Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary information

High Performance Sulfide All-Solid-State Batteries Enabled by $Li_{1.26}Mg_{0.12}Zr_{1.86}(PO_4)_3$ Coating of Iron Fluorides Cathodes

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b

materials	a (Å)	b (Å)	c (Å)	Volume (Å^3)
bare n-FeF_2	4.70287	4.70287	3.30586	73.1156
n-FeF_2@0.5%LMZP	4.703	4.703	3.306	73.1227
n-FeF_2@1%LMZP	4.70298	4.70298	3.30597	73.1215
n-FeF_2@2%LMZP	4.70312	4.70312	3.30613	73.1294

Figure S1. a) Digital photographs of each LMZP-coated samples and b) the corresponding lattice parameters of n-FeF_2@LMZP.

b materials	a (Å)	b (Å)	c (Å)	Volume (Å^3)
bare m-FeF_3	5.201	5.201	13.326	360.473
m-FeF_3@0.5%LMZP	5.199	5.199	13.324	360.142
m-FeF_3@1%LMZP	5.2	5.2	13.323	360.254
m-FeF_3@2%LMZP	5.198	5.198	13.32	359.896

Figure S2. a) Digital photographs and b) the corresponding lattice parameters of m-FeF_3@LMZP.

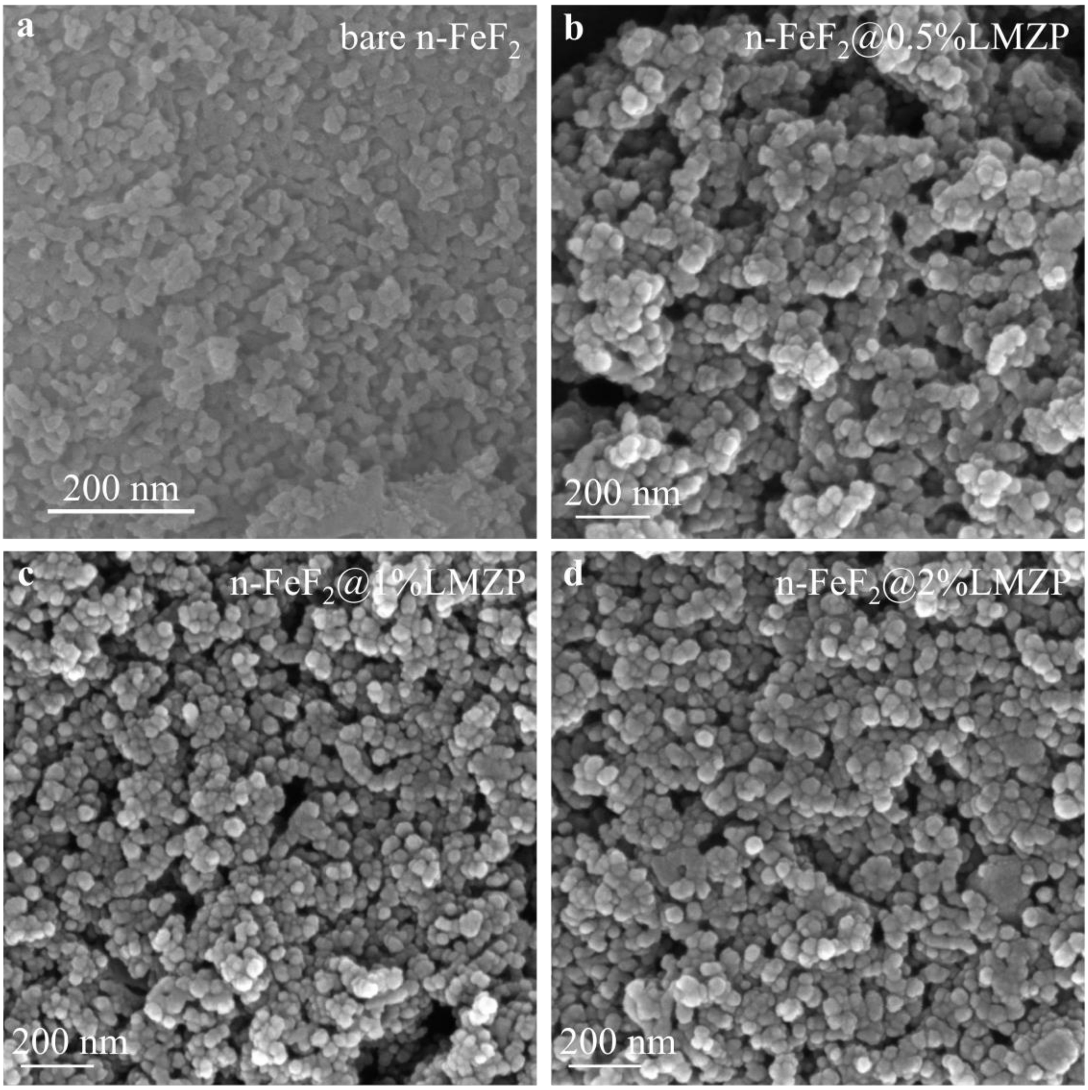


Figure S3. SEM images of a) bare n-FeF_2, b) n-FeF_2@0.5%LMZP, c) n-FeF_2@1%LMZP and d) n-FeF_2@2%LMZP.

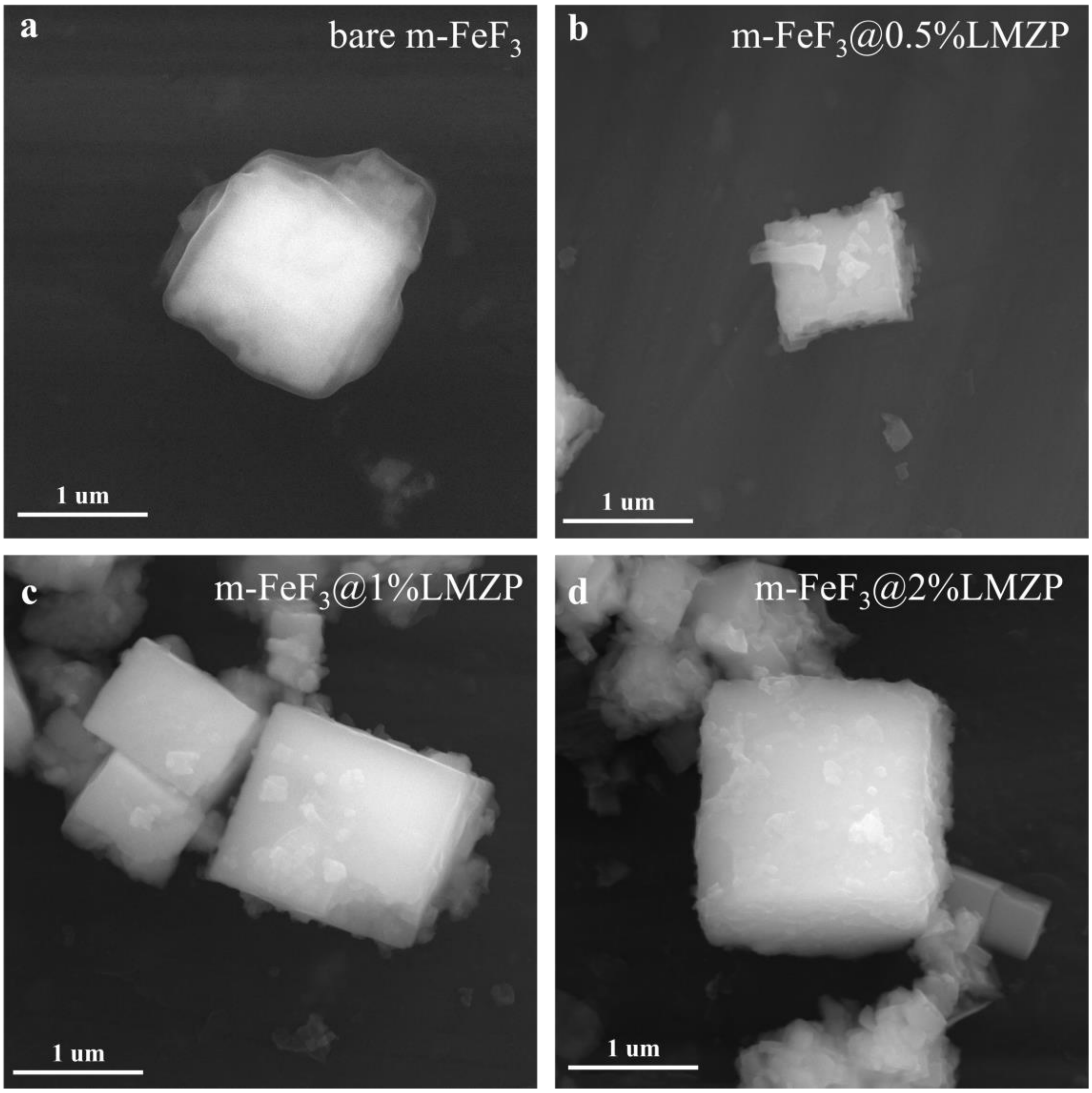


Figure S4. SEM images of a) bare m-FeF_3, b) m-FeF_3@0.5%LMZP, c) m-FeF_3@1%LMZP and d) m-FeF_3@2%LMZP. Bare m-FeF_3 particles display a slight increase in roughness after LMZP coating.

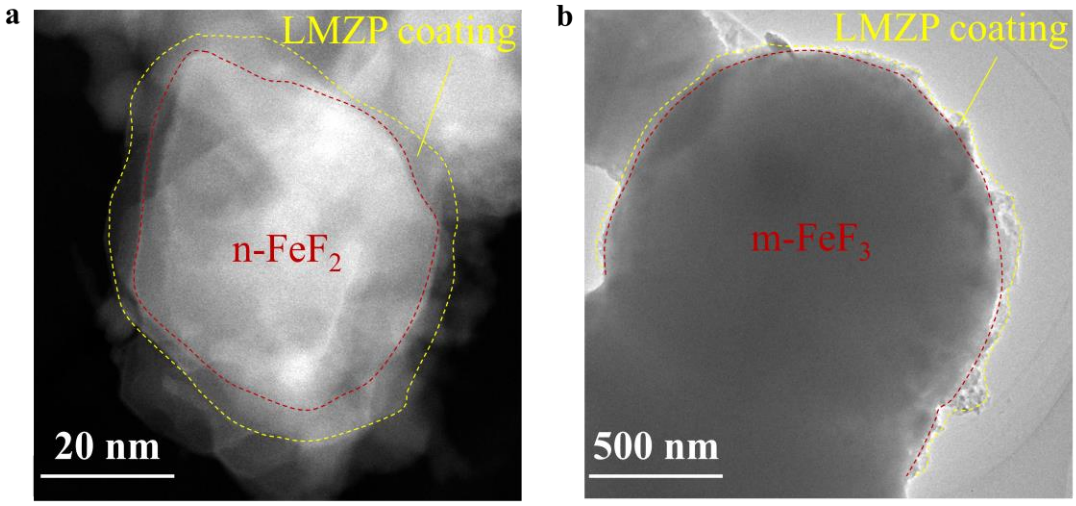


Figure S5. TEM characterizations of a) single n-FeF_2@1%LMZP and b) m-FeF_3@1%LMZP particle.

