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

Electronic Supplementary Information for

Degradation analysis during fast lifetime cycling of sulfide-based all-solid-state Li-metal batteries using in-situ electrochemical impedance spectroscopy

Young Jung Kim,[#ab] Hyeseong Jeong,[#ac] Sahn Nam,[b] Dongwook Shin,[c] Jong-Ho Lee,*[a] and Hyoungchul Kim*[d]

[a]*Center for Hydrogen Energy Materials, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea*

[b]*Department of Materials Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea*

[c]*Division of Materials Science and Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea*

[d]*Department of Mechanical and System Design Engineering, Hongik University, 94 Wausan-ro, Mapo-gu, Seoul 04066, Republic of Korea*

[#]These authors contributed equally to this work

*Corresponding authors. E-mail address: jongho@kist.re.kr (J.-H. Lee), hyoungchul@hongik.ac.kr (H. Kim)

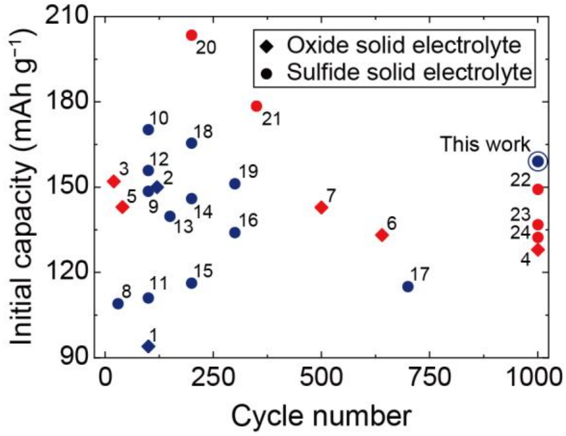

Fig. S1 Comparison of electrochemical performance with that previously reported all-solid-state Li-metal batteries (ASSLMBs). The color of the symbol indicates the following: Red indicates operation at high temperatures (60–80 °C). Blue indicates operation at room temperature (25–35 °C).

