

## Electronic Supplementary Material

### Stable lithium metal batteries enabled by Al-Li/LiF composite artificial interfacial layer

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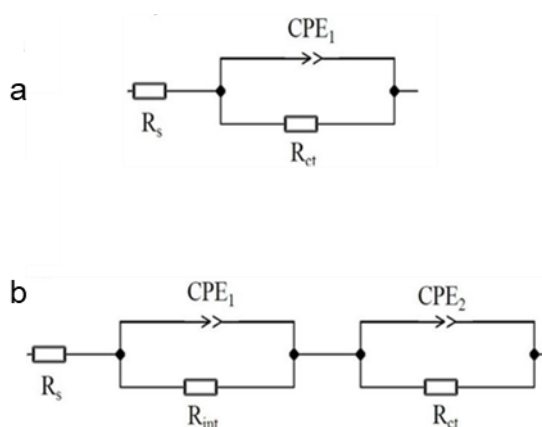


Figure S1. The equivalent circuit for fitting Nyquist plot with a single (a) and double (b) semicircle, respectively.

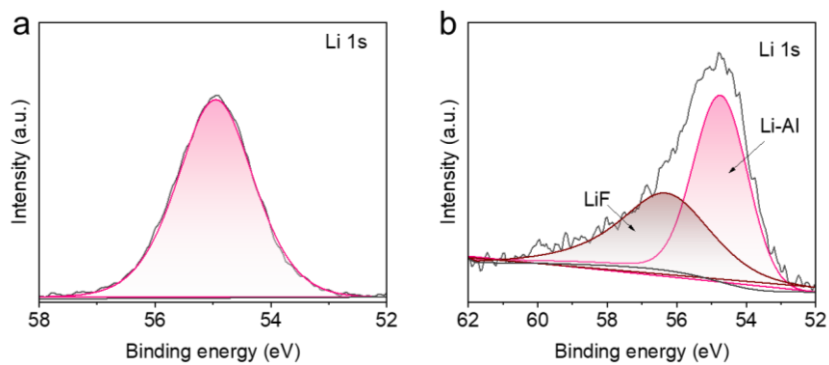


Figure S2. XPS spectra of lithium (a) before processing and (b) after processing.

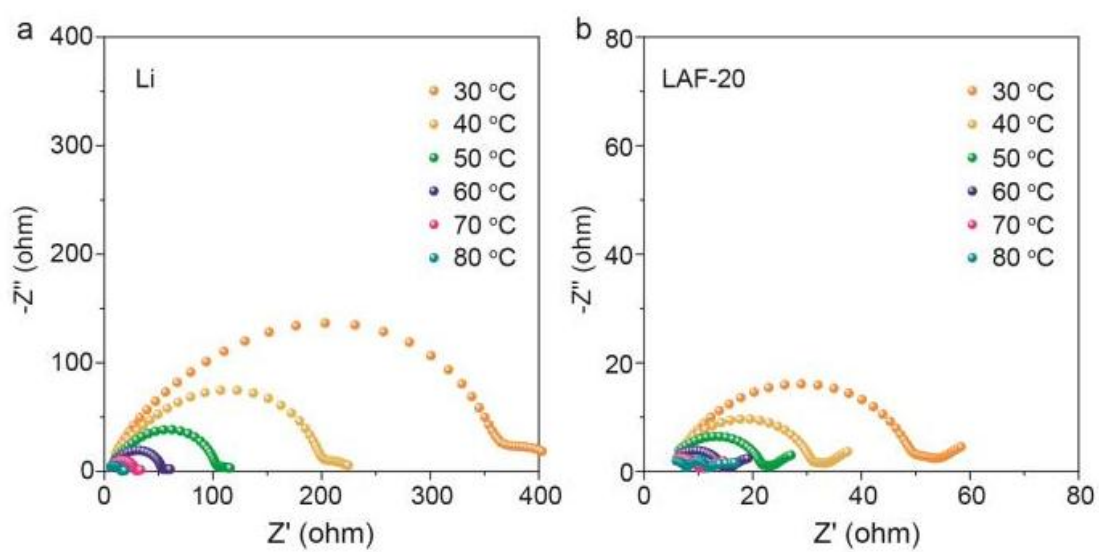


Figure S3. Nyquist plot of bare Li (a) and LAF-20 (b) electrode symmetrical cells at different temperatures.