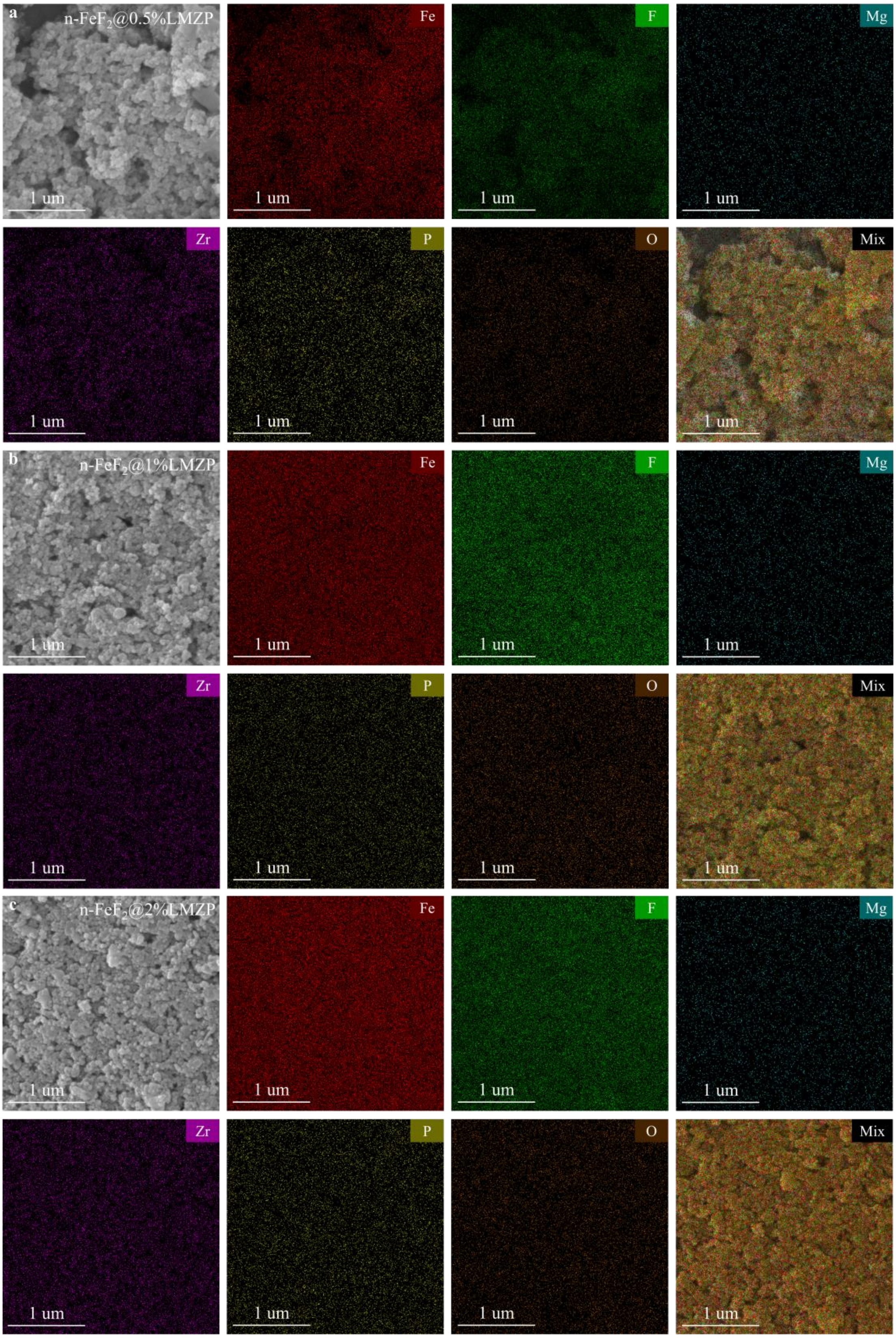


Figure S6. SEM images and the corresponding EDS mappings of Fe, F, Mg, Zr, P and O elements of a) n-FeF_2@0.5%LMZP, b) n-FeF_2@1%LMZP and c) n-FeF_2@2%LMZP.

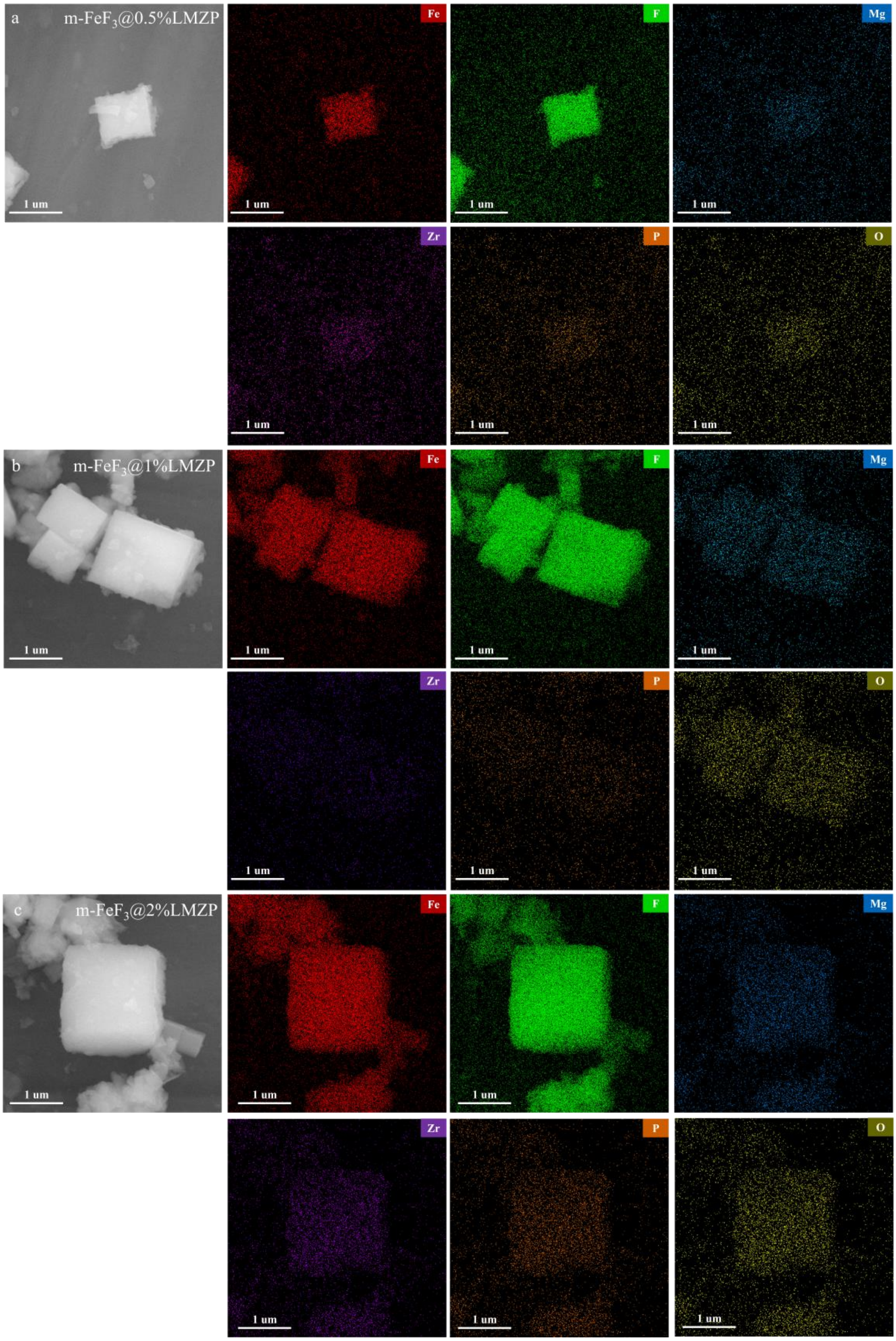


Figure S7. SEM images and the corresponding EDS mappings of Fe, F, Mg, Zr, P and O elements of a) m-FeF_3@0.5%LMZP, b) m-FeF_3@1%LMZP and c) m-FeF_3@2%LMZP.

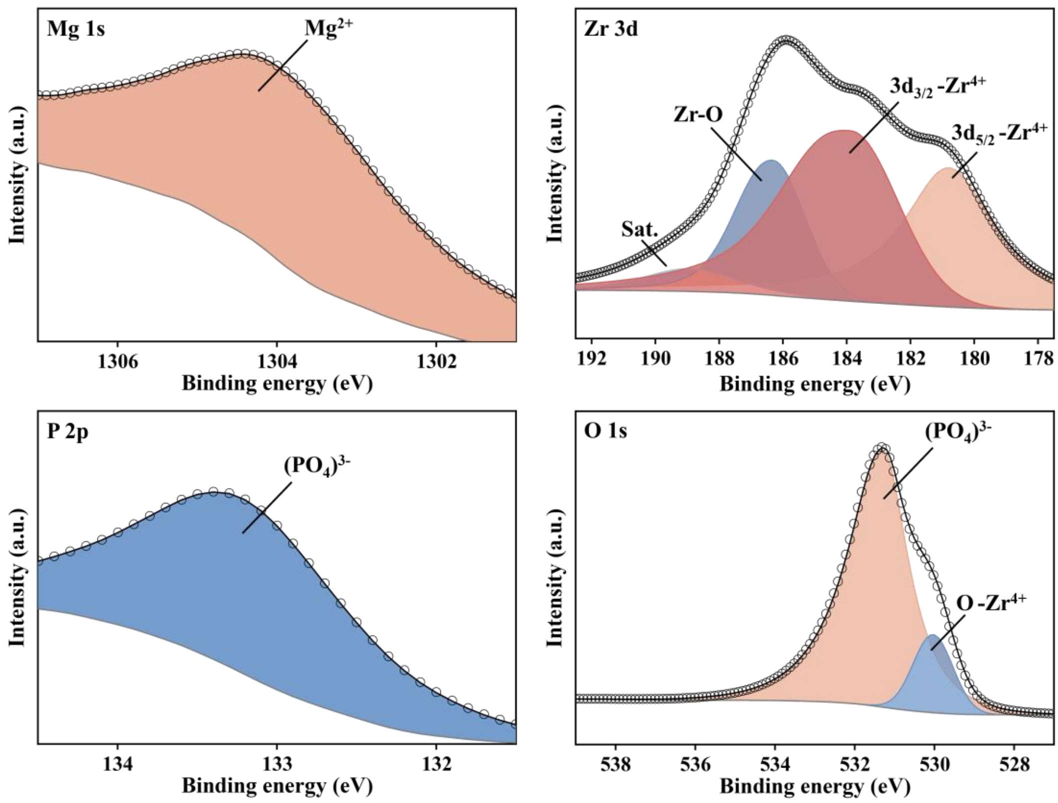


Figure S8. XPS characterizations of Mg 1s, Zr 3d, P 2p and O 1s spectra on the surface of n-FeF_2@1%LMZP.