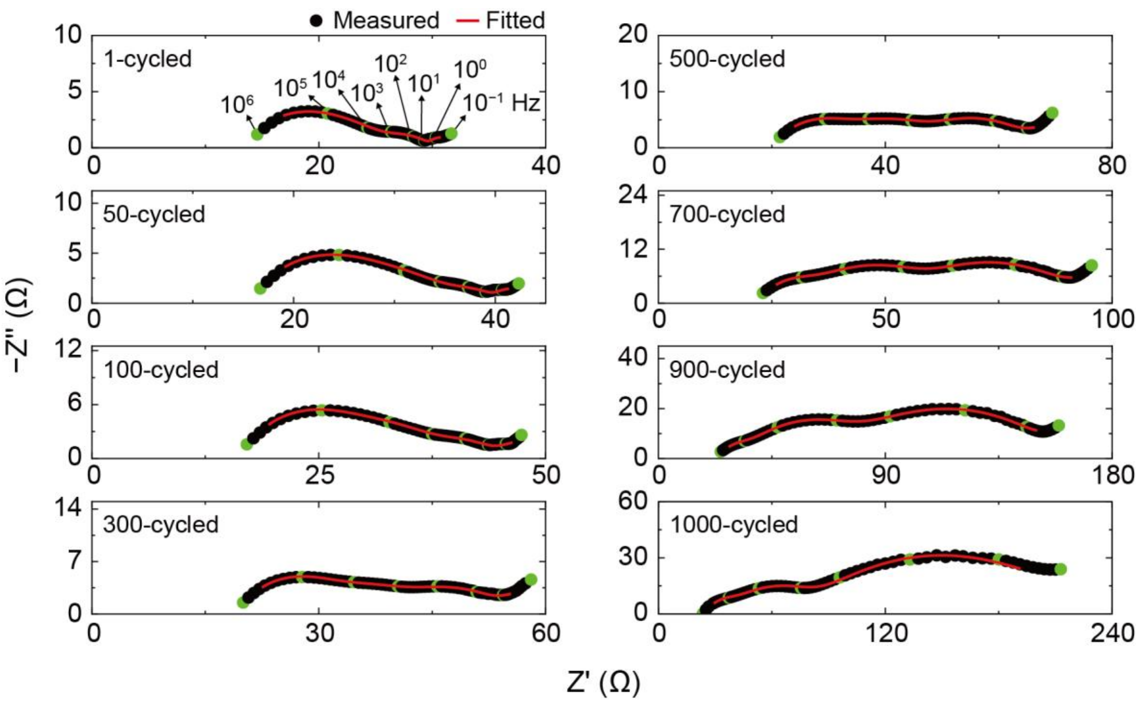

Fig. S2 Nyquist plots of electrochemical impedance spectroscopy (EIS) for the ASSLMB (1-, 50-, 100-, 300-, 500-, 700-, 900-, and 1000-cycled), measured over a frequency range of 10^6 to 10^{-1} Hz. The black and red lines represent the raw and fitted data, respectively.