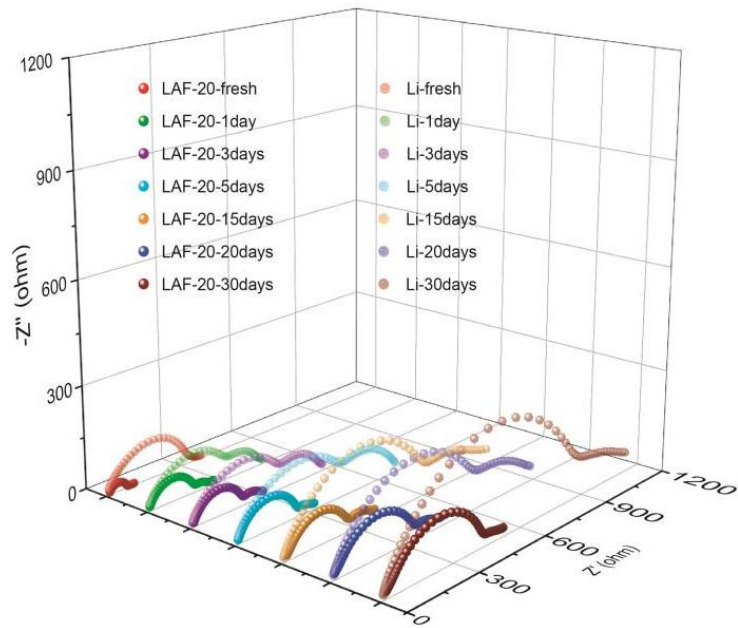


Figure S4. Nyquist plot of bare Li and LAF-20 electrode symmetrical cells at different standing time.

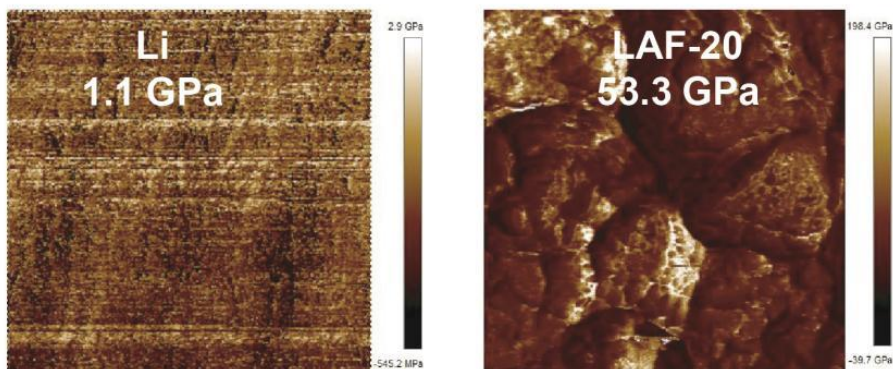


Figure S5. Young's modulus analysis of bare Li (a) and LAF-20 (b).

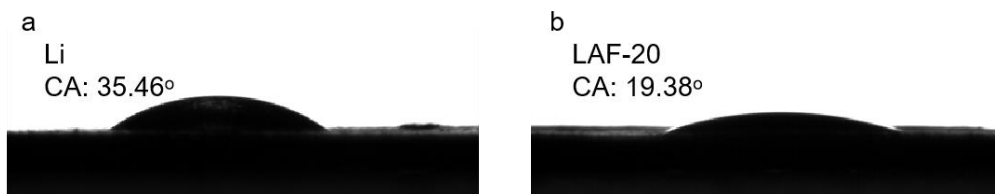


Figure S6. The contact angle measurement of bare Li (a) and LAF-20 (b).

