

Electronic Supplementary Information for

A “two-in-one” integrated electrode design for high-energy rechargeable bipolar Li batteries

Qianqian Liu ^{a,b}, Yan Liu ^a, Yifei Xu ^a, Jianghao Wang ^a, Zerui Chen ^a and Hao Bin Wu ^{a,*}

^a*Institute for Composites Science Innovation (InCSI) and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

^b*Key Laboratory of Electronic Materials and Devices of Tianjin, School of Electronics and Information Engineering, Hebei University of Technology, Tianjin, 300401, China*

* *Corresponding Author: hbwu@zju.edu.cn (H. B. W.)*

Calculation of cell-level energy density with Al anode. First of all, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode was chosen for pairing with graphite anode, Li metal anode and Al anode. When NCM111|Li cell was charged to 4.3 V, the specific capacity of 160 mAh g⁻¹ and an average discharge voltage of 3.8 V were obtained. The areal capacity of NMC111 cathode was set as 4 mAh cm⁻², which is similar in commercial lithium-ion batteries. The cathode was made of 96 wt% active material, 2 wt% binder and 2 wt% conductive carbon. The graphite anode was made of 93 wt% active material, 3 wt% binder and 4 wt% conductive carbon. The press density of NCM111 cathode and graphite anode is 3.7 g cm⁻³ and 1.5 g cm⁻³, respectively. Detailed parameters of cell components were shown in Table 1 and 2. For comparison, “model lithium cell” containing half Al|Cu current collector, one cathode, one separator and one anode (Figure S1) is used for energy density calculation ¹⁻³.

The volumetric energy (E_{vol} , in Wh L⁻¹) of a cell was calculated as follows:

$$E_{vol} = \frac{E \times Q}{d}$$

The specific (gravimetric) energy densities (E_{grav} , in Wh g⁻¹) of a cell was calculated as follows:

$$E_{grav} = \frac{E \times Q}{W}$$

Where, E is the cell volage (V), Q is the areal capacity (mAh cm⁻²), d is the total cell thickness (cm) and W is the total weight (mg cm⁻²).

Supplemental Figures and Tables

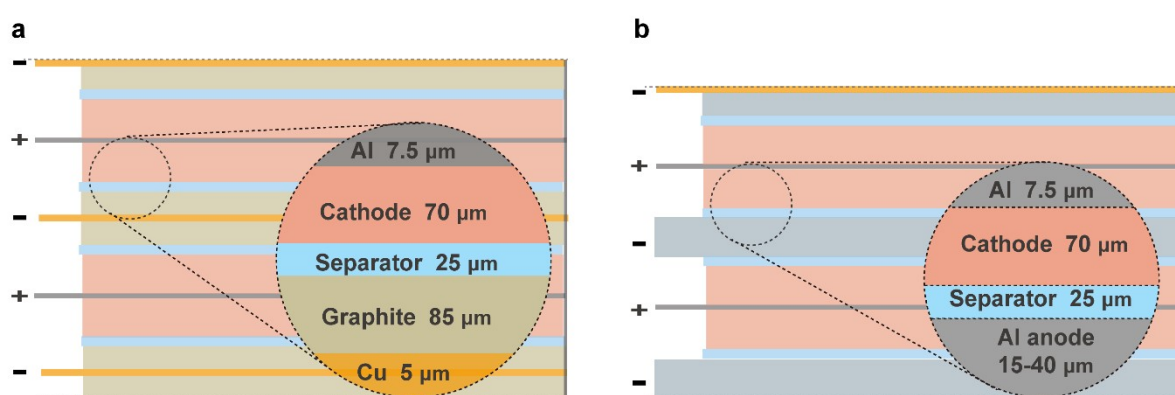


Fig. S1 Schematic of a laminate-type cell with a) a commercial graphite anode and b) Al anode.

The LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM111) was chosen as cathode. In the NCM111|Al configuration, Al foil acts as both anode and current collector, replacing conventional anode including active materials (graphite) and Cu current collector.