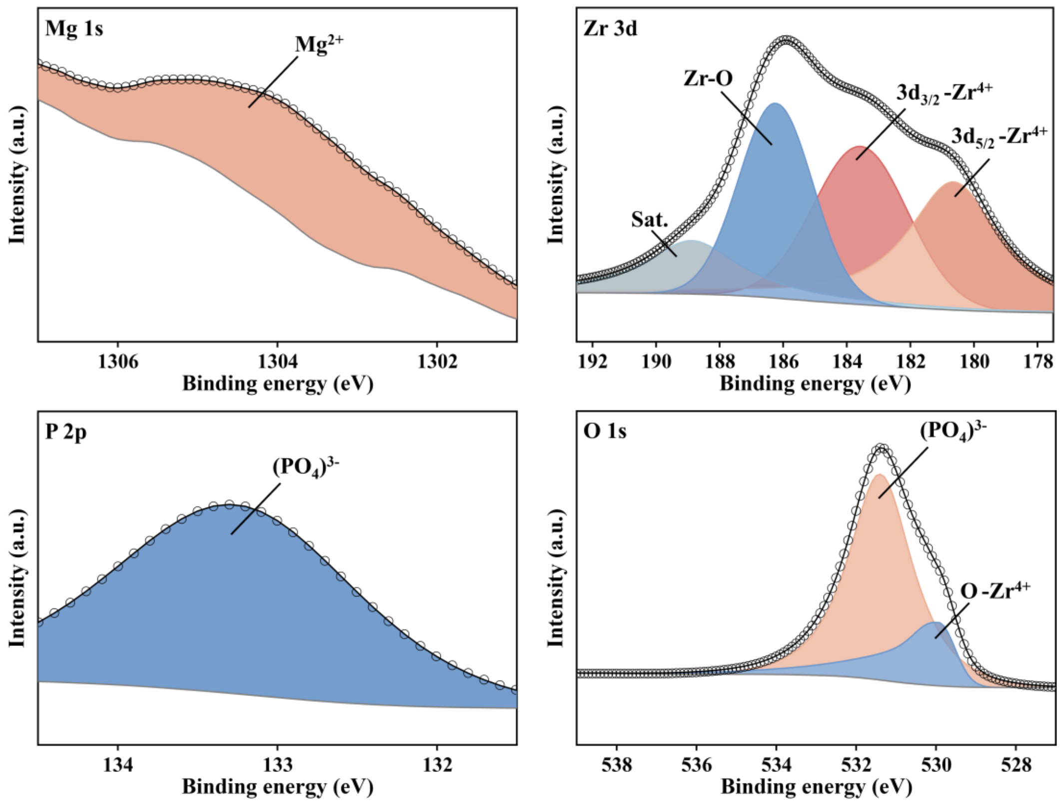


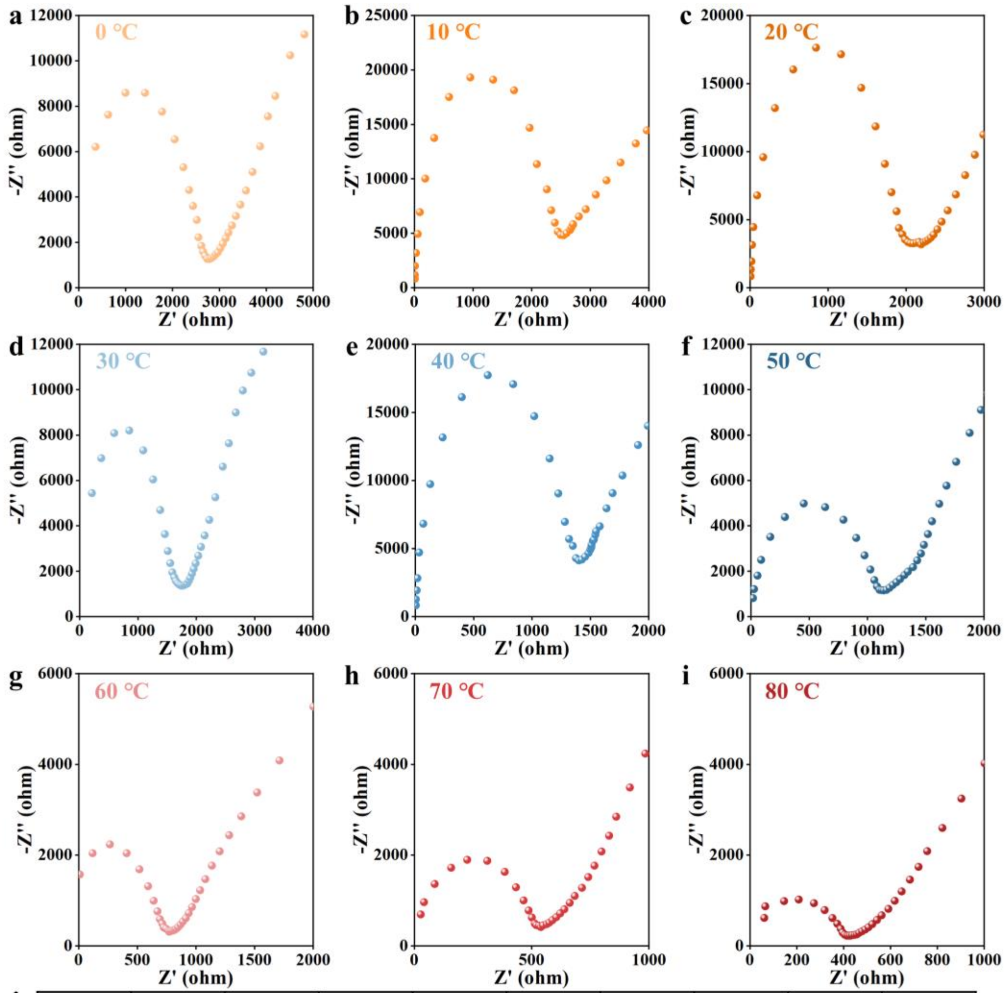
Figure S9. XPS characterizations of Mg 1s, Zr 3d, P 2p and O 1s spectra on the surface of m-FeF_3@1%LMZP.

Figure S10. The digital photo of the pure LMZP powder.

Element	Li	Mg	Zr
Content (wt.%)	1.9	0.6	36.3

Figure S11. The ICP test result of the content of Li, Mg and Zr in LMZP.

Figure S12. The thickness of the pellet of 80 mg LMZP powder after 5 MPa pressure is shown with a thickness of about 0.41 mm.



j

T (°C)	0	10	20	30	40	50	60	70	80
R (Ω)	2783	2544	2194	1740	1400	1123	803	539	426

Figure S13. The a-i) EIS curves of LMZP slice from 0 °C to 80 °C and j) impedance change.

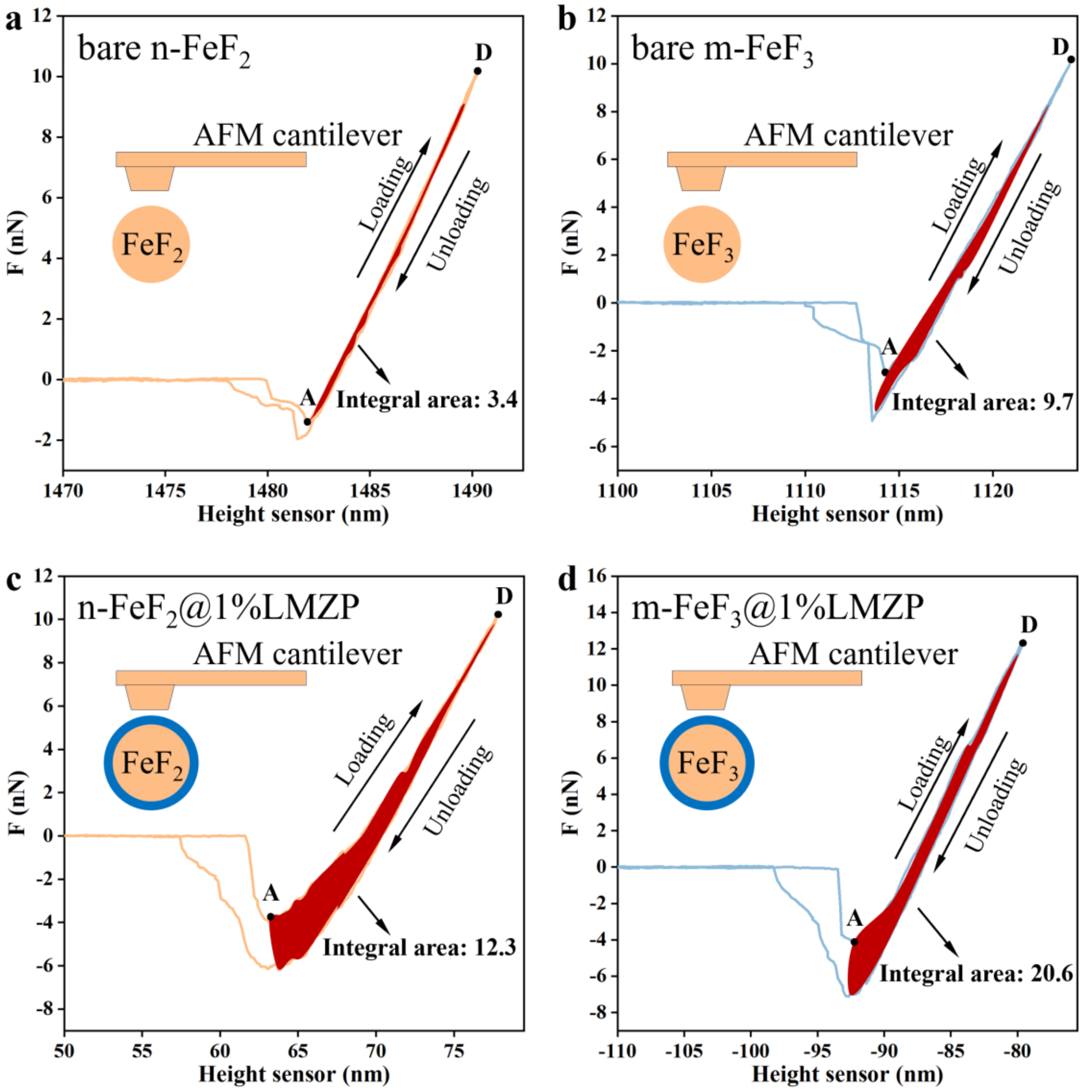


Figure S14. AFM tests of a) bare n-FeF_2, b) bare m-FeF_3, c) n-FeF_2@1%LMZP and d) m-FeF_3@1%LMZP. For bare n-FeF_2 and bare m-FeF_3, the integral area is only 3.4 and 9.7, respectively. For n-FeF_2@1%LMZP and m-FeF_3@1%LMZP, the integral area increases to 12.3 and 20.6, respectively.

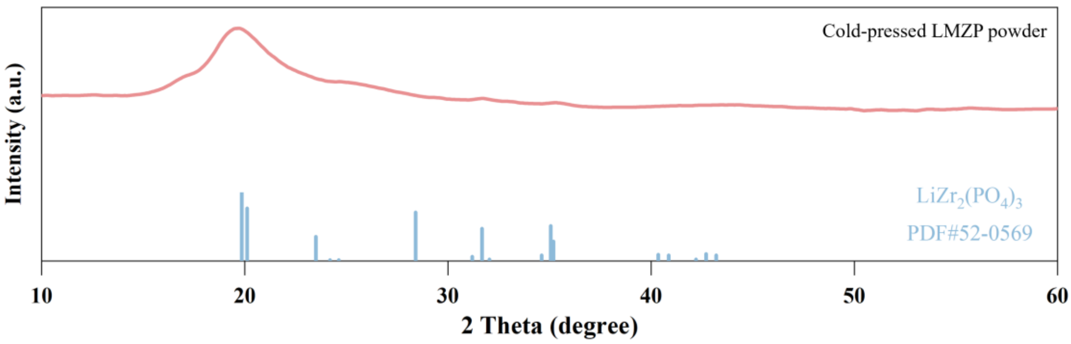


Figure S15. The XRD pattern of the cold-pressed LMZP powder.

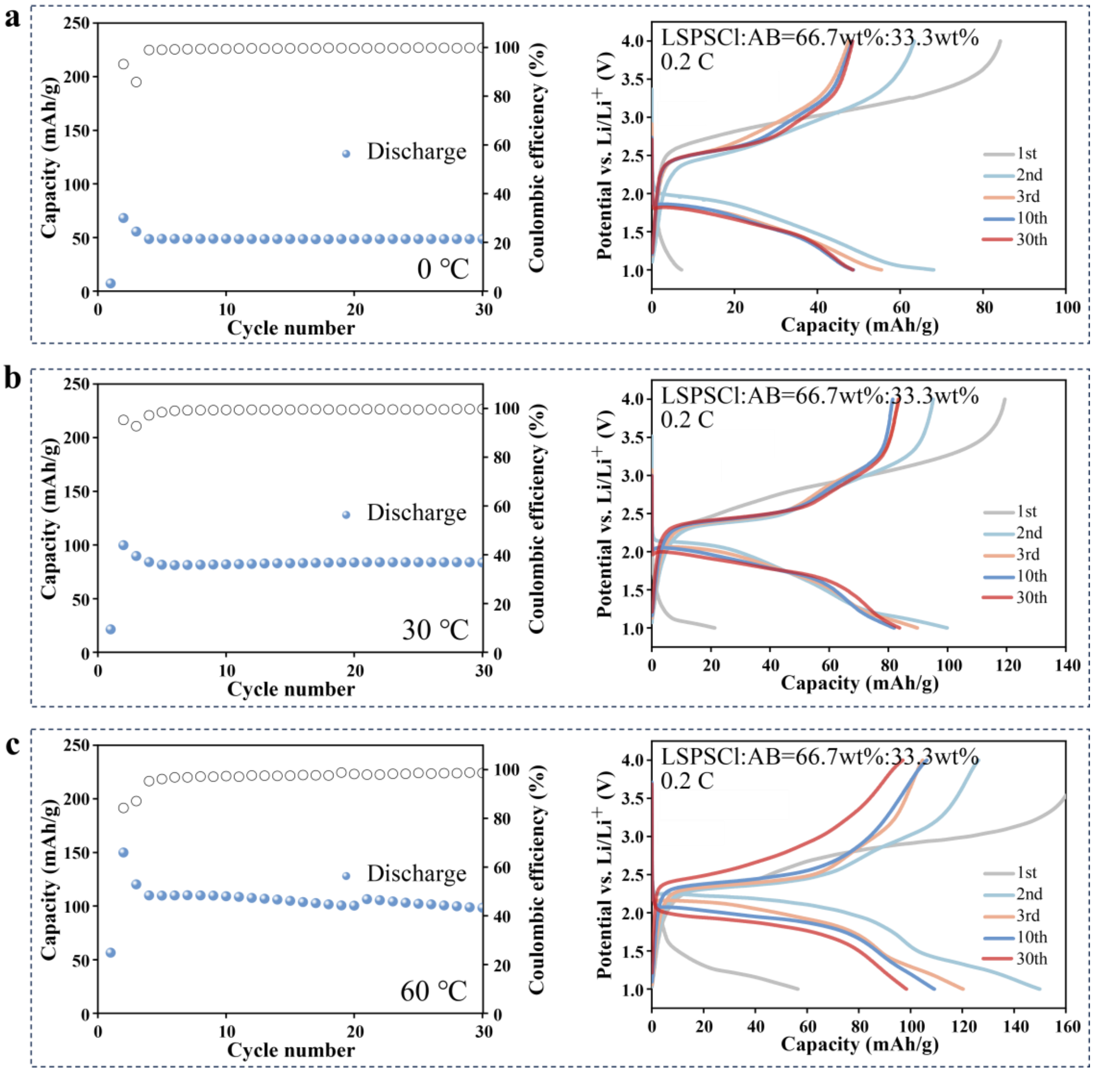


Figure S16. The capacity of ASSBs with AB only as the cathodes at a) 0 °C, b) 30 °C and c) 60 °C.

