	1.2-4.2	0.2 C	100	60	[39]
34	FeF_3/C/RGO film	Liquid lithium battery	1.0-4.0	0.2 C	220	200	[40]
35	FeF_3 nanocrystal	Liquid lithium battery	1.0-4.0	0.2 C	410	120	[41]
36	$FeF_3\cdot 0.33H_2O$/ rGO	Liquid lithium battery	1.5-4.5	0.24 C	378	100	[42]
37	FeF_3-V_2O_5/C	Liquid lithium battery	1.0-4.5	0.2468 C	218	30	[43]
38	LiF@C-coated $FeF_3\cdot 0.33H_2O$	Liquid lithium battery	1.3-4.3	0.4 C	231	50	[44]
39	HTB-FeF_3	Solid-state lithium battery	1.2-3.9	0.1 C	346.5	100	[15]
40	HTB-FeF_3	Solid-state lithium battery	1.2-3.9	0.1 C	300	200	[18]
41	HTB-FeF_3	Solid-state lithium battery	1.2-3.9	0.1 C	300	240	[14]
42	5%rGO-FeF_3	All-solid-state	1.2-3.0	0.4 C	567.51	120	This

		lithium battery					work
43	5%rGO-FeF_3	All-solid-state lithium battery	1.2-3.0	1 C	409.16	300	This work

a. The unit of mA g^{-1} is converted into current rate if the original unit "C" in the literature is clealy defined.

1. Q. Chu, Z. Xing, X. Ren, A. M. Asiri, A. O. Al-Youbi, K. A. Alamry and X. Sun, *Electrochimica Acta*, 2013, **111**, 80-85.
2. W. Li, Y. Li, M. Fang, X. Yao, T. Li, M. Shui and J. Shu, *Ionics*, 2018, **24**, 1561-1569.
3. R. Ma, M. Wang, P. Tao, Y. Wang, C. Cao, G. Shan, S. Yang, L. Xi, J. C. Chung and Z. Lu, *Journal of Materials Chemistry A*, 2013, **1**, 15060-15067.
4. X. Zhou, J. Ding, J. Tang, J. Yang, H. Wang and M. Jia, *Journal of Electroanalytical Chemistry*, 2019, **847**, 113227.
5. L. Li, F. Meng and S. Jin, *Nano letters*, 2012, **12**, 6030-6037.
6. X. Zhou, H. Sun, H. Zhou, J. Ding, Z. Xu, W. Bin, J. Tang and J. Yang, *Journal of Electroanalytical Chemistry*, 2018, **810**, 41-47.
7. Y. Lu, S. Huang, Z. Zhang, X. Huang, L. Lan, L. Lu, S. Li, J. Li, C. Pan and F. Zhao, *Ionics*, 2019, **25**, 5221-5228.
8. M. Liu, Q. Wang, B. Chen, H. Lei, L. Liu, C. Wu, X. Wang and Z. Yang, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 15651-15660.
9. H. Jung, H. Song, T. Kim, J. K. Lee and J. Kim, *Journal of Alloys and Compounds*, 2015, **647**, 750-755.
10. T. Kim, W. Jae, H. Kim, M. Park, J.-M. Han and J. Kim, *Journal of Materials Chemistry A*, 2016, **4**, 14857-14864.
11. X. Fan, Y. Zhu, C. Luo, T. Gao, L. Suo, S.-C. Liou, K. Xu and C. Wang, *Journal of Power Sources*, 2016, **307**, 435-442.
12. R. Zhang, X. Wang, S. Wei, X. Wang, M. Liu and H. Hu, *Journal of Alloys and Compounds*, 2017, **719**, 331-340.
13. J. Chun, C. Jo, S. Sahgong, M. G. Kim, E. Lim, D. H. Kim, J. Hwang, E. Kang, K. A. Ryu and Y. S. Jung, *Acs Applied Materials & Interfaces*, 2016, **8**, 35180-35190.
14. X. Wu, K. Chen, Z. Yao, J. Hu, M. Huang, J. Meng, S. Ma, T. Wu, Y. Cui and C. Li, *Journal of Power Sources*, 2021, **501**, 229946.
15. M. Lei, S. Fan, Y. Yu, J. Hu, K. Chen, Y. Gu, C. Wu, Y. Zhang and C. Li, *Energy Storage Materials*, 2022, **47**, 551-560.
16. Y. Zhang, J. Meng, K. Chen, H. Wu, J. Hu and C. Li, *ACS Energy Letters*, 2020, **5**, 1167-1176.
17. Y. Zhang, J. Meng, K. Chen, Q. Wu, X. Wu and C. Li, *ACS Applied Materials & Interfaces*, 2020, **12**, 33729-33739.
18. J. Hu, K. Chen, Z. Yao and C. Li, *Science Bulletin*, 2021, **66**, 694-707.
19. A. Pohl, M. Faraz, A. Schröder, M. Baunach, W. Schabel, A. Guda, V. Shapovalov, A. Soldatov, V. S. K. Chakravadhanula and C. Kübel, *Journal of Power Sources*, 2016, **313**, 213-222.
20. S.-T. Myung, S. Sakurada, H. Yashiro and Y.-K. Sun, *Journal of Power Sources*, 2013, **223**, 1-8.
21. J. Hu, Y. Zhang, D. Cao and C. Li, *Journal of Materials Chemistry A*, 2016, **4**, 16166-16174.
22. X. Zhou, H. Sun, H. Zhou, Z. Xu and J. Yang, *Journal of Alloys and Compounds*, 2017, **723**, 317-326.