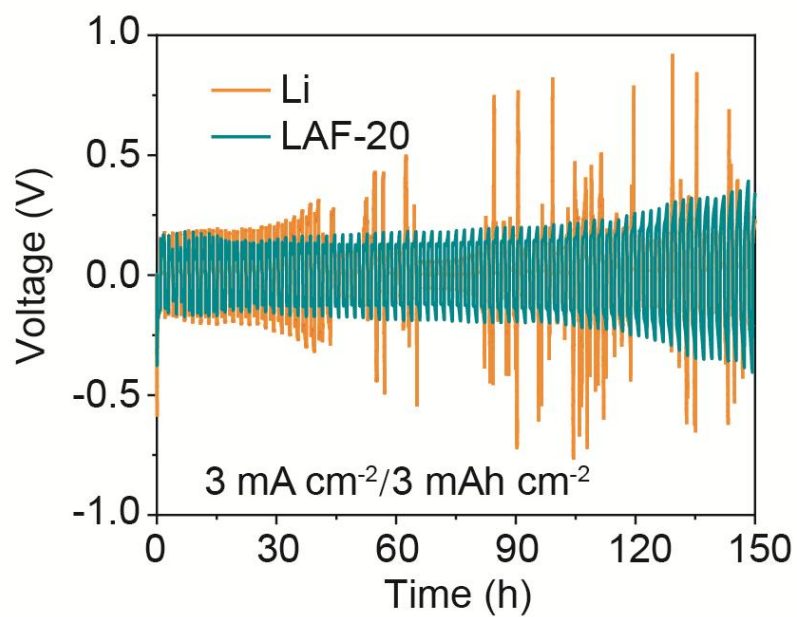


Figure S7. Plating/stripping profile of Li and LAF-20 electrode symmetrical cells at 3 mA cm<sup>-2</sup>.

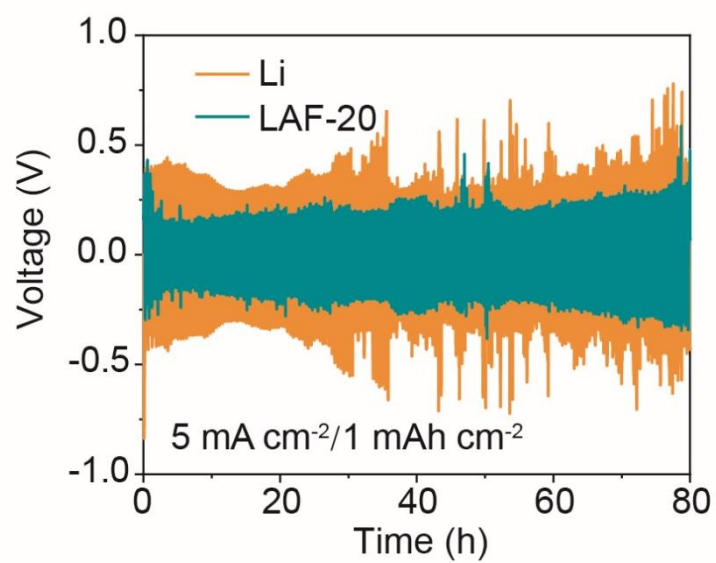


Figure S8. Plating/stripping profile of Li and LAF-20 electrode symmetrical cells at 5 mA cm<sup>-2</sup>.

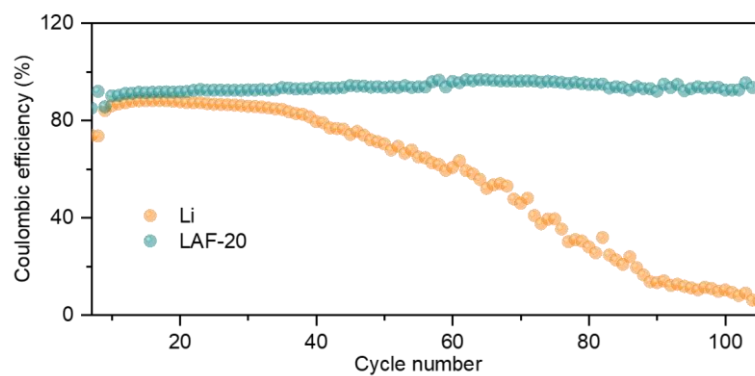


Figure S9. Comparison of CE of Li||Cu cell and Li||AlF<sub>3</sub> modified Cu cell at a current density of 0.5 mA cm<sup>-2</sup> with a capacity of 0.5 mAh cm<sup>-2</sup>. (1 mol L<sup>-1</sup> LiPF<sub>6</sub> in EC/DEC (volume ratio of 1:1)).