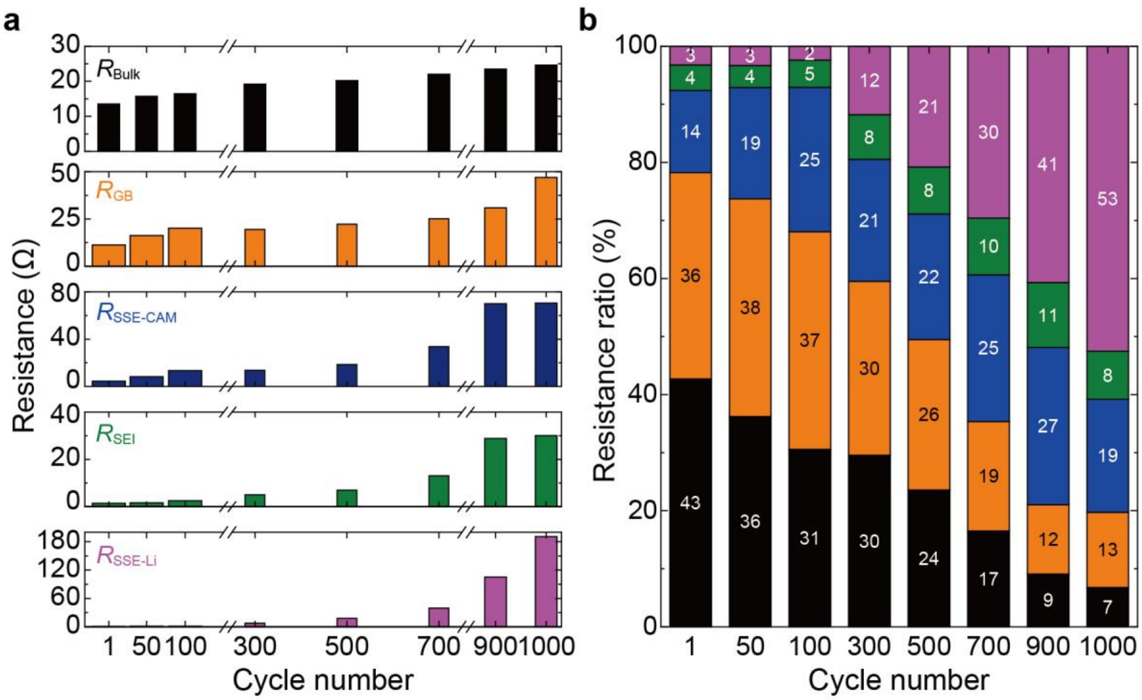

Fig. S3 Variation of each internal resistance component as a function of cycling, calculated by the distribution of relaxation times (DRT). (a) Separated histogram for the absolute value of each resistance component. (b) Stacked histogram for the proportion of each resistance component. Equivalent circuit consisting of bulk resistance of electrolyte (R_{Bulk}), grain boundary resistance of electrolyte (R_{GB}), interfacial resistance of electrolyte-cathode active material ($R_{SSE-CAM}$), interfacial resistance of solid electrolyte interphase (R_{SEI}), and interfacial resistance of electrolyte-Li metal (R_{SSE-Li}). SSE, CAM, and SEI indicate sulfide solid electrolyte, cathode active material, and solid electrolyte interface, respectively.