Table 1. Parameters for calculation of volumetric energy densities of NCM111|anode (graphite, Li and Al) batteries

Cell type	NCM Graphite (N/P=1.1)	NCM Li (N/P=1/1)	NCM Li (N/P=2/1)	NCM 20- $\mu\text{m Al}$	NCM 40- $\mu\text{m Al}$
Cell voltage (V)	3.7	3.8	3.8	3.4	3.4
Areal capacity (mAh cm ⁻²)	4	4	4	4	4
Cathode thickness (μm)	70	70	70	70	70
Anode thickness (μm)	85	20	40	20	40
Separator thickness (μm)	25	25	25	25	25
Cu thickness (μm)	5	5	5	0	0
Al thickness (μm)	7.5	7.5	7.5	7.5	7.5
Total thickness (μm)	191.5	127.5	147.5	115	135
Volumetric energy density (Wh L ⁻¹)	768.8	1192.1	1030.5	1182.6	1007

Table 2. Parameters for calculation of gravimetric energy densities of NCM111|anode (graphite, Li and Al) batteries

Cell type	NCM Graphite	NCM Li	NCM 20- μm Al	NCM 40- μm Al
	(N/P=1.1)	(N/P=2/1)		
Cell voltage (V)	3.7	3.8	3.4	3.4
Areal capacity (mAh cm ⁻²)	4	4	4	4
Cathode mass (mg cm ⁻²)	26.0	26.0	26.0	26.0
Anode mass (mg cm ⁻²)	12.7	2.1	5.4	10.8
Electrolyte mass (mg cm ⁻²)	12	12	12	12
Cu mass (mg cm ⁻²)	4.5	4.5	0	0
Al mass (mg cm ⁻²)	2	2	2	2
Total mass (mg cm ⁻²)	57.2	46.6	43.4	48.8
Gravimetric energy density (Wh kg ⁻¹)	258.5	325.7	313.0	278.5

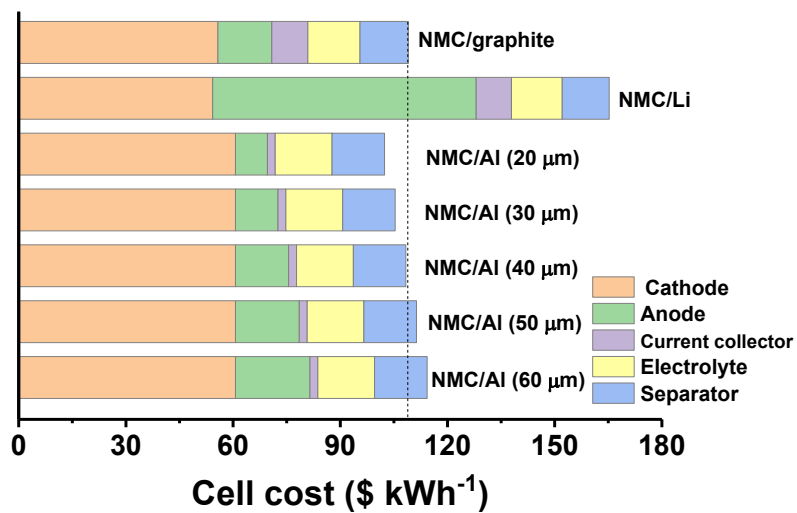


Fig. S2 Cost estimation on NCM111|anode (graphite, Li and Al) batteries based on the material cost.

Table 3. Parameters for calculating cost of NCM111|anode (graphite, Li and Al) batteries. The material cost was collected from reference ^{1,2}

Cell type	NCM Graphite (N/P=1.1)	NCM Li (N/P=2/1)	NCM 20- μm Al	NCM 40- μm Al
Cathode cost (\$ kWh ⁻¹)	55.7	54.3	60.7	60.7
Anode cost (\$ kWh ⁻¹)	15.0	73.7	6.0	12.0
Electrolyte cost (\$ kWh ⁻¹)	14.6	14.2	15.9	15.9
Cu cost (\$ kWh ⁻¹)	8.1	7.8	0	0
Al cost (\$ kWh ⁻¹)	2.0	1.97	2.2	2.2
Separator (\$ kWh ⁻¹)	13.5	13.2	14.7	14.7
Total cost (\$ kWh ⁻¹)	109.0	165.3	102.4	108.3