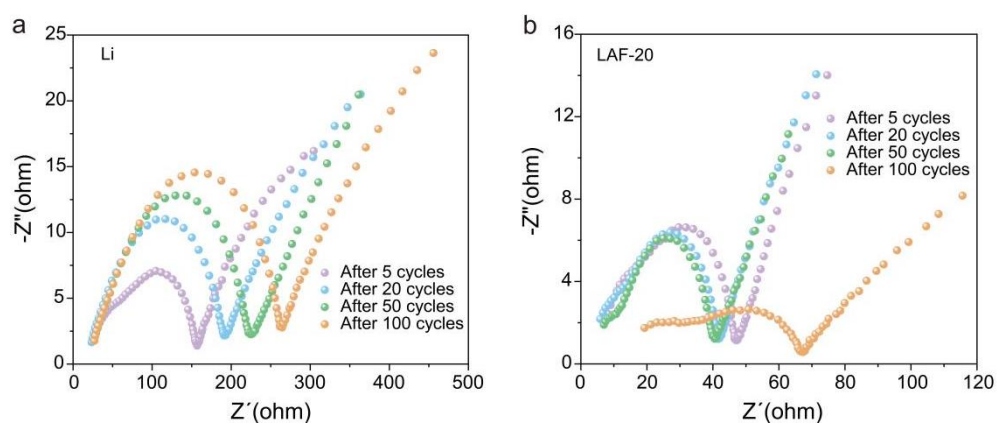


Figure S10. Nyquist plot of (a) bare Li and (b) LAF-20 symmetrical cells after 5 cycles, 20 cycles, 50 cycles, and 100 cycles at 0.5 mA cm<sup>-2</sup>, respectively.

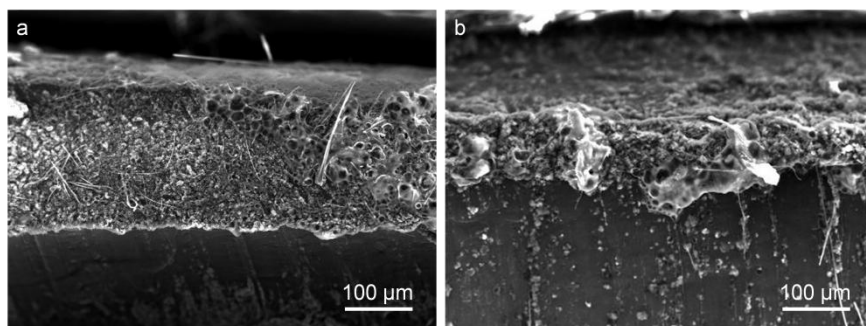


Figure S11. Cross-sectional SEM images of the bare Li (a) and LAF-20 (b) anodes after cycling.