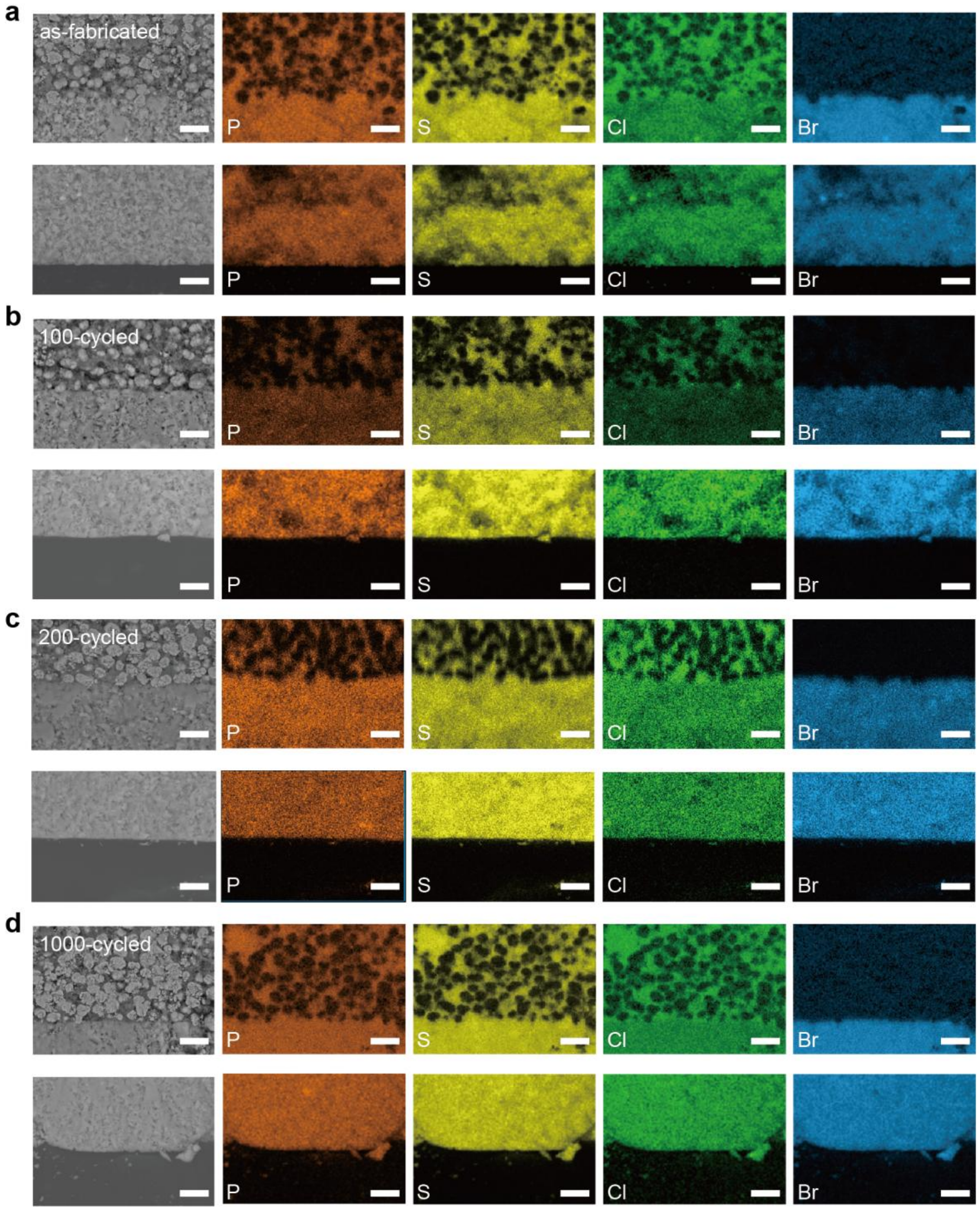

Fig. S4 Scanning electron microscopy and energy dispersive spectroscopy analysis of ASSLMB microstructure. Elemental mappings of cathode-electrolyte (top) and electrolyte -Li metal (bottom) interface of (a) the as-fabricated, (b) the 100-cycled, (c) the 200-cycled, and (d) the 1000-cycled cells. All scale bars correspond to 10 μm.