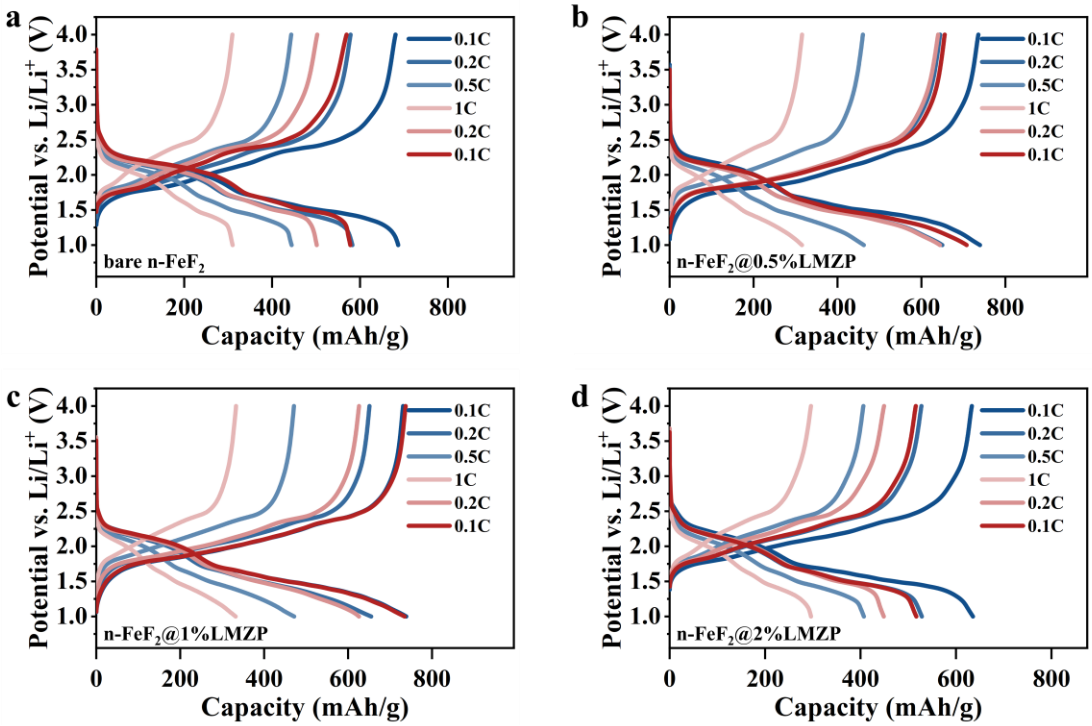


Figure S17. The C-rate C-D curves of a) bare n-FeF_2, b) n-FeF_2@0.5%LMZP, c) n-FeF_2@1%LMZP and d) n-FeF_2@2%LMZP at 60 ℃.

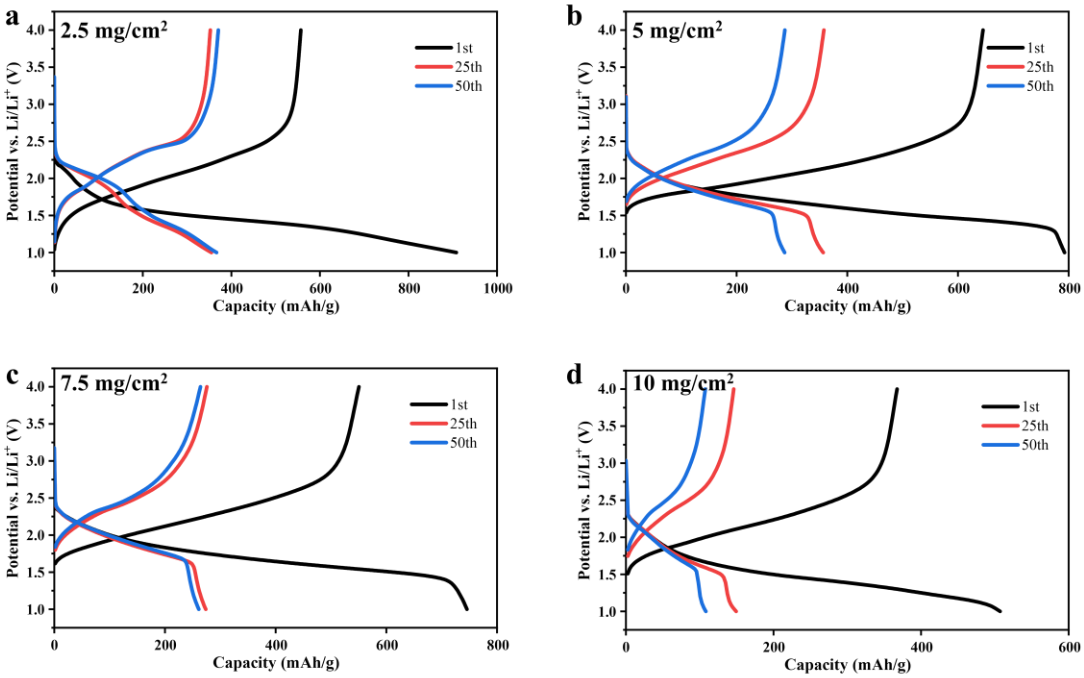


Figure S18. The C-D curves of n-FeF_2@1%LMZP with mass loading of a) 2.5 mg/cm^2, b) 5 mg/cm^2, c) 7.5 mg/cm^2 and d) 10 mg/cm^2.

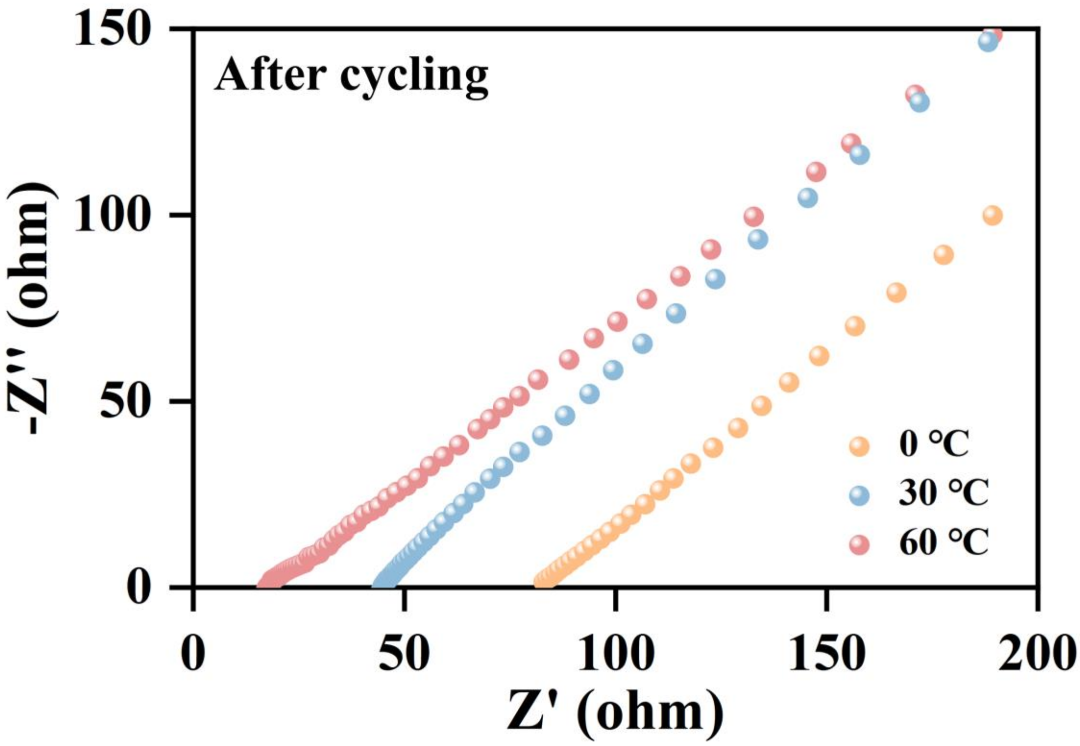


Figure S19. The EIS tests of ASSBs with n-FeF_2@1%LMZP cathode at 0 °C, 30 °C and 60 °C after cycling.

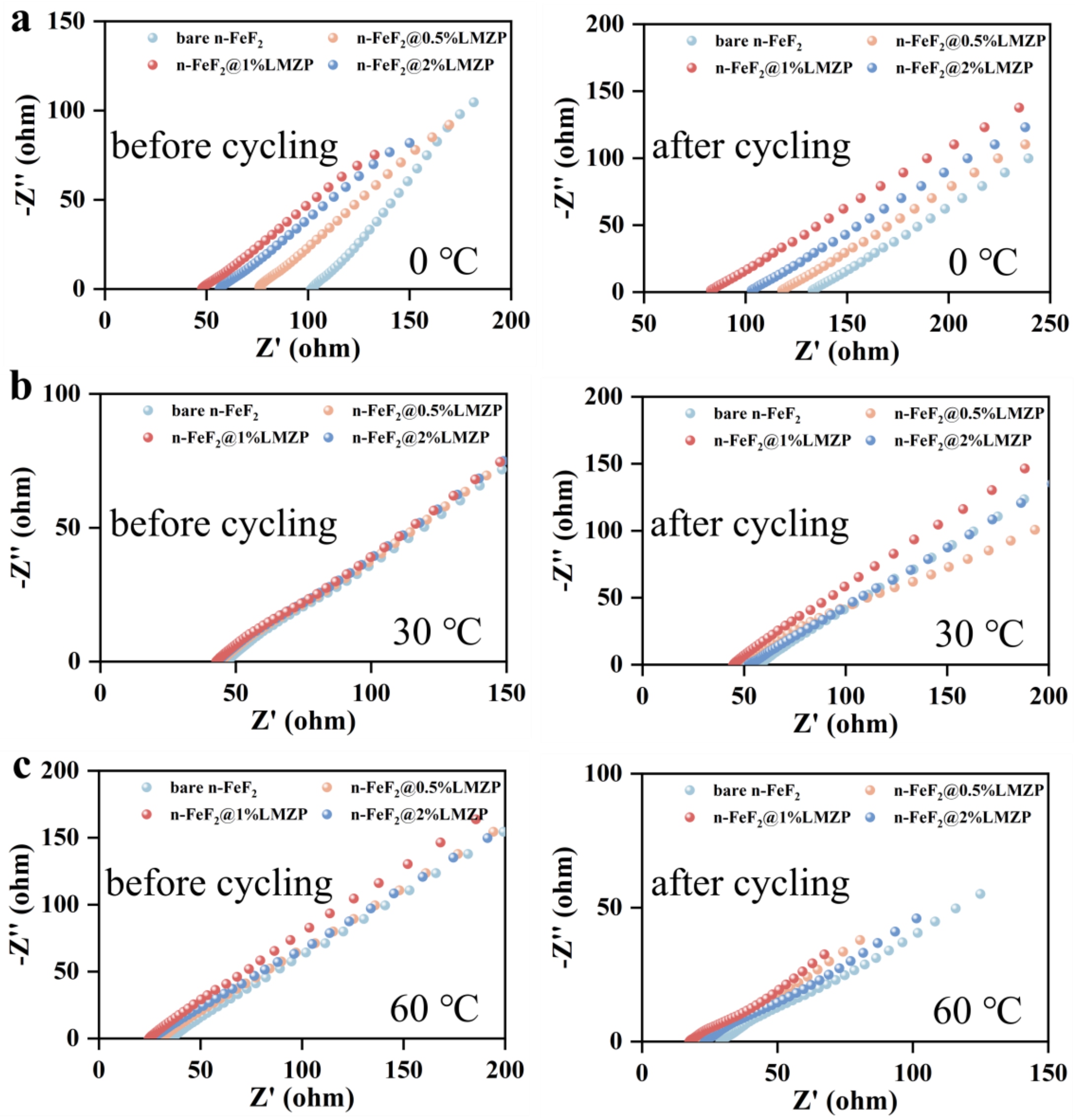


Figure S20. The EIS tests of n-FeF$_2$@LMZP before/after cycling at a) 0 °C, b) 30 °C and c) 60 °C.