Note, the cost of cathode, graphite, Li metal, electrolyte, Al and Cu is 33 \$ kg⁻¹, 19 \$ kg⁻¹, 100 \$ kg⁻¹, 18 \$ kg⁻¹, 15 \$ kg⁻¹, and 25 \$ kg⁻¹, respectively. The cost of binder and conductive carbon is ignored due to the small ratio. For simple comparison, the cost of material scrap rate, process cost, and overheads are all ignored here.

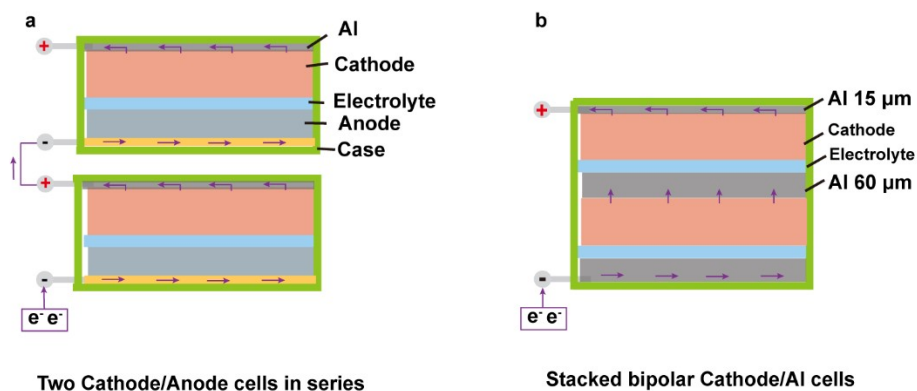


Fig. S3 Schematic illustration of electron flow in a) conventional external-serial connected cells and b) a stacked bipolar cell. The pathway of electron flow is significantly shortened in bipolar-type cells, which would improve power density.

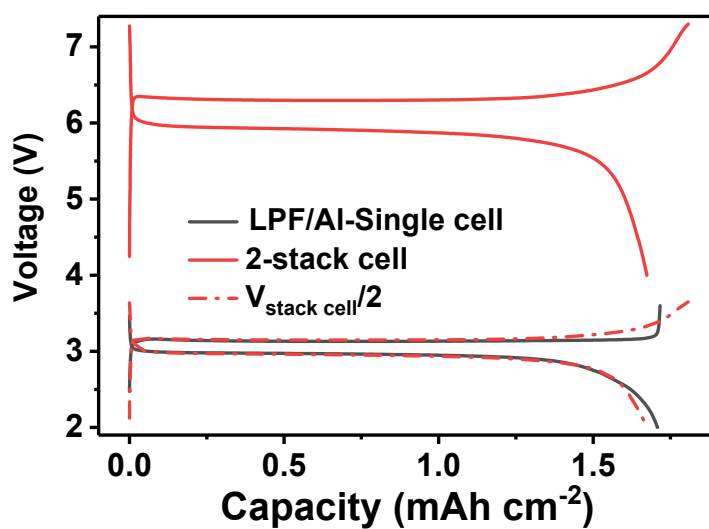


Fig. S4 Voltage profiles of LPF|Al coin cells and two-unit stacked bipolar LPF|Al pouch cells.