23. L. Zhao, H. Xu, H. Ru, Y. Shi, Q. Zhuang, Y. Cui, Z. Ju and Y. Cui, *Journal of The Electrochemical Society*, 2021, **168**, 030501.
24. R. Prakash, C. Wall, A. K. Mishra, C. Kübel, M. Ghafari, H. Hahn and M. Fichtner, *Journal of Power Sources*, 2011, **196**, 5936-5944.
25. R. Ma, Z. Lu, C. Wang, H.-E. Wang, S. Yang, L. Xi and J. C. Chung, *Nanoscale*, 2013, **5**, 6338-6343.
26. Y. Bai, X. Zhou, Z. Jia, C. Wu, L. Yang, M. Chen, H. Zhao, F. Wu and G. Liu, *Nano Energy*, 2015, **17**, 140-151.
27. S. Wei, X. Wang, R. Yu, R. Zhang, M. Liu, Z. Yang and H. Hu, *Journal of Alloys and Compounds*, 2017, **702**, 372-380.
28. J. Lin, S. Chen, L. Zhu, Z. Yuan and J. Liu, *Electrochimica Acta*, 2020, **364**, 137293.
29. L. Liu, H. Guo, M. Zhou, Q. Wei, Z. Yang, H. Shu, X. Yang, J. Tan, Z. Yan and X. Wang, *Journal of Power Sources*, 2013, **238**, 501-515.
30. C. Li, X. Mu, P. A. van Aken and J. Maier, *Advanced Energy Materials*, 2013, **3**, 113-119.
31. J. Liu, W. Liu, S. Ji, Y. Wan, M. Gu, H. Yin and Y. Zhou, *Chemistry–A European Journal*, 2014, **20**, 5815-5820.
32. S. W. Kim, D. H. Seo, H. Gwon, J. Kim and K. Kang, *Advanced Materials*, 2010, **22**, 5260-5264.
33. H. Torii, K. Uematsu, T. Ishigaki, K. Toda and M. Sato, *Journal of the Ceramic Society of Japan*, 2014, **122**, 473-476.
34. J. Ding, X. Zhou, H. Wang, J. Yang, Y. Gao and J. Tang, *ACS Applied Materials & Interfaces*, 2019, **11**, 3852-3860.
35. R. Rao, V. Pralong and U. Varadaraju, *Solid State Sciences*, 2016, **55**, 77-82.
36. M. Tang, Z. Zhang, Z. Wang, J. Liu, H. Yan and J. Peng, *Journal of Materials Engineering and Performance*, 2018, **27**, 624-629.
37. J. Liu, Y. Wan, W. Liu, Z. Ma, S. Ji, J. Wang, Y. Zhou, P. Hodgson and Y. Li, *Journal of materials chemistry A*, 2013, **1**, 1969-1975.
38. J. Lin, L. Zhu, S. Chen, Q. Li, Z. He, Z. Cai, L. Cao, Z. Yuan and J. Liu, *Journal of The Electrochemical Society*, 2019, **166**, A2074.
39. E. Zhao, O. Borodin, X. Gao, D. Lei, Y. Xiao, X. Ren, W. Fu, A. Magasinski, K. Turcheniuk and G. Yushin, *Advanced Energy Materials*, 2018, **8**, 1800721.
40. D. He, Y. Zhang, D. Cao, M. Sun, J. Xia, Y. Yang, Y. Ding and H. Chen, *Journal of Alloys and Compounds*, 2022, **909**, 164702.
41. Y. Yang, L. Gao, L. Shen and N. Bao, *Journal of Alloys and Compounds*, 2021, **873**, 159799.
42. J. Lian, Y. Wu, Y. Guo, Z. Zhao, Q. Zhang, Y. Hou, L. Chen, B. Lu, X. Pan and Z. Ye, *Chinese Chemical Letters*, 2021.
43. A. Kitajou, M. Hokazono, N. Taguchi, S. Tanaka and S. Okada, *Journal of Alloys and Compounds*, 2021, **856**, 157449.
44. C. Zeng and C. Huang, *ACS omega*, 2021.