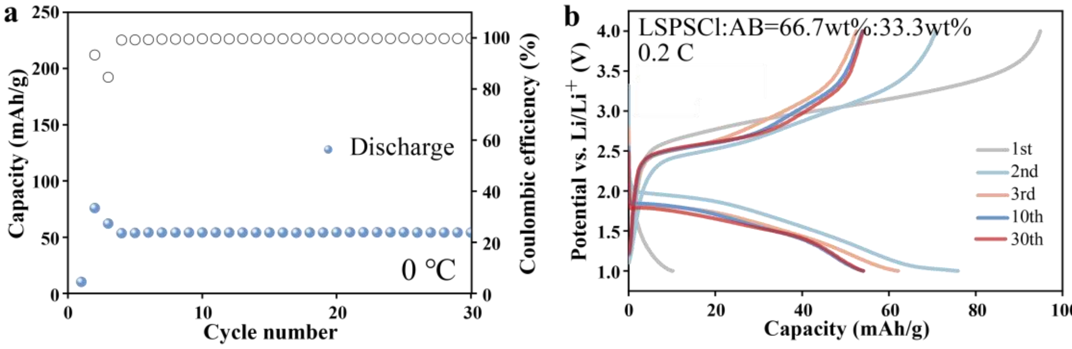


Figure S21. The a) discharge capacity and b) the corresponding C-D curves of ASSBs with AB as cathode at 0 ℃.

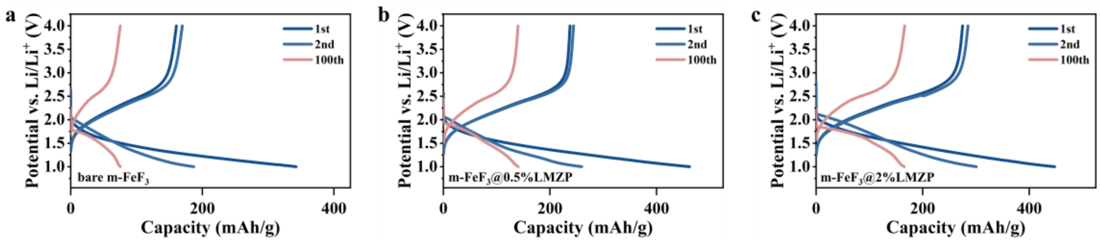


Figure S22. The C-D curves of the a) bare m-FeF_3, b) m-FeF_3@0.5%LMZP and c) m-FeF_3@2%LMZP at 0 °C.

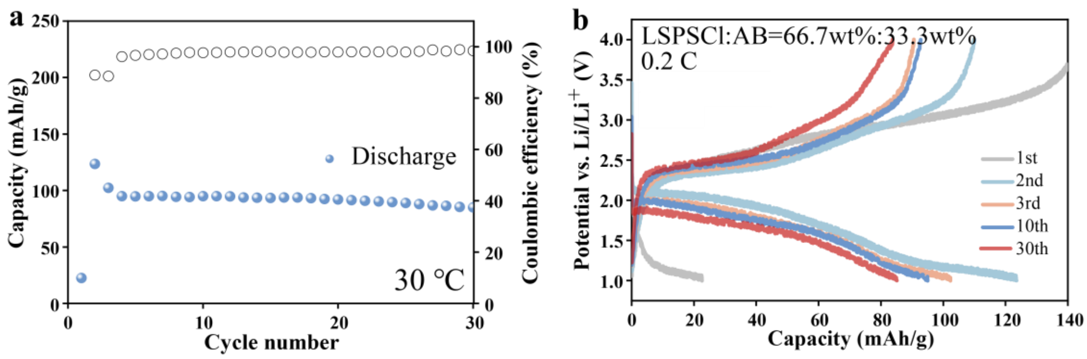


Figure S23. The a) discharge capacity and b) the corresponding C-D curves of ASSBs with AB as cathode at 30 ℃.

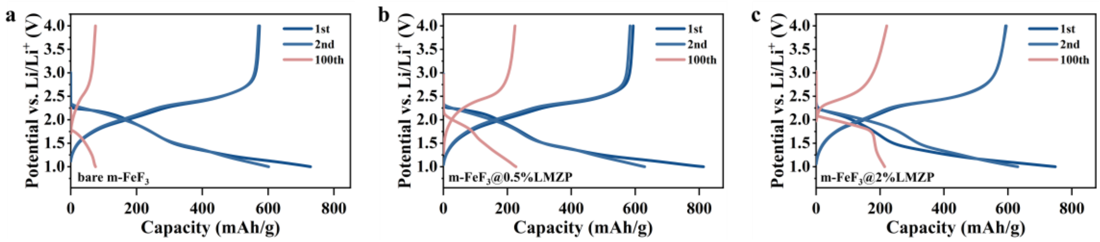


Figure S24. The C-D curves of ASSBs with a) bare m-FeF_3, b) m-FeF_3@0.5%LMZP and c) m-FeF_3@2%LMZP as cathodes at 30 ℃.

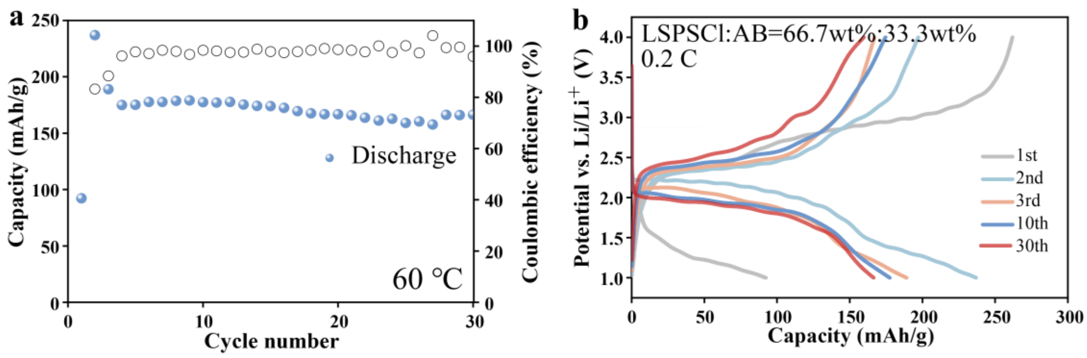


Figure S25. The a) discharge capacity and b) the corresponding C-D curves of ASSBs with AB as cathode at 60 °C.

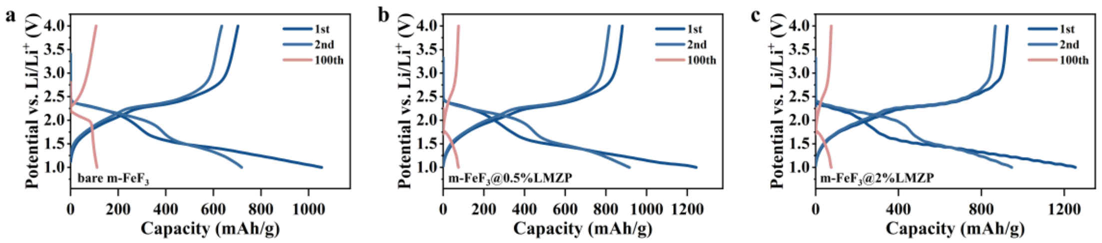


Figure S26. The C-D curves of ASSBs with the a) bare m-FeF_3, b) m-FeF_3@0.5%LMZP and c) m-FeF_3@2%LMZP as cathodes at 60 ℃.

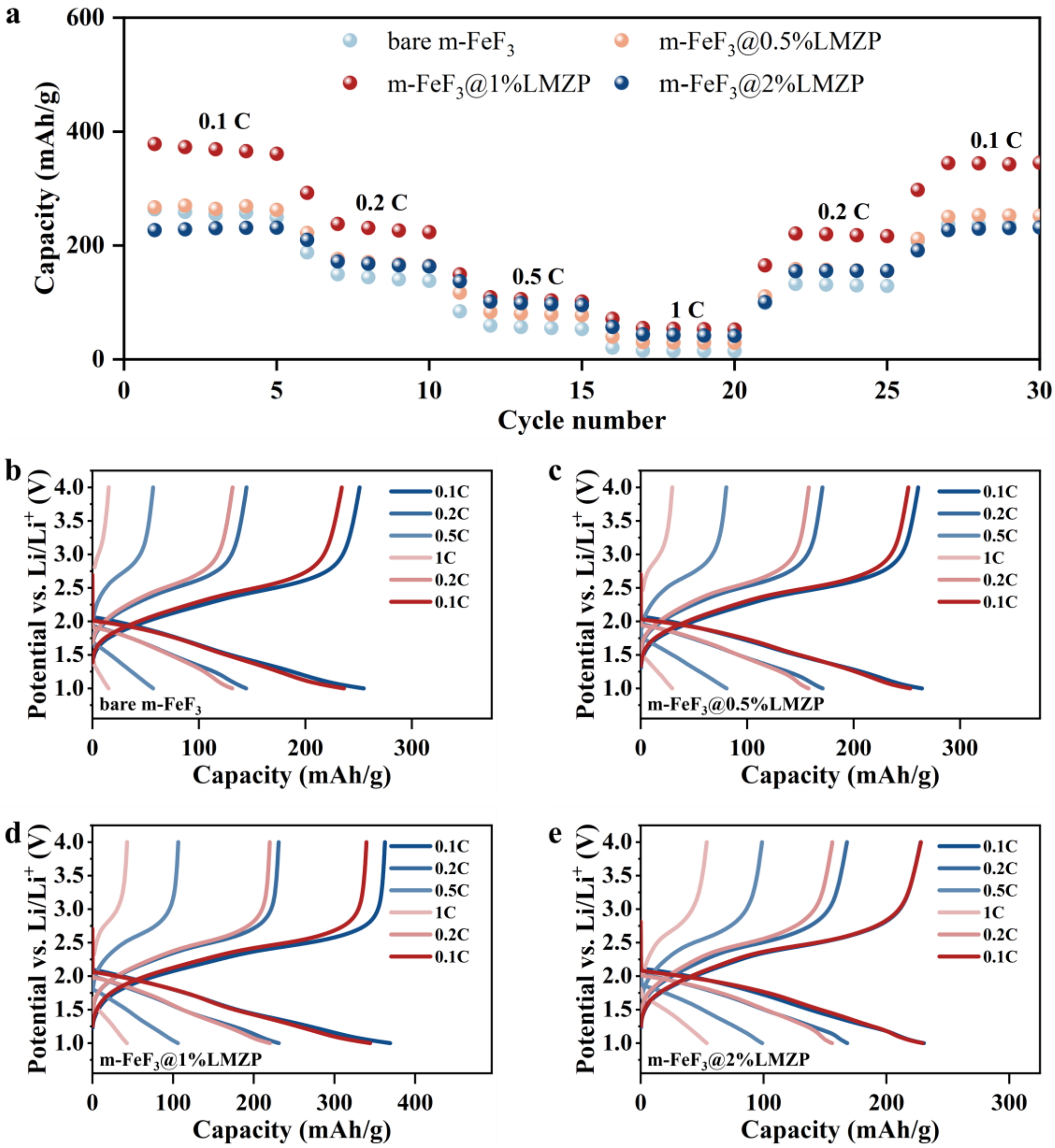


Figure S27. a) Rate tests of ASSBs with m-FeF_3@LMZP at 0 °C. The corresponding C-D curves of b) bare m-FeF_3, c) m-FeF_3@0.5%LMZP, d) m-FeF_3@1%LMZP and e) m-FeF_3@2%LMZP.