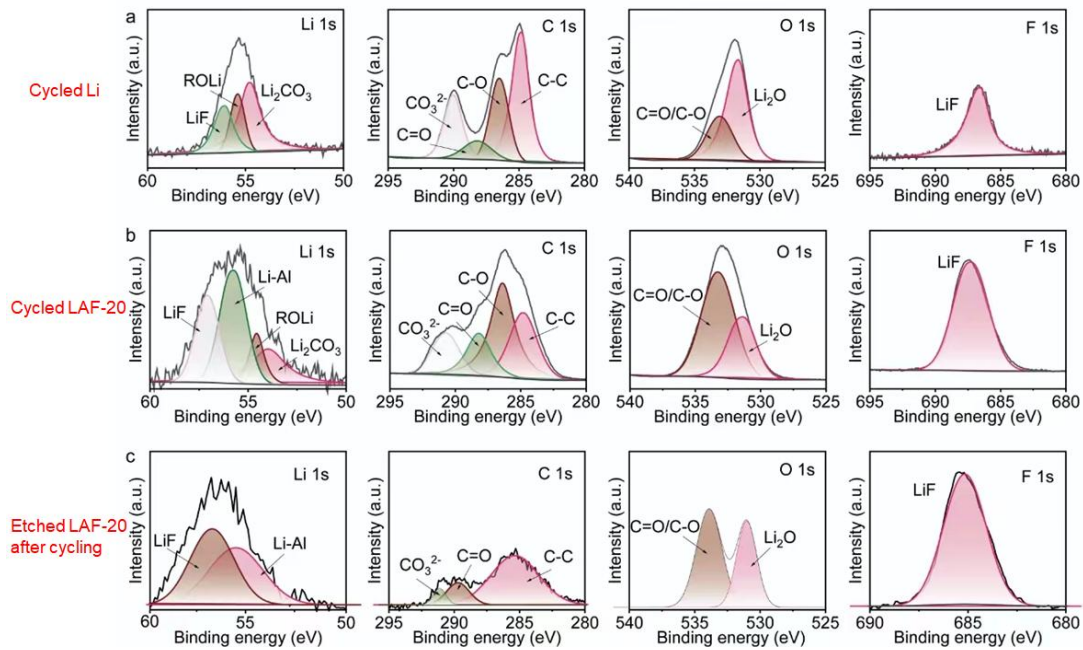


Figure S12. XPS spectra of (a) pure lithium and (b) LAF-20 anode after 20 cycles at a current density of  $1 \text{ mA cm}^{-2}$  with a capacity of  $1 \text{ mAh cm}^{-2}$ . (c) XPS depth profiles of LAF-20 anode after 20 cycles at a current density of  $1 \text{ mA cm}^{-2}$  with a capacity of  $1 \text{ mAh cm}^{-2}$  by Ar sputtering with 100 nm etching depth.

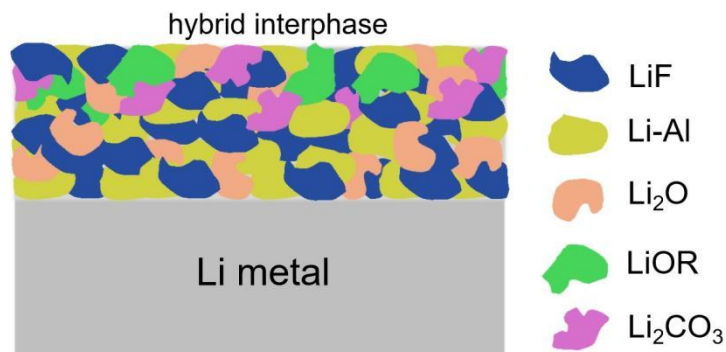


Figure S13. Schematic illustration of the SEI layer formed on the Li metal anode.

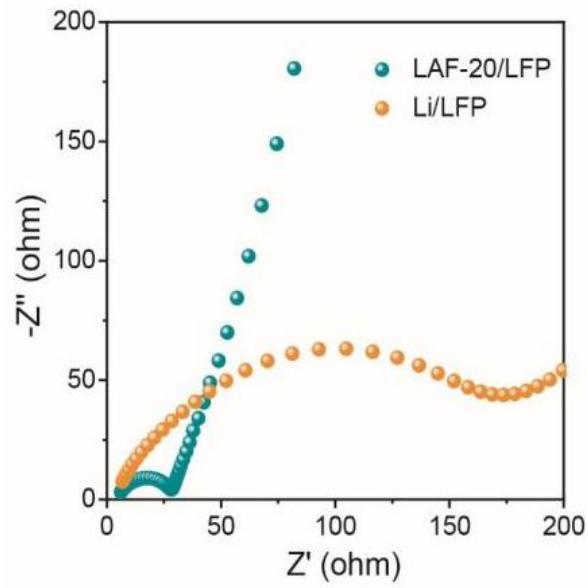


Figure S14. EIS measurement of LFP coupled with bare Li and LAF-20 anode.

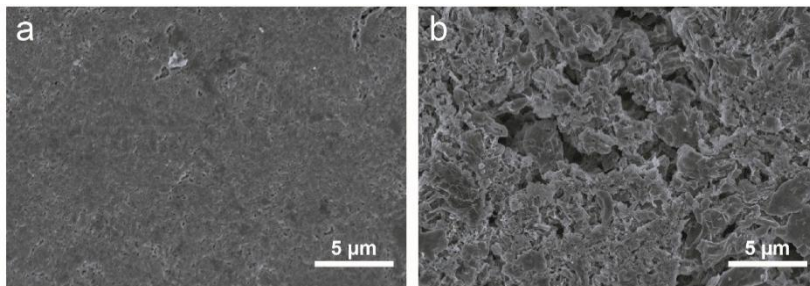


Figure S15. The SEM images of LAF-20 electrodes (a) and pure Li (b) after the 100th cycles.