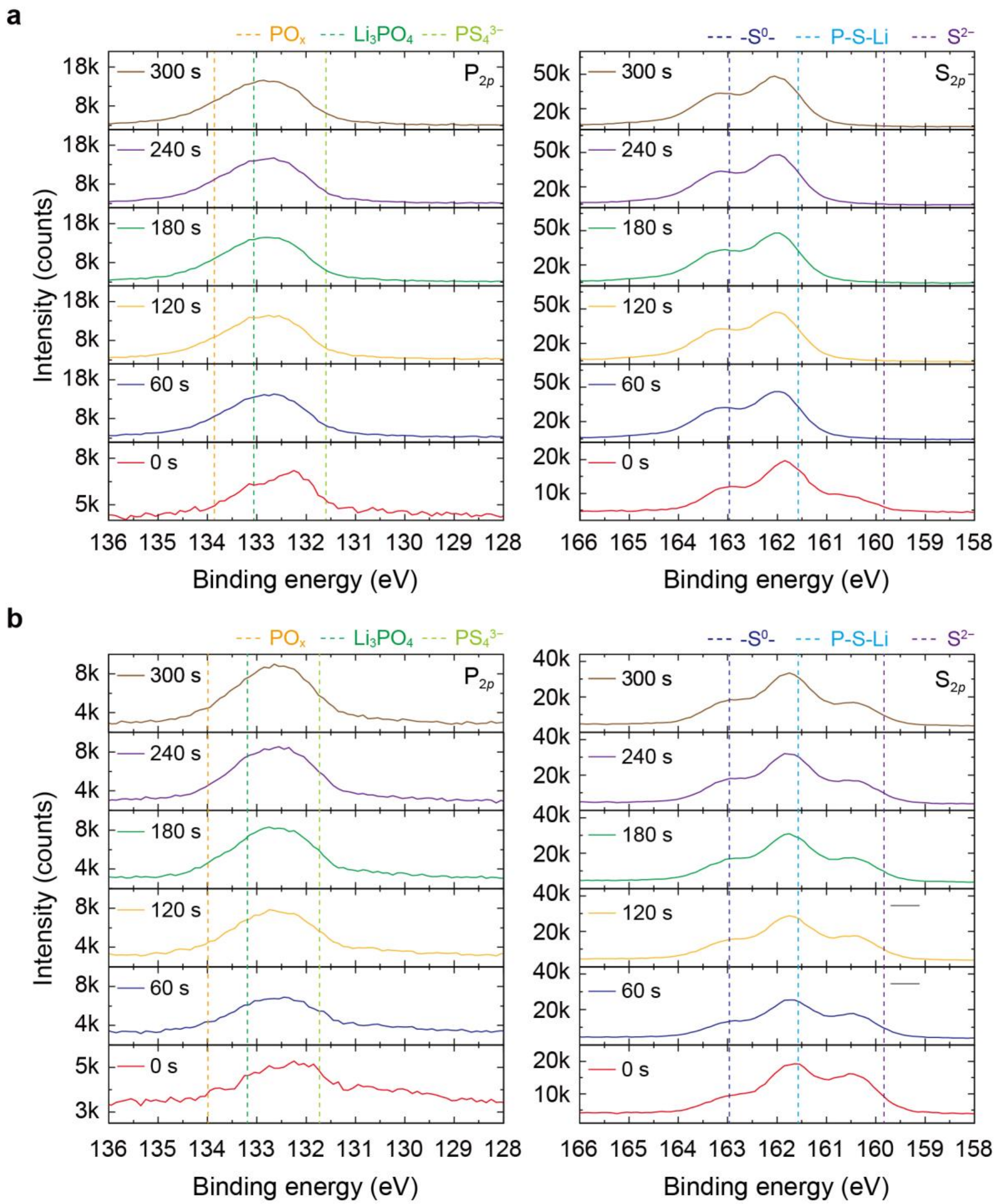

Fig. S5 X-ray photoelectron spectroscopy analysis of P 2*p* and S 2*p* in SSEs as a function of etching time at the end of regime 4: (a) cathode/SSE and (b) SSE/anode interfaces.