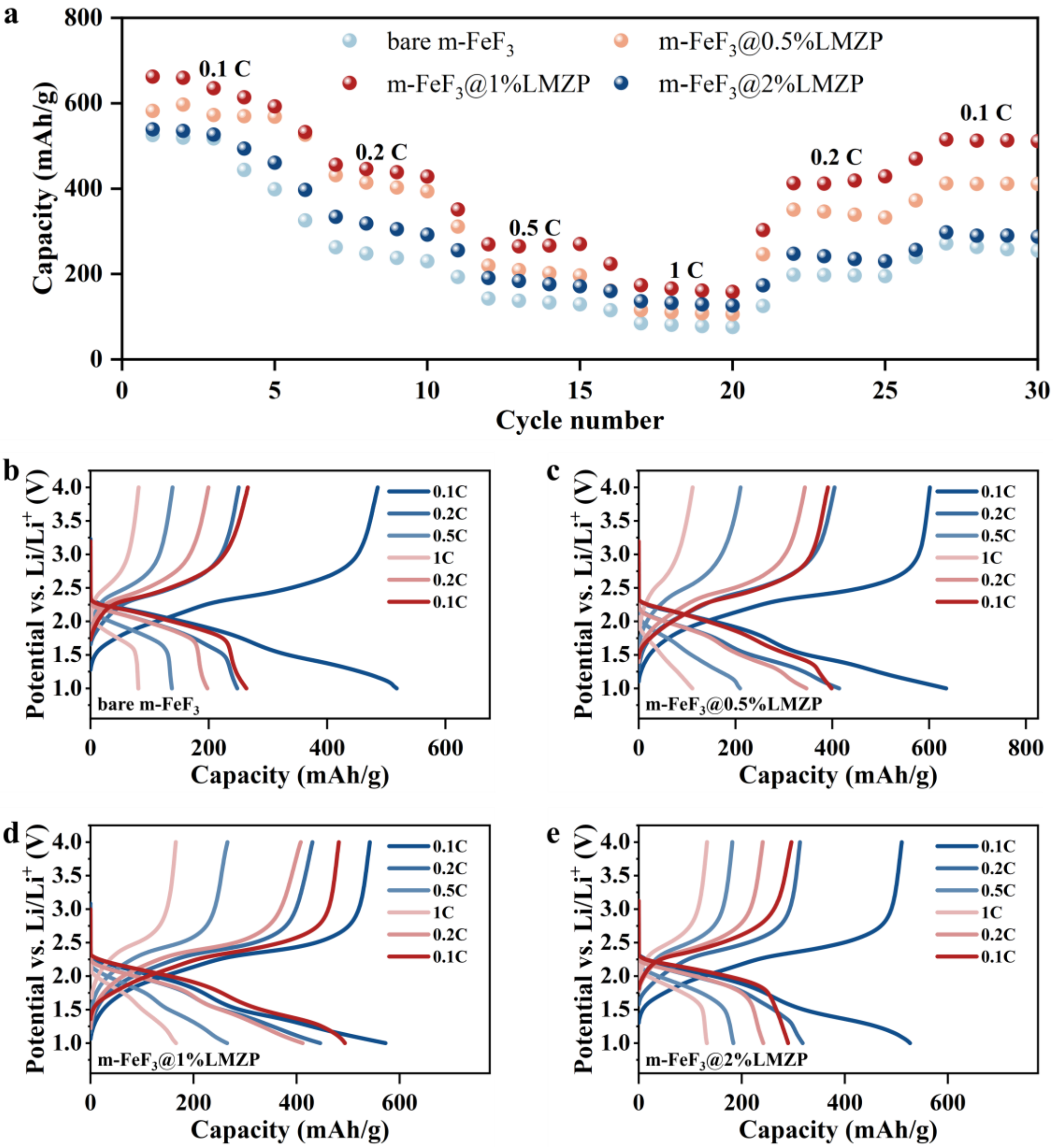


Figure S28. a) Rate tests of ASSBs with m-FeF_3@LMZP at 30 °C. The corresponding C-D curves of ASSBs with b) bare m-FeF_3, c) m-FeF_3@0.5%LMZP, d) m-FeF_3@1%LMZP and e) m-FeF_3@2%LMZP.

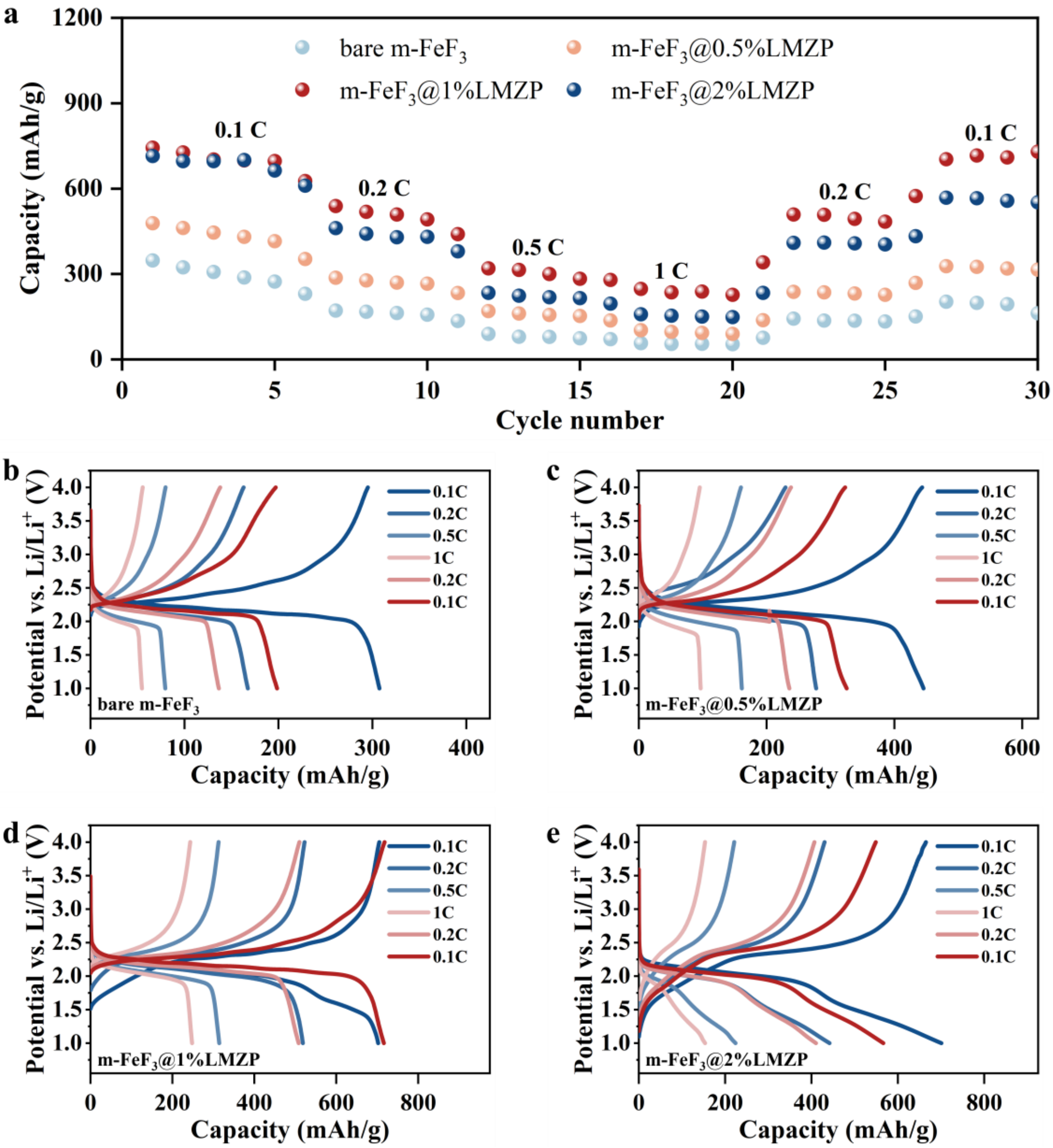


Figure S29. a) Rate tests of ASSBs with m-FeF_3@LMZP at 60 °C. The corresponding C-D curves of b) bare m-FeF_3, c) m-FeF_3@0.5%LMZP, d) m-FeF_3@1%LMZP and e) m-FeF_3@2%LMZP.

Sample	Particle size	Mass loading (mg/cm^2)	Areal capacity (mAh/cm^2)	Electrolytes	Journal
n-FeF_2@LMZP	**~50 nm**	**7.5**	**2**	**Solid-State Electrolyte**	**This Work**
m-FeF_3@LMZP	**1-2 um**	**7.5**	**3.1**		
FeF_2	~200 nm	2.5	1.5	Solid-State Electrolyte	Adv. Funct. Mater.
FeF_3	3-5 um	1.34	0.7	Solid-State Electrolyte	Adv. Energy Mater.
FeF_3	~4 um	1.34	1	Solid-State Electrolyte	J. Mater. Chem. A
FeF_2	~20 nm	2	0.8	Solid-State Electrolyte	Nat. Mater.
FeF_3	~100 nm	1	0.3	Solid-State Electrolyte	Energy Stor. Mater.
FeF_2	~50 nm	1.2	0.6	Liquid Electrolyte	Adv. Sci.
FeF_2	~50 nm	0.7	0.1	Liquid Electrolyte	Small
FeF_2	~50 nm	1	0.3	Liquid Electrolyte	Adv. Funct. Mater.
FeF_2	~20 nm	2	0.8	Liquid Electrolyte	Adv. Funct. Mater.
FeF_2	~50 nm	3	1.2	Liquid Electrolyte	Energy Stor. Mater.
FeF_2	~100 nm	1.5	0.3	Liquid Electrolyte	J. Mater. Sci.
FeF_2	~20 nm	0.75	0.3	Liquid Electrolyte	Adv. Funct. Mater.
FeF_2	~50 nm	1.5	0.6	Liquid Electrolyte	Adv. Energy Mater.
FeF_2	~100 nm	1	0.5	Liquid Electrolyte	J. Am. Chem. Soc.
FeF_2	~200 nm	1.5	0.4	Liquid Electrolyte	ACS Appl. Mater. Inter.
FeF_2	~50 nm	2	0.4	Liquid Electrolyte	Adv. Energy Mater.
FeF_2	~20 nm	1	0.5	Liquid Electrolyte	Nat. Mater.
FeF_2	~10 nm	1.5	0.7	Liquid Electrolyte	J. Mater. Chem. A
FeF_2	~10 nm	3.5	1.2	Liquid Electrolyte	Adv. Energy Mater.
FeF_3	~100 nm	4.5	1.8	Liquid Electrolyte	Matter
FeF_3	~50 nm	5.3	1	Liquid Electrolyte	Adv. Mater.
FeF_3	~50 nm	2	0.5	Liquid Electrolyte	Nano Energy
FeF_3	~50 nm	2	0.3	Liquid Electrolyte	Adv. Energy Mater.
FeF_3	~150 nm	2	0.4	Liquid Electrolyte	Nano Lett.
FeF_3	~10 nm	2	0.4	Liquid Electrolyte	J. Mater. Chem. A
FeF_3	~10 nm	1.5	0.2	Liquid Electrolyte	Adv. Mater.
FeF_3	~10 nm	2	0.4	Liquid Electrolyte	ACS Nano
FeF_3	~1 um	2	0.4	Liquid Electrolyte	Adv. Energy Mater.
FeF_3	~10 nm	0.88	0.2	Liquid Electrolyte	J. Mater. Chem. A
FeF_3	~40 nm	0.5	0.3	Liquid Electrolyte	ACS Appl. Mater. Inter.
FeF_3	~500 nm	1.5	0.2	Liquid Electrolyte	J. Energy Chem.
FeF_3	~10 nm	1.5	0.7	Liquid Electrolyte	Adv. Funct. Mater.
FeF_3	~25 nm	1	0.2	Liquid Electrolyte	Nano Energy
FeF_3	~30 nm	1	0.2	Liquid Electrolyte	J. Alloys Compd.
FeF_3	~500 nm	2	0.3	Liquid Electrolyte	Nanoscale
FeF_3	~500 nm	2.5	0.5	Liquid Electrolyte	Ionics
FeF_3	~100 nm	2	0.2	Liquid Electrolyte	J. Mater. Chem. A
FeF_3	~1 um	1.5	0.3	Liquid Electrolyte	ACS Sustain. Chem. Eng.
FeF_3	~50 nm	2	0.4	Liquid Electrolyte	J. Mater. Chem. A
FeF_3	~100 nm	1	0.5	Liquid Electrolyte	ACS Energy Lett.
FeF_3	~100 nm	1.5	0.7	Liquid Electrolyte	ACS Appl. Mater. Inter.
FeF_3	~100 nm	0.6	0.2	Liquid Electrolyte	Sci. Bull.
FeF_3	~1 um	2.5	0.5	Liquid Electrolyte	Solid State Sci.
FeF_3	~50 nm	1.5	0.2	Liquid Electrolyte	J. Mater. Chem. A
FeF_3	~50 nm	1.5	0.5	Liquid Electrolyte	J. Alloys Compd.