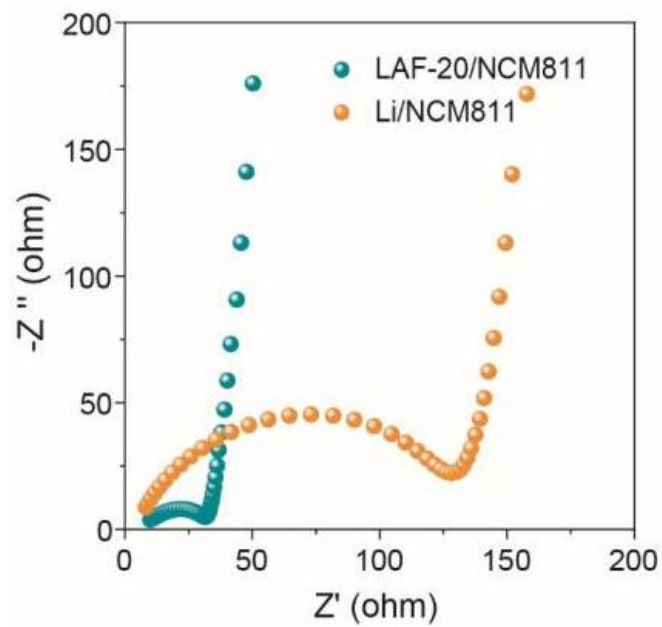


Figure S16. EIS measurement of NCM811 coupled with bare Li and LAF-20 anode.

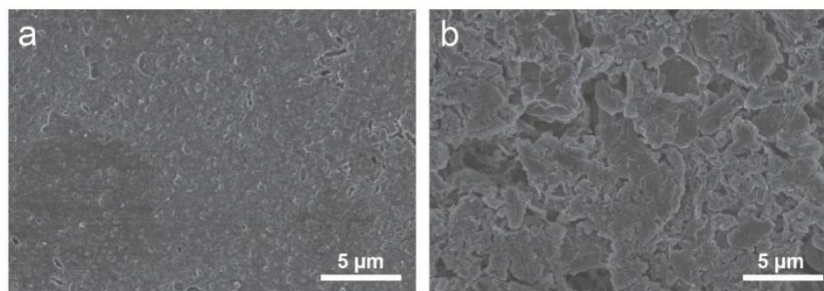


Figure S17. The SEM images of LAF-20 electrodes (a) and pure Li (b) after the 100th cycles.

Table S1. The comparison of plating/stripping hours of this work with previous reports

Artificial layer type	Electrolyte	Density/Capacity (mA cm <sup>-2</sup> / mAh cm <sup>-2</sup> )	Plating/stripping (hours)	Ref.
Surface fluorination of Li using fluoropolymer	1M LiPF <sub>6</sub> -EC/DEC (1:1, v/v)	1/1	~ 600	28
		3/1	~ 120	
Mo <sub>6</sub> S <sub>8</sub> /carbon coated Li	1 M LiPF <sub>6</sub> -EC/DMC (1:1, v/v)	1/1	~ 600	41
Coating cyclic ether group-containing polymer on Li	1M LiPF <sub>6</sub> -EC/EMC/FEC (3:7:1, v/v/v)	0.5/1	~ 300	42
Ag/LiF coated Li	1M LiPF <sub>6</sub> -EC/DMC (1:2)	0.5/1	~ 1000	43
Al <sub>2</sub> O <sub>3</sub> thin film sputtered on Li	1 M LiPF <sub>6</sub> -EC/DEC/DMC (1:1:1, v/v/v)	0.5/0.5	~ 1200	44
MPDMS coated Li	1 M LiPF <sub>6</sub> -EC/EMC/DEC (1:1:1, v/v/v)	0.5/0.25	~500	45
P(St-MaI) coated Li	1M LiPF <sub>6</sub> -EC/EMC (3:7, v/v)	1/1	~900	46
Octaphenylsilsesquioxane coated Li	1M LiPF <sub>6</sub> -EC/DEC (1:1, v/v)+10 wt%FEC+1wt%VC	1/1	~800	47
LiF/Al-Li coated Li	1M LiPF <sub>6</sub> -EC/DEC (1:1, v/v)	0.5/1	~ 2300	This work
		1/1	~ 700	