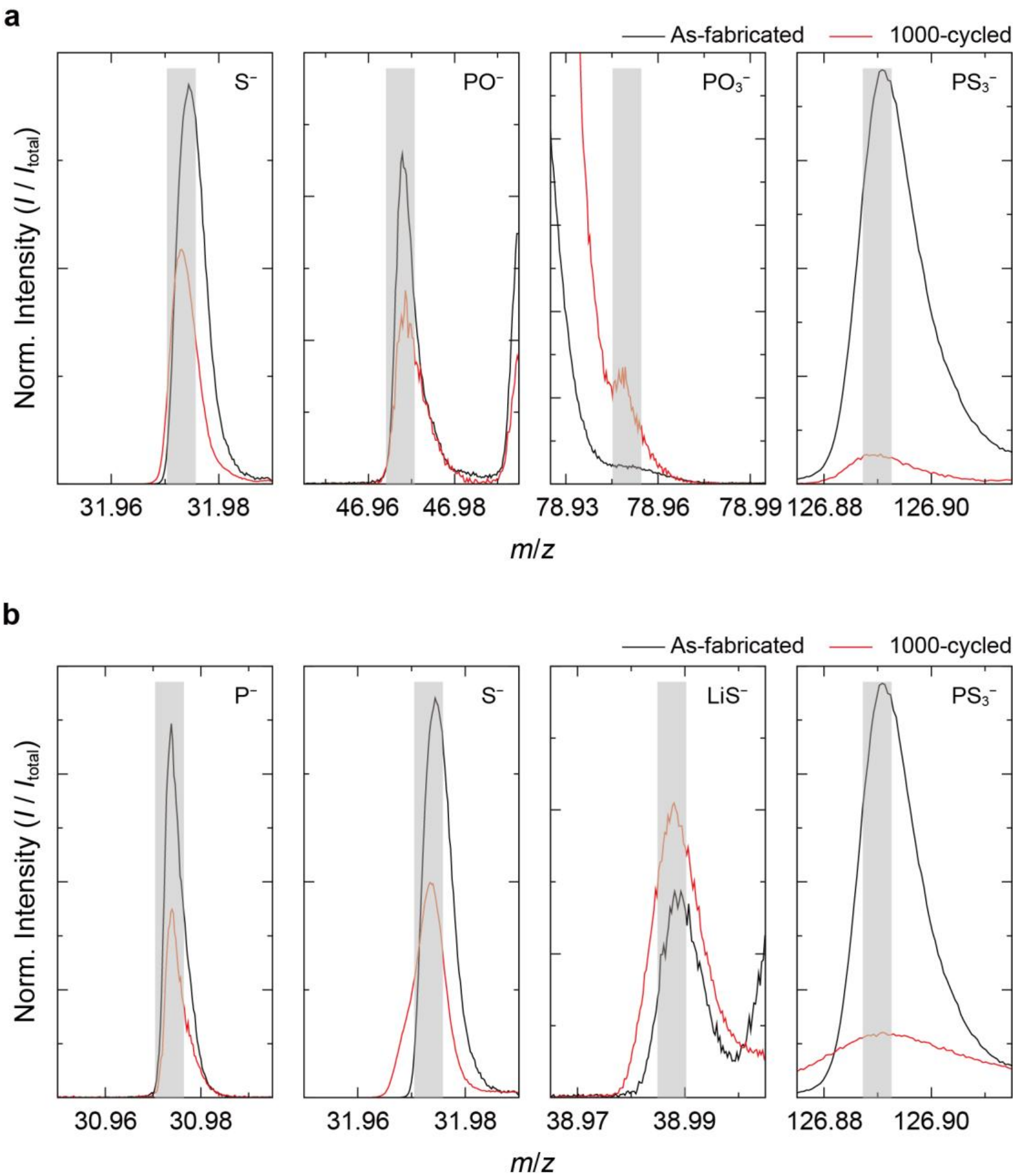

Fig. S6 Mass-spectra analysis of time-of-flight secondary ion mass spectrometry mass for the lifetime of ASSLMBs: (a) cathode/SSE and (b) SSE/anode interfaces. Degradation behaviors lead to an increase in signal intensity of PO_3^- and LiS^- fragments.

Table S1 Comparison of the operating conditions of this study with those of the previously reported ASSLMBs.

Electrolyte type	Operating temperature (°C)	Cycle number	C-rate	Initial capacity (mAh g^{-1})	Ref.
Oxide	25	100	0.05C	94.00	1
Oxide	25	120	0.4C	150.00	2
Oxide	60	20	0.05C	152.00	3
Oxide	60	1000	5C	128.00	4
Oxide	65	40	100, 200 μA cm^{-2}	143.00	5
Oxide	65	640	0.2, 0.5, 0.6C	133.14	6
Oxide	80	500	1C	142.96	7
Sulfide	25	30	0.1C	109.00	8
Sulfide	25	100	0.1C	148.54	9
Sulfide	25	100	0.1C	170.20	10
Sulfide	25	100	0.1C	111.00	11
Sulfide	25	100	0.5C	155.85	12
Sulfide	25	150	0.1C	139.71	13
Sulfide	25	200	0.1C	145.96	14
Sulfide	25	200	0.5C	116.20	15
Sulfide	25	300	1C	134.01	16
Sulfide	25	700	1C	115.00	17
Sulfide	30	200	0.5C	165.47	18
Sulfide	35	300	0.5C	151.17	19
Sulfide	60	200	0.35C	203.43	20
Sulfide	60	350	0.5C	178.47	21
Sulfide	60	1000	1C	149.20	22
Sulfide	60	1000	1C	136.77	23
Sulfide	60	1000	1C	132.30	24
Sulfide	**25**	**1000**	**0.5C**	**159.28**	**This work**

Table S2. Individual fitting component values over the cycle number obtained from EIS curves.