Figure S30. Comparison of areal capacity of the previously reported IBFs cathodes in ASSBs and liquid electrolytes-based batteries with this study.

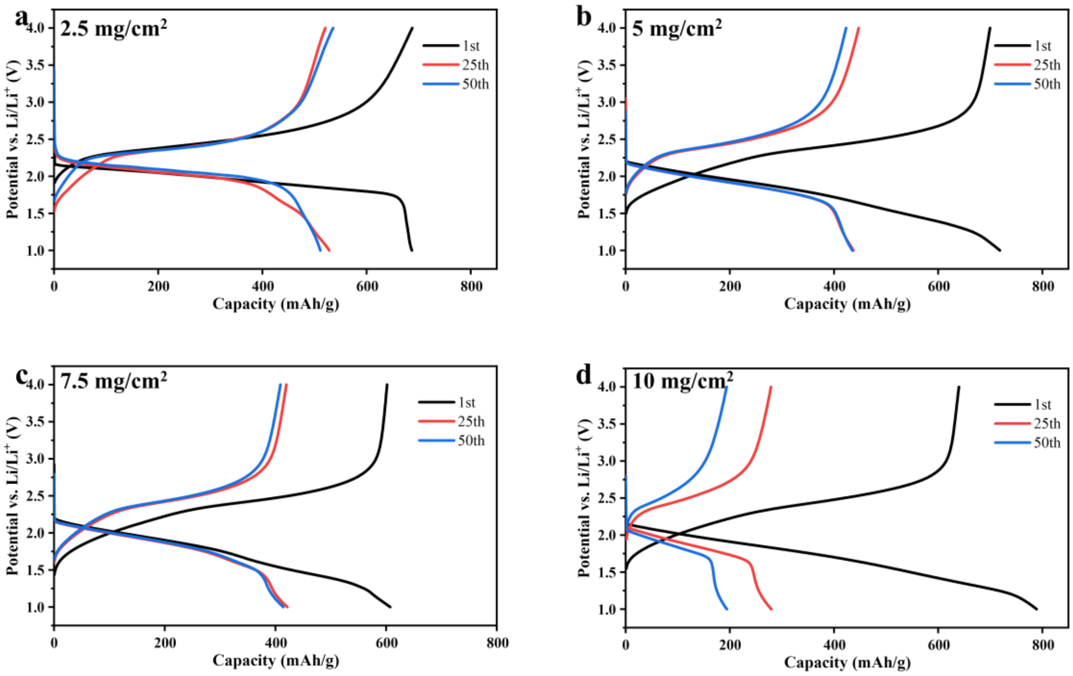


Figure S31. The C-D curves of ASSBs with m-FeF_3@1%LMZP at the mass loading of a) 2.5 mg/cm^2, b) 5 mg/cm^2, c) 7.5 mg/cm^2 and d) 10 mg/cm^2.

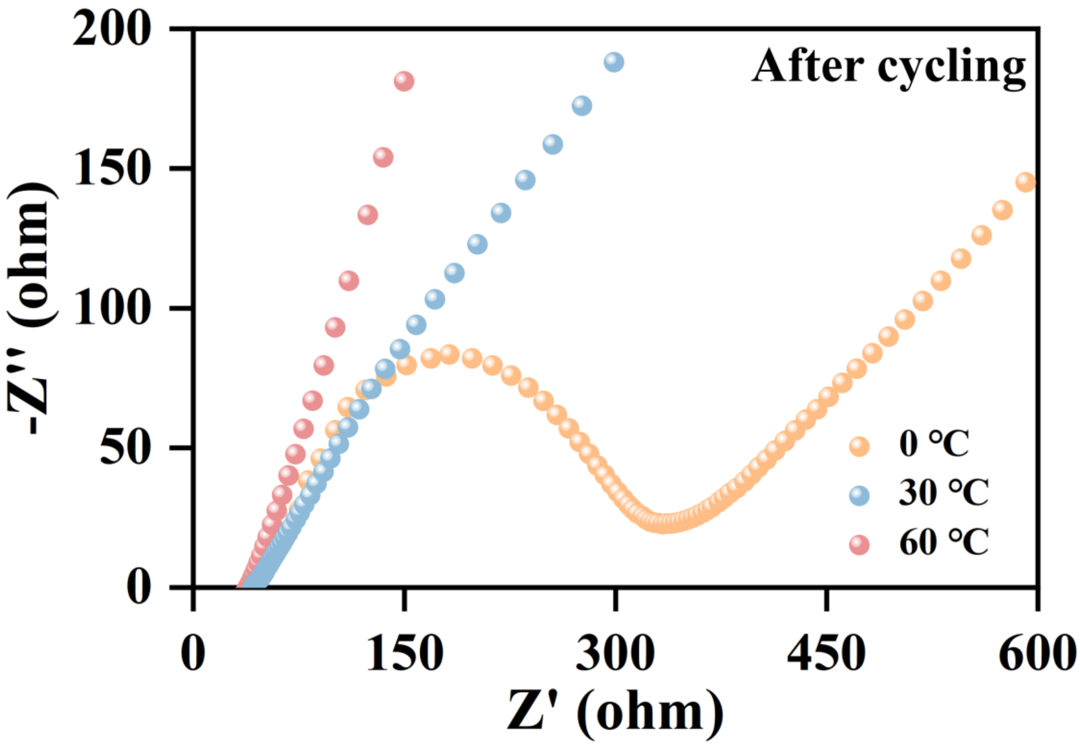


Figure S32. The EIS test of ASSB with m-FeF_3@1%LMZP after cycling at 0 ℃, 30 ℃ and 60 ℃.

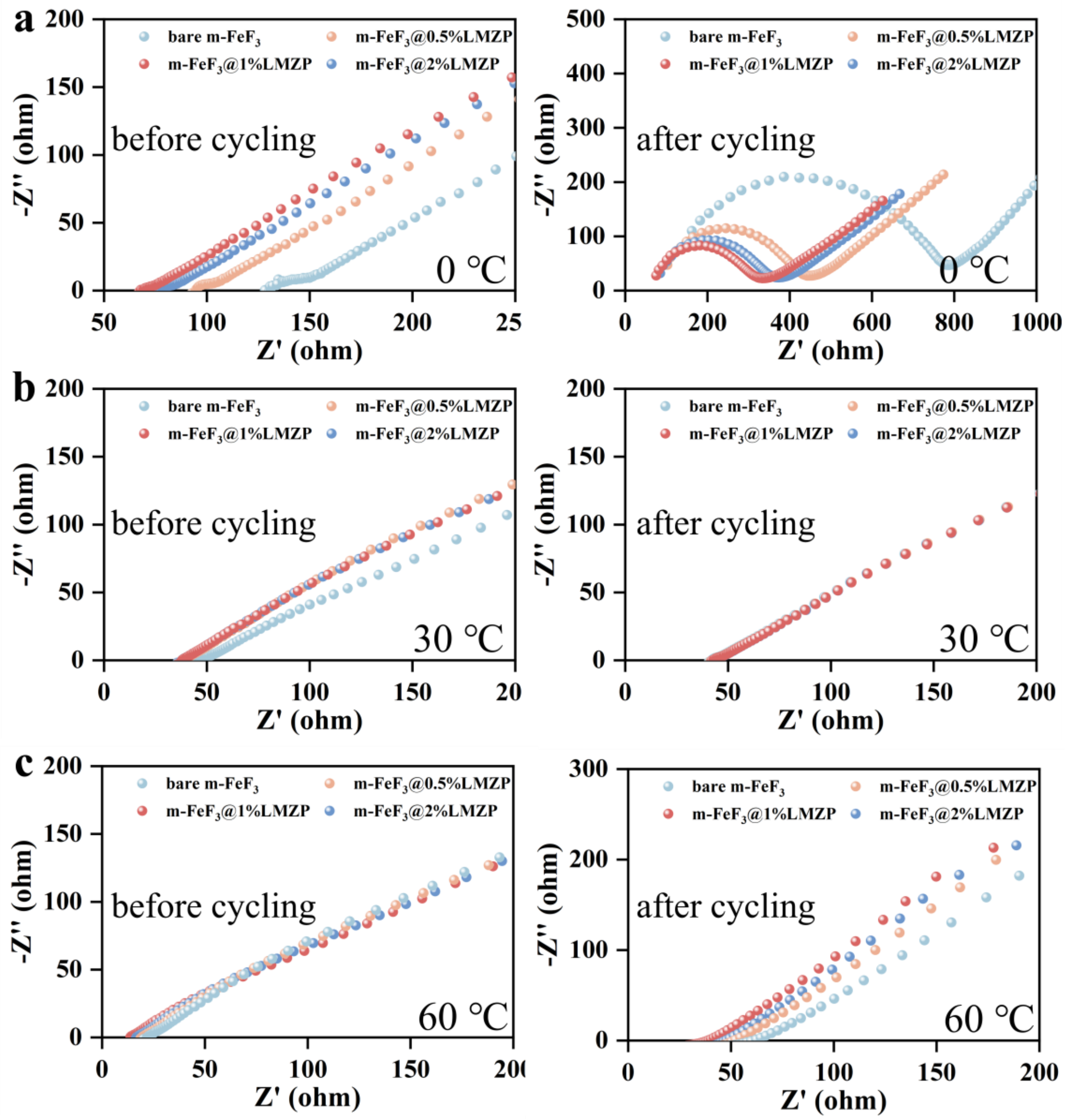


Figure S33. The EIS tests of m-FeF₃@LMZP before/after cycling at a) 0 °C, b) 30 °C and c) 60 °C.

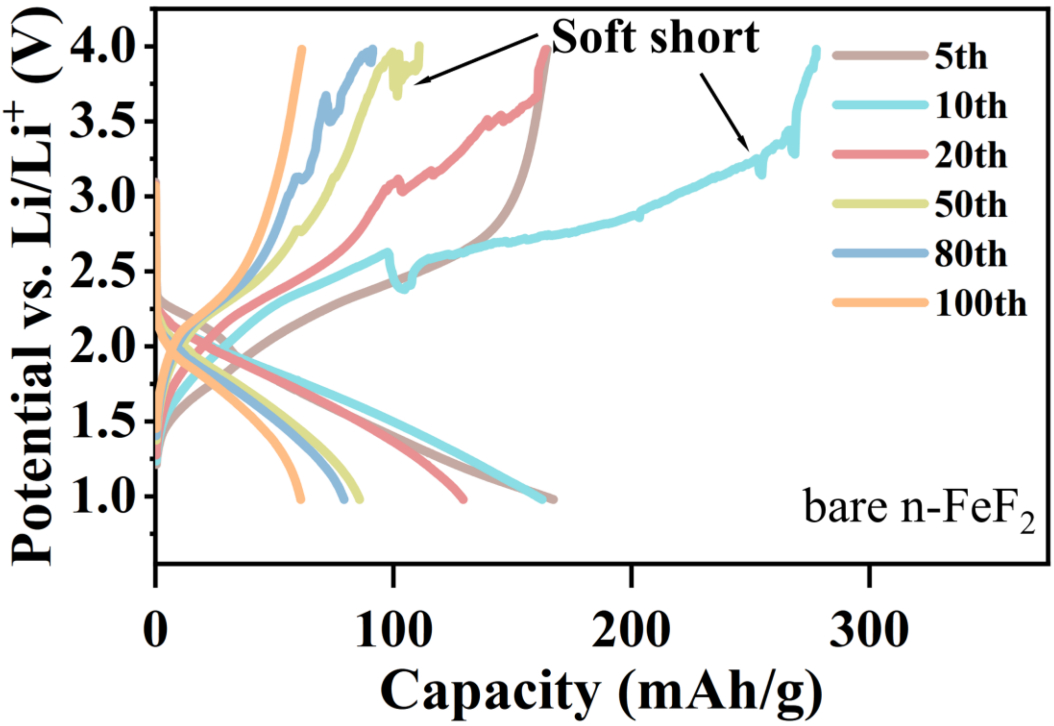


Figure S34. The C-D curves of ASSBs with bare n-FeF_2 as cathode and Li metal as anode.