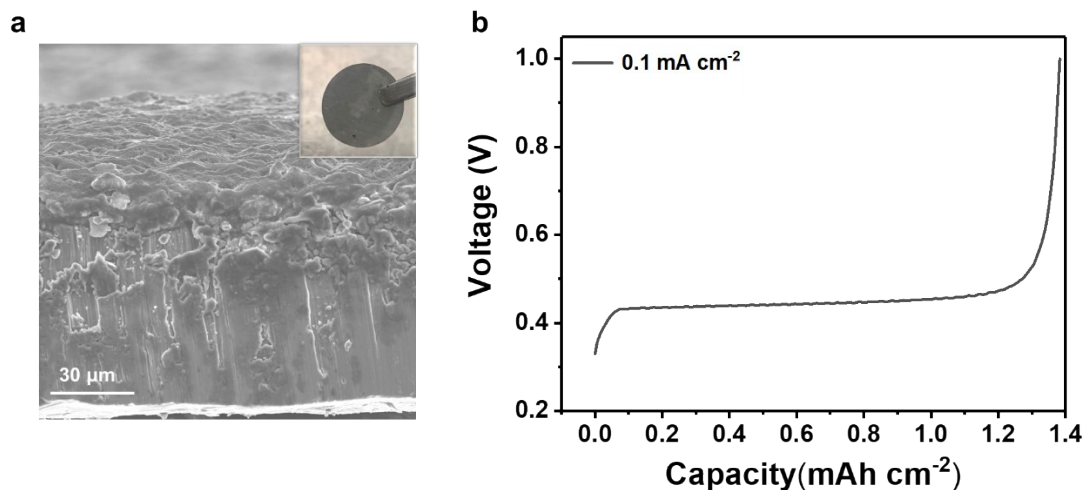


Fig. S5 a) Cross-section SEM images of prelithiated Al. Inset is the optical image of Al foil after prelithiation. Prelithiation was performed by short-circuiting Li foil and Al foil with electrolyte between them. Uniform and dense LiAl layer was deposited on the top layer of Al foil, suggesting the feasibility of the method for prelithiation. b) Charge profiles of prelithiated Al to determine available capacity of prelithiation. The charge capacity is around 1.40 mAh cm^{-2} , which is enough to compensate for irreversible capacity in subsequent cycles.

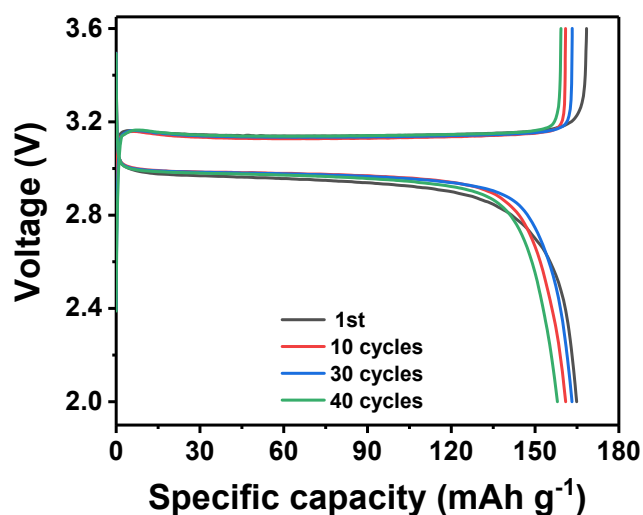


Fig. S6 Voltage profiles of one-unit LPF|Al cell during cycling at 0.2C.