	Cycle number							
	1	50	100	300	500	700	900	1000
R_{Bulk} (Ω)	13.520	15.710	16.460	19.210	20.210	22.040	23.490	24.650
R_{GB} (Ω)	4.000	9.145	11.040	13.000	15.980	23.240	39.510	39.630
CPE-T_{GB} ($Fs^{\alpha-1}$)	1.66E−04	1.80E−04	1.11E−04	3.76E−04	2.17E−04	6.72E−05	3.08E−05	3.12E−05
CPE-P_{GB} (α)	0.599	0.555	0.589	0.513	0.569	0.645	0.678	0.660
C_{GB} (F)	1.23E−06	1.06E−06	1.03E−06	2.41E−06	2.99E−06	1.91E−06	1.27E−06	1.00E−06
$R_{SSE\text{-}CAM}$ (Ω)	4.684	5.707	6.858	11.320	15.030	31.940	82.680	135.500
CPE-$T_{SSE\text{-}CAM}$ ($Fs^{\alpha-1}$)	5.36E−03	8.14E−03	4.09E−03	4.14E−03	2.67E−03	1.82E−03	1.05E−03	1.22E−03
CPE-$P_{SSE\text{-}CAM}$ (α)	0.500	0.487	0.530	0.554	0.625	0.575	0.544	0.528
$C_{SSE\text{-}CAM}$ (F)	1.34E−04	3.20E−04	1.73E−04	3.52E−04	3.90E−04	2.23E−04	1.34E−04	2.43E−04
R_{SEI} (Ω)	7.825	9.940	10.040	10.640	12.430	12.440	12.720	15.440
CPE-T_{SEI} ($Fs^{\alpha-1}$)	4.85E−06	2.96E−06	1.55E−06	3.41E−06	5.46E−06	4.48E−06	4.13E−06	2.01E−06
CPE-P_{SEI} (α)	0.709	0.750	0.799	0.742	0.695	0.705	0.705	0.750
C_{SEI} (F)	7.35E−08	9.14E−08	9.54E−08	9.80E−08	8.01E−08	7.44E−08	6.69E−08	6.30E−08
$R_{SSE\text{-}Li}$ (Ω)	1.842	3.027	9.610	11.000	22.400	43.810	100.000	147.800
CPE-$T_{SSE\text{-}Li}$ ($Fs^{\alpha-1}$)	2.10E−01	1.66E−01	1.63E−01	1.48E−01	1.11E−01	1.04E−01	1.19E−01	1.00E−01
CPE-$P_{SSE\text{-}Li}$ (α)	0.889	0.829	0.512	0.627	0.494	0.490	0.865	0.595
$C_{SSE\text{-}Li}$ (F)	1.86E−01	1.44E−01	2.51E−01	1.98E−01	2.80E−01	5.08E−01	1.76E−01	6.26E−01

Table S3. Detailed Resistance values over the cycle number obtained from EIS-DRT method.

	Cycle number							
	1	50	100	300	500	700	900	1000
R_{Bulk} (Ω)	13.52	15.71	16.46	19.21	20.21	22.04	23.49	24.65
R_{GB} (Ω)	11.25	16.27	20.19	19.49	22.22	25.15	30.87	47.02
$R_{SSE-CAM}$ (Ω)	4.47	8.31	13.39	13.65	18.55	33.73	70.03	70.60
R_{SEI} (Ω)	1.40	1.64	2.50	5.00	6.94	13.07	28.83	30.03
R_{SSE-Li} (Ω)	1.01	1.44	1.30	7.66	17.82	39.49	105.18	190.72

References

1 F. Han, J. Yue, C. Chen, N. Zhao, X. Fan, Z. Ma, T. Gao, F. Wang, X. Guo and C. Wang, *Joule*, 2018, **2**, 497–508.

2 X. Zhang, T. Liu, S. Zhang, X. Huang, B. Xu, Y. Lin, B. Xu, L. Li, C. W. Nan and Y. Shen, *J. Am. Chem. Soc.*, 2017, **139**, 13779–13785.

3 J. F. Wu, W. K. Pang, V. K. Peterson, L. Wei and X. Guo, *ACS Appl. Mater. Interfaces*, 2017, **9**, 12461–12468.

4 Y. Fu, K. Yang, S. Xue, W. Li, S. Chen, Y. Song, Z. Song, W. Zhao, Y. Zhao, F. Pan, L. Yang and X. Sun, *Adv. Funct. Mater.*, 2023, **33**, 2210845.