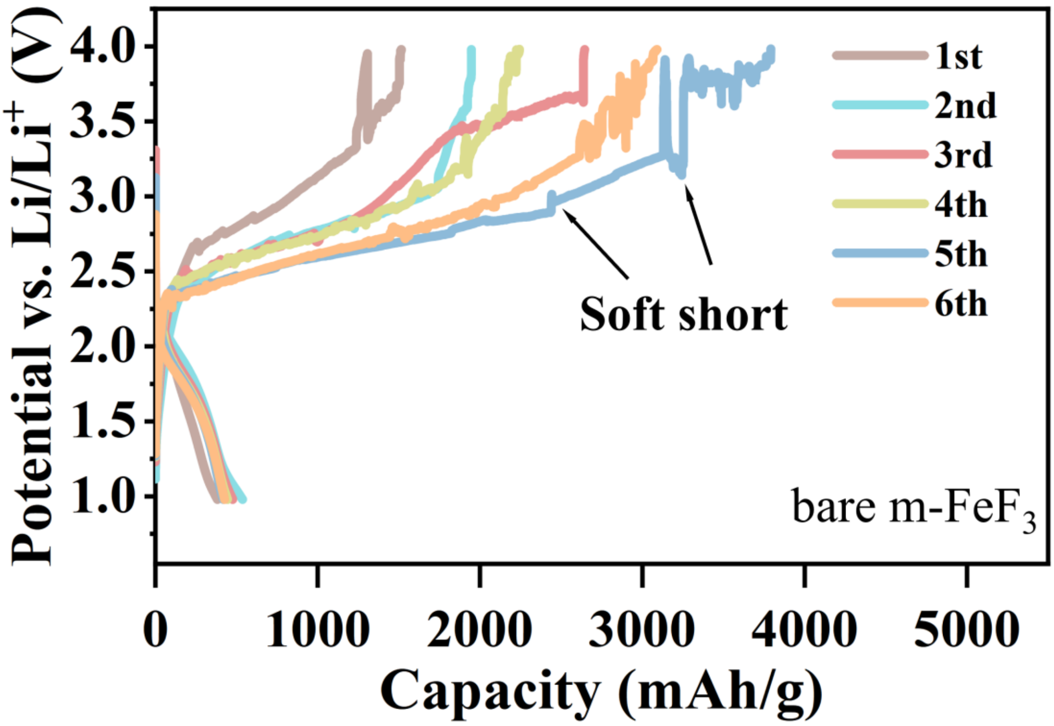


Figure S35. The C-D curves of ASSBs with bare m-FeF_3 as cathode and Li metal as anode.

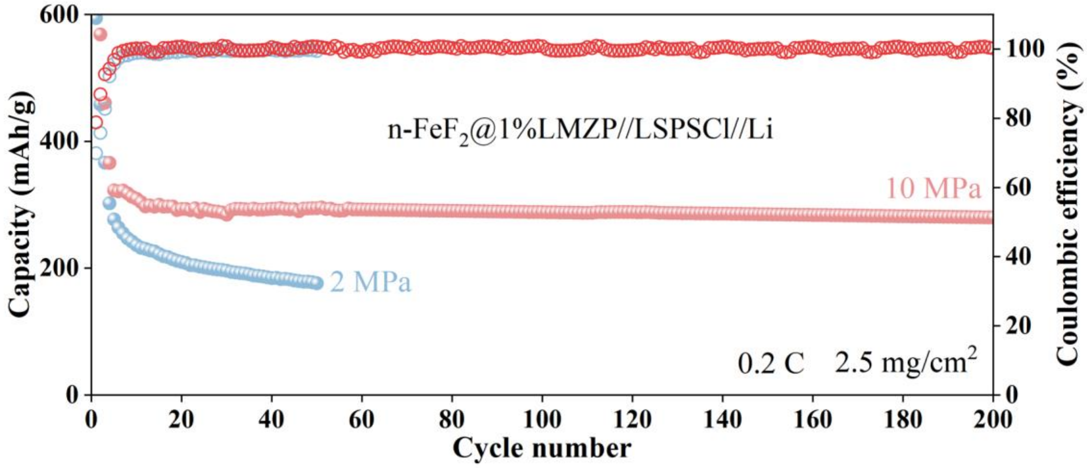


Figure S36. The cycle performance of ASSB with n-FeF_2@1%LMZP cathode and Li metal anode at a reduced stack pressure of 2 MPa.

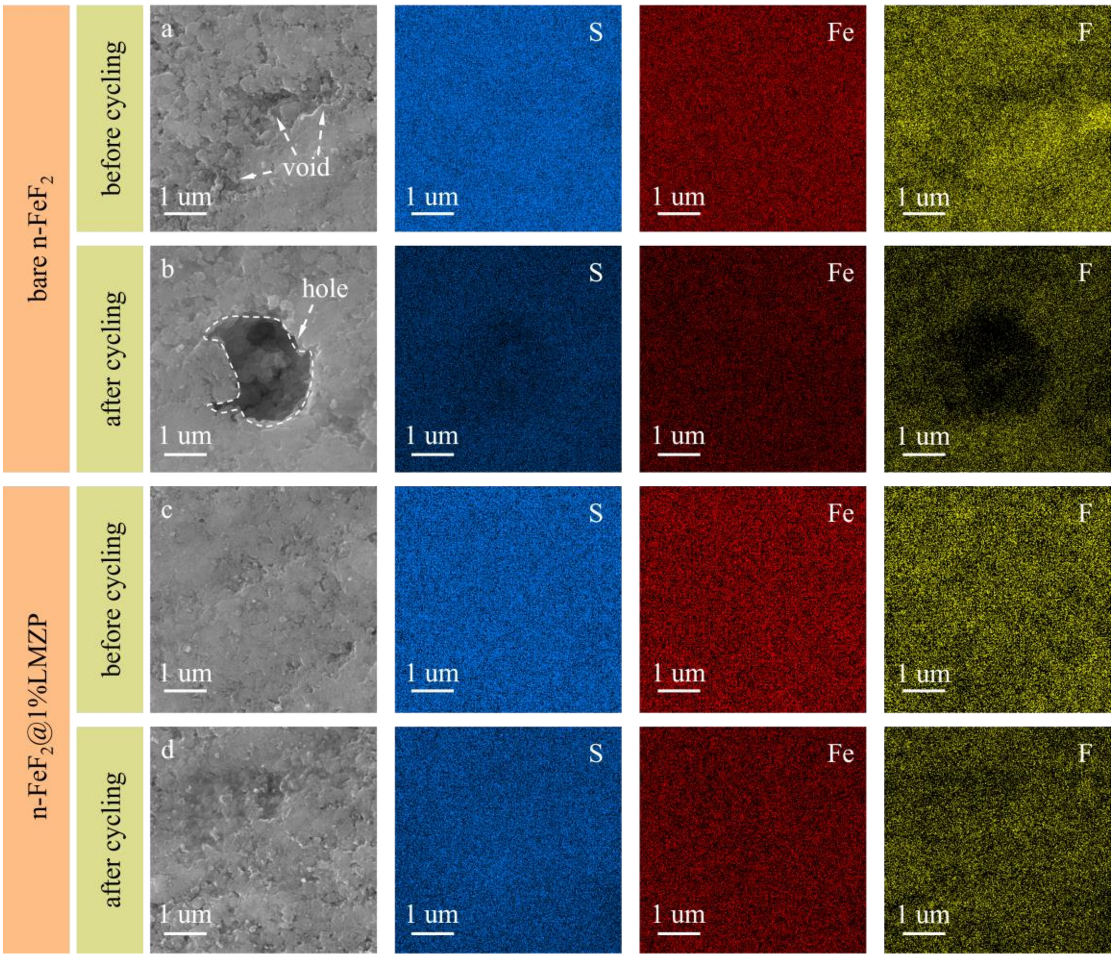


Figure S37. Cross-section SEM images of the solid electrodes with bare n-FeF_2 a) before and b) after cycling. Solid electrodes with n-FeF_2@1%LMZP c) before and d) after cycling.

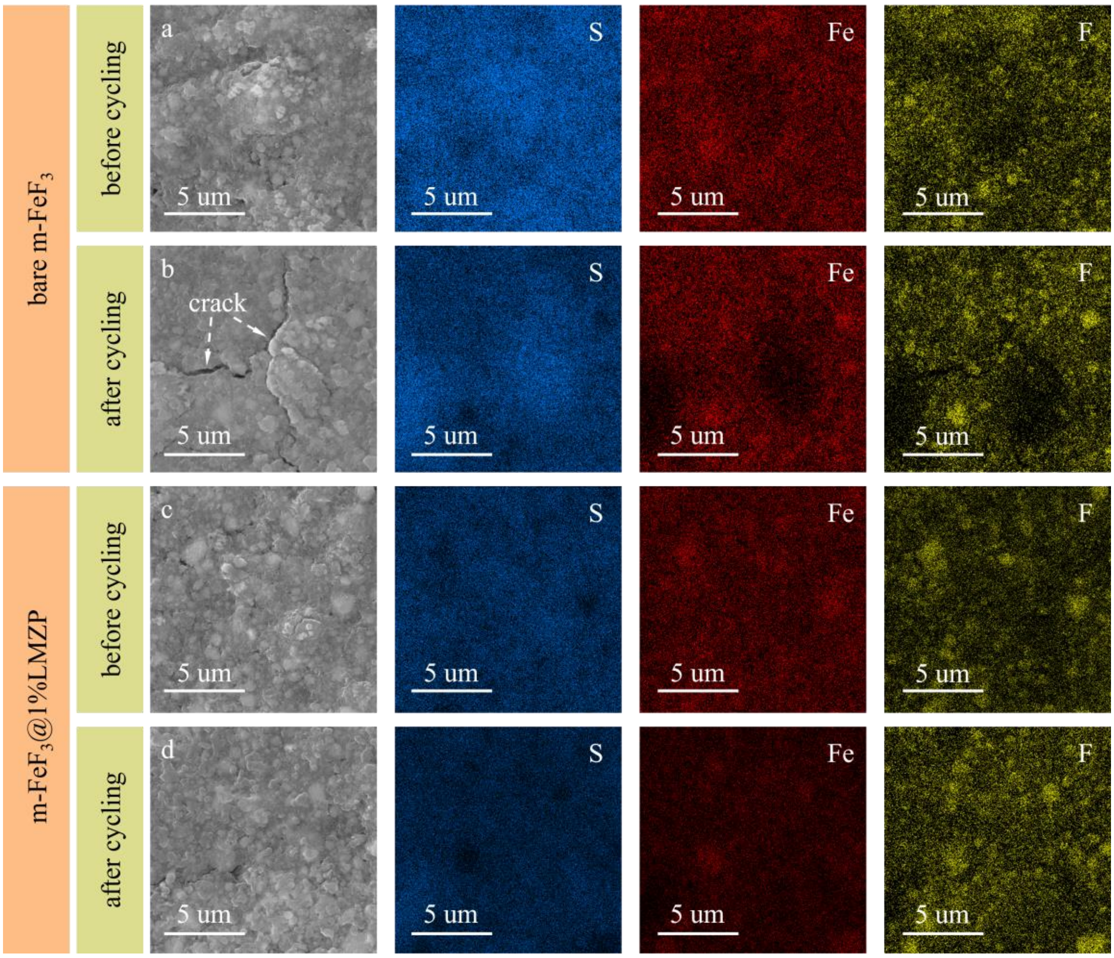


Figure S38. Cross-section SEM images of the solid electrodes with bare m-FeF_3 a) before and b) after cycling and m-FeF_3@1%LMZP c) before and d) after cycling.