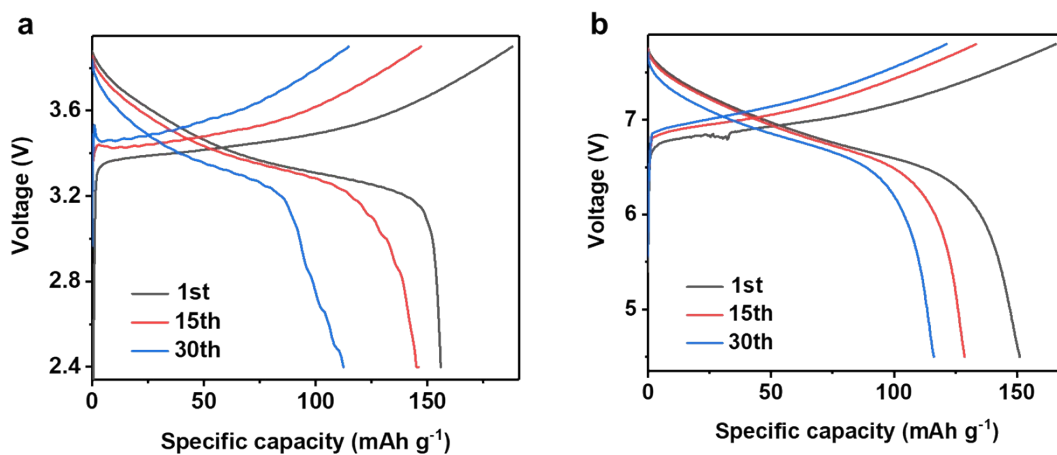


Fig. S7 Voltage profiles of a) one-unit NMC|Al cell and b) two-unit bipolar NMC|Al cell during cycling at 0.2C.

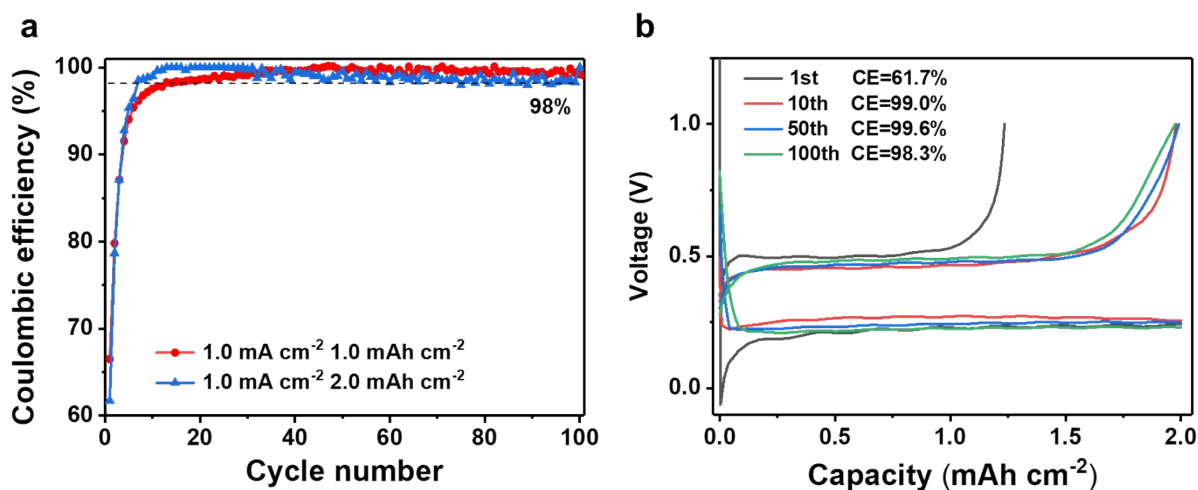


Fig. S8 a) Coulombic efficiency (CE) of Al anode during cycling with cycled capacities of 1.0 mAh cm⁻², 2.0 mAh cm⁻² at 1.0 mA cm⁻². b) Voltage-capacity profiles of Al anode with a cycled capacity of 2.0 mAh cm⁻² at 1.0 mA cm⁻². The initial CE of Al anode cycled at a higher capacity of 2 mAh cm⁻² is slightly lower than that at a capacity of 1 mAh cm⁻², probably due to higher irreversible deformation with deeper alloying/dealloying. While the voltage polarization shows no obvious increase during cycling.