5 Y. Li, X. Chen, A. Dolocan, Z. Cui, S. Xin, L. Xue, H. Xu, K. Park and J. B. Goodenough, *J. Am. Chem. Soc.*, 2018, **140**, 6448–6455.

6 W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram and J. B. Goodenough, *J. Am. Chem. Soc.*, 2016, **138**, 9385–9388.

7 X. Ban, W. Zhang, N. Chen and C. Sun, *J. Phys. Chem. C*, 2018, **122**, 9852–9858.

8 Y. Tao, S. Chen, D. Liu, G. Peng, X. Yao and X. Xu, *J. Electrochem. Soc.*, 2015, **163**, 96–101.

9 J. Kim, M. J. Kim, J. Kim, J. W. Lee, J. Park, S. E. Wang, S. Lee, Y. C. Kang, U. Paik, D. S. Jung and T. Song, *Adv. Funct. Mater.*, 2023, **33**, 2211355.

10 R. Rajagopal, Y. Subramanian, Y. J. Jung, S. Kang and K.-S. Ryu, *J. Mater. Sci. Tech.*, 2024, **191**, 8–16.

11 S. Li, S. J. Yang, G. X. Liu, J. K. Hu, Y. L. Liao, X. L. Wang, R. Wen, H. Yuan, J. Q. Huang and Q. Zhang, *Adv. Mater.*, 2024, **36**, 2307768.

12 J. Y. Jung, H. Jeong, Y. J. Kim, S. M. Cho, Y. Jang and H. Kim, *J. Mater. Chem. A*, 2024, **12**, 12405–12411.

13 S. Feng, R. H. Yeerella, J. Zhou, N. Harpak, C. Li, S. Cai and P. Liu, *ACS Energy Lett.*, 2024, **9**, 748–757.

14 Y. Subramanian, R. Rajagopal and K.-S. Ryu, *J. Energy Storage*, 2024, **78**, 109943.

15 C. Wei, C. Yu, R. Wang, L. Peng, S. Chen, X. Miao, S. Cheng and J. Xie, *J. Power Sources*, 2023, **559**, 232659.

16 H. Yuan, W. Lin, C. Tian, T. Huang and A. Yu, *Nano Energy*, 2024, **128**, 109835.

17 H. Duan, C. Wang, R. Yu, W. Li, J. Fu, X. Yang, X. Lin, M. Zheng, X. Li, S. Deng, X. Hao, R. Li, J. Wang, H. Huang and X. Sun, *Adv. Energy Mater.*, 2023, **13**, 2300815.

18 T. Lee, H. Park, S. Joo, H. Kim, J. Kim, T. Kim, W. Lee, Y. Kim, J. Kim, K. Kim, W. Cho and S. Kim, *ACS Energy Lett.*, 2024, **9**, 4493–4500.

19 R. Fang, Y. Liu, Y. Li, A. Manthiram and J. B. Goodenough, *Mater. Today*, 2023, **64**, 52–60.

20 J. Sung, S. Y. Kim, A. Harutyunyan, M. Amirmaleki, Y. Lee, Y. Son and J. Li, *Adv. Mater.*, 2023, **35**, 2210835.

21 Z. Wang, J. Xia, X. Ji, Y. Liu, J. Zhang, X. He, W. Zhang, H. Wan and C. Wang, *Nat. Energy*, 2024, **9**, 251–262.

22 J. Xu, J. Li, Y. Li, M. Yang, L. Chen, H. Li and F. Wu, *Adv. Mater.*, 2022, **34**, 2203281.

23 G. Liu, J. Zhang, J. Yang, J. Chen, X. Xiao and X. Yao, *J. Energy Chem.*, 2025, **100**, 50–58.

24 Z. Zhang, Y. Zhao, S. Chen, D. Xie, X. Yao, P. Cui and X. Xu, *J. Mater. Chem. A*, 2017, **5**, 16984–16993.