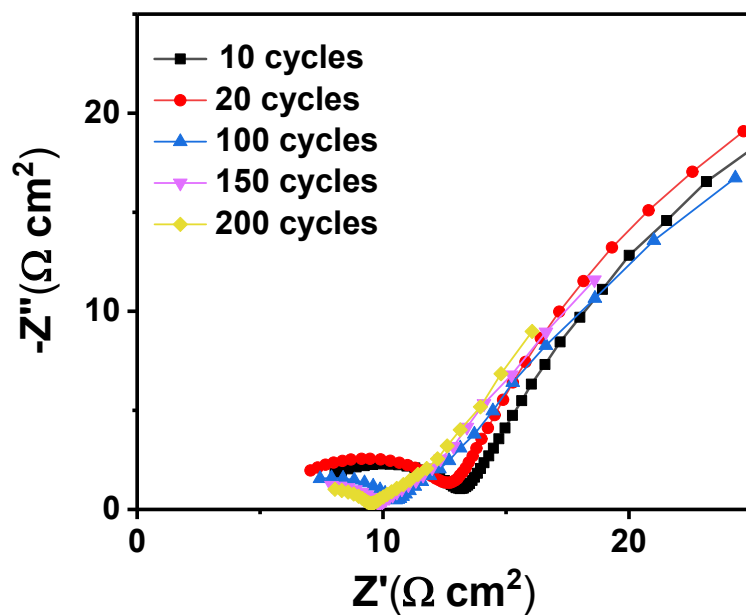


Fig. S9 Nyquist plots of Al|Li coin cell during cycling with a cycled capacity of 1.0 mAh cm^{-2} at 1.0 mA cm^{-2} .

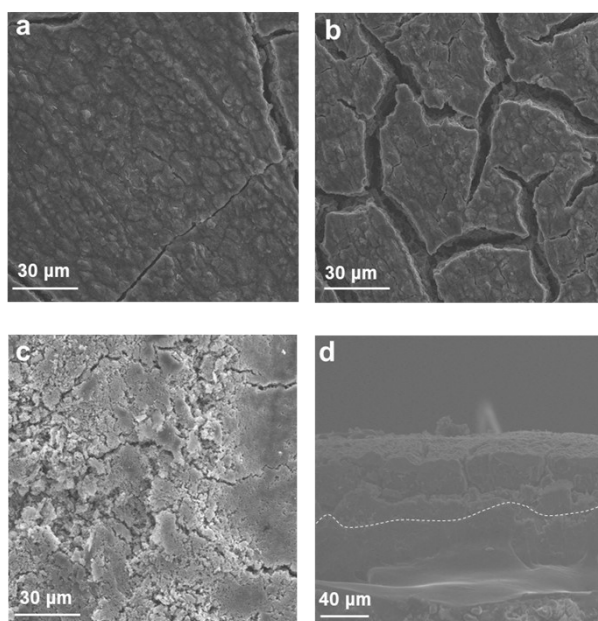


Fig. S10 Surface SEM images of Al anode with cycled capacities of 2.0 mAh cm^{-2} after a) 3rd lithiation, b) 3rd delithiation, c) 20 cycles, d) cross-section images of Al anode after 20 cycles.

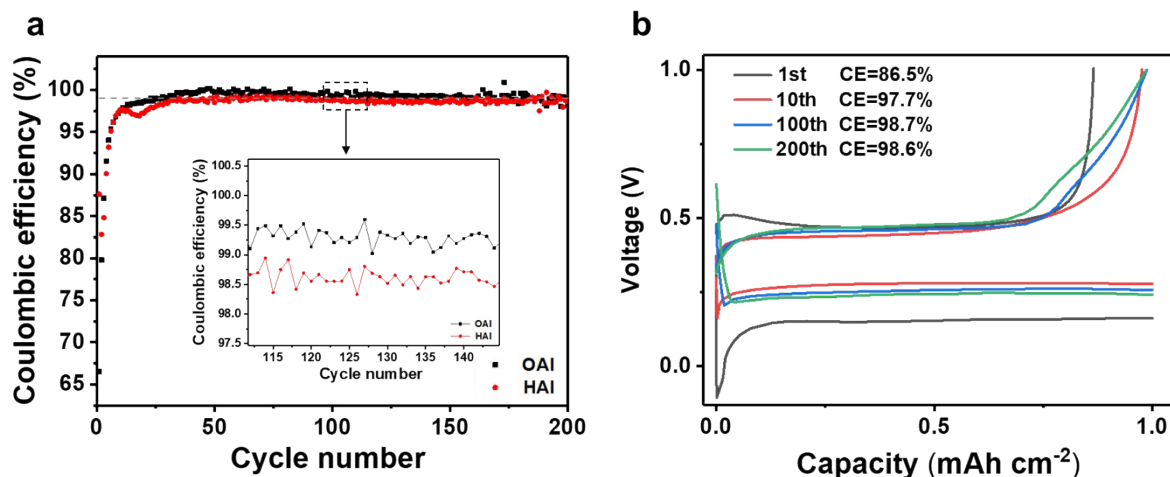


Fig. S11 a) Coulombic efficiency of Al anode with different hardness during cycling with a capacity of 1.0 mAh cm⁻² at 1.0 mA cm⁻². b) Voltage-capacity profiles of unannealed Al with higher hardness (HAI) at selected cycles. The unannealed Al with higher hardness exhibits a larger voltage polarization during first alloying/dealloying process. In addition, the coulombic efficiency of HAI keeps below 99% during 200 cycles.

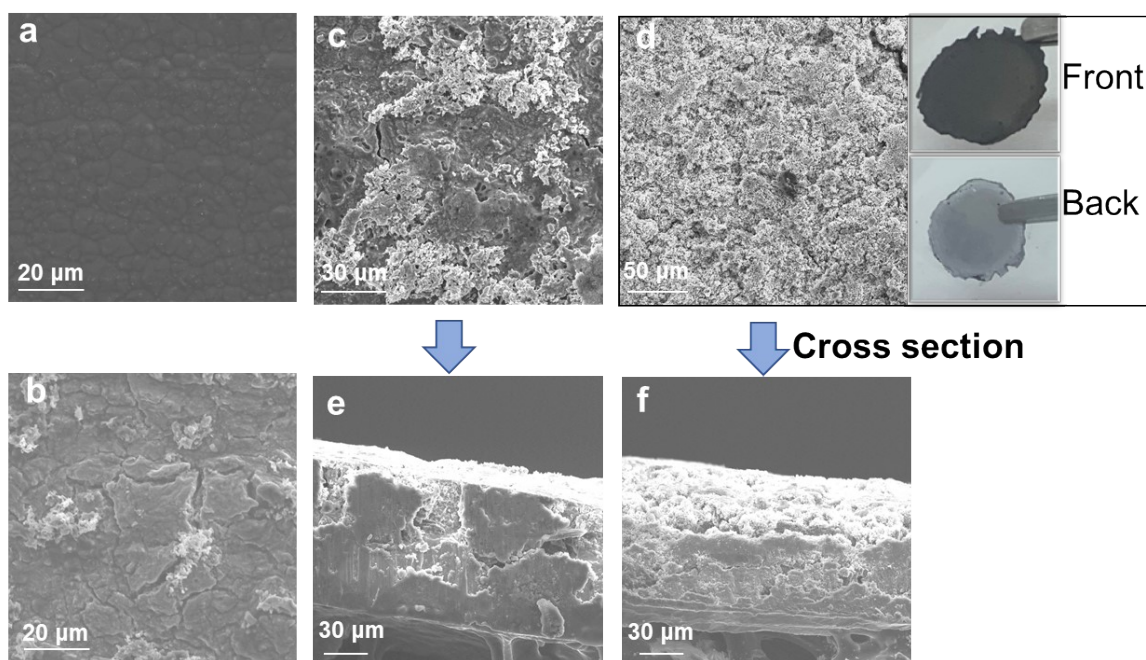


Fig. S12 Surface SEM images of unannealed Al anode after a) the first lithiation, b) 3 cycles, c) 100 cycles, d) 200 cycles, e), h) cross-section images of Al anode after 100 and 200 cycles.

REFERENCES

- 1 G. Patry, R. A., M. S. and F. D., *Energy Science and Engineering*, 2015, **3**, 71–82.
- 2 E. J. Berg, C. Villeveille, D. Streich, S. Trabesinger and P. Nov'akz, *J Electrochem Soc*, 2015, **162**, A2468-A2475.
- 3 Y. F. Xu, L. N. Gao, L. Shen, Q. Q. Liu, Y. Y. Zhu, Q. Liu, L. S. Li, X. Q. Kong, Y. F. Lu and H. B. Wu, *Matter*, 2020, **3**, 1685-1700.