# **Electronic Supplementary Information**

# A Large-Capacity, Superhigh-Rate Integrated Lithium Metal Anode with Top-Down Composition Gradient Enabled by Polyantimonic Acid

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## Part I. Supplementary Notes

### Note S1. Computational methods in details

# a) Adsorption energy

The structures of crystal Li<sub>3</sub>Sb, Li<sub>2</sub>O, and LiOH adopt the group of P63/mmc (No.194), Fm-3m (No.225), and P4/nmm (No.129), respectively, according to the experimental characterization results, which were further geometry optimized with convergent criteria of 0.02 eV Å<sup>-1</sup>.

To determine the Li adsorption on these secondary products (including Li<sub>2</sub>O, Li<sub>3</sub>Sb, and LiOH), slab models of  $3 \times 3$  supercell for Li<sub>2</sub>O (111),  $2 \times 2$  supercell for Li<sub>3</sub>Sb (002),  $2 \times 2$  supercell for LiOH (001) containing 81, 32, 80 atoms were built as the substrate, respectively. A vacuum space of 15 Å was introduced along the z-direction to avoid the interactions of each compositional component among slabs. A geometry optimization was considered convergent when the energy change was smaller than 0.02 eV Å<sup>-1</sup>. The adsorption energy of Li atoms on different surfaces was calculated as:

$$E_{ads} = E_{total} - E_{surf} - E_{Li}$$
(S1)

 $E_{\text{total}}$ ,  $E_{\text{surf}}$ , and  $E_{\text{Li}}$  are the energies of the adsorption configuration, the pristine surface, and a single Li atom, respectively.

### b) Surface energy and interfacial energy

The stability of a surface is delineated by its surface energy ( $\gamma_{surf}$ ), denoting the surplus energy inherent to surface atoms. For a given slab model with a specified Miller index (*hkl*), the surface energy ( $\gamma_{surf}$ ) of X can be mathematically expressed as follows: <sup>1,2</sup>

$$\gamma_{surf} = \frac{1}{2A} (E_{slab} - E_{bulk} \times n_{slab})$$
(S2)

Where  $E_{slab}$  is the total energy of the slab model containing n nuits,  $E_{bulk}$  is the unit

bulk energy,  $n_{slab}$  is the total number of formula units in the slab model, A is the cross-section surface area of the slab structure, the factor of 2 in the denominator represents the two surfaces in the slab models.

The interfacial energy can be defined as the interaction at the interface without the strain effects. For the Li/X interface model containing a vacuum slab, the following expression can calculate it:<sup>3,4</sup>

$$\gamma_{X-Li} = \frac{1}{2A} (E_{X-Li} - E_X - E_{Li}) + \gamma_X + \gamma_{Li}$$
(S3)

Where  $E_{X-Li}$  is the total energy of the X/Li interface cell,  $E_{X}$ , and  $E_{Li}$  are the energies of the isolated slab of the interface structure,  $\gamma_X$  and  $\gamma_{Li}$  are the surface energies of the isolated slab of this interface structure. A is the interface area.

## Note S2. Thermodynamic analysis for the phase separation

Phase separation in the X-Li-Li<sub>2</sub>O system

According to the formula derivation of thermodynamic analysis<sup>4</sup>, the internal energy

U of this system can be quantified as:

$$U = 0.5n_{\chi} \times (\gamma_{\chi - Li} + \gamma_{\chi - Li,0}) \times S_{\chi} + N_{\chi} \times \gamma_{\chi - Li} \times S_{\chi}$$
(S4)

Where  $N_X$  is the number of X particles within Li,  $n_X$  is the number of X particles on the surface of Li;

 $S_x$  is the surface area per X particles;

 $\gamma_{{\scriptscriptstyle X-Li}}$  and  $\gamma_{{\scriptscriptstyle X-Li_2O}}$  are the interfacial energies for X-Li and X-Li\_2O, respectively.

U: internal energy;

F: the Gibbs free energy of the system.

$$F = U - TS \tag{S5}$$

$$S = k \ln W$$
 (S6)

k and T are the Boltzmann constant and the absolute temperature, respectively.

$$W = \frac{N!n!}{N_{x}!N_{Li}!n_{x}!n_{Li}!} (N = N_{x} + N_{Li}, n = n_{x} + n_{Li})$$
(S7)

$$F = 0.5n_{X} \times (\gamma_{X-Li} + \gamma_{X-Li_{2}O}) \times S_{X} + N_{X} \times \gamma_{X-Li} \times S_{X} - kT \ln(\frac{N!n!}{N_{X}!N_{Li}!n_{X}!n_{X}!n_{Li}!})$$
(S8)

$$\frac{dF}{dN_x} = -\frac{dF}{dn_x}, \frac{d\ln W}{dN_x} = \ln \frac{N - N_x}{N_x} - \ln \frac{n - n_x}{n_x} = \ln \left(\frac{N_{Li}n_x}{N_x n_{Li}}\right)$$
(S9)

$$(\frac{dF}{dn})_{T} = 0.5(\gamma_{X-Li} + \gamma_{X-Li_{2}O}) \times S_{X} - \gamma_{X-Li} \times S_{X} + kT \ln(\frac{N_{Li}n_{X}}{N_{X}n_{Li}}) = 0$$
(S10)

$$\ln(\frac{N_{Li}n_{X}}{N_{X}n_{Li}}) = -\frac{0.5(\gamma_{X-Li_{2}O} - \gamma_{X-Li}) \times S_{X}}{kT}$$
(S11)

$$\frac{n_x}{n_{Li}} = \frac{N_x}{N_{Li}} \times e^{\left(-\frac{0.5(V_{X-Li_2O} - Y_{X-Li}) \times S_X}{kT}\right)} = \frac{N_x}{N_{Li}} \times e^{\left(-\frac{\Delta E}{kT}\right)}$$
(S12)

For LiOH, due to  $\gamma_{LiOH-Li_2O} - \gamma_{LiOH-Li} = 0.69 \text{ J/m}^2 > 0$ ,  $\frac{n_{LiOH}}{n_{Li}} < \frac{N_{LiOH}}{N_{Li}}$ , thus LiOH may

tend to concentrate in the bulk Li; Meanwhile, considering LiOH is lithiophobic (

 $\gamma_{LiOH} - \gamma_{LiOH-Li} = -0.22$  J m<sup>-2</sup>), thus the enrichment of LiOH could be at the Li<sub>2</sub>O-Li interface act as a bridge to link lithiophobic Li<sub>2</sub>O and lithiophilic Li<sub>3</sub>Sb layer.

For Li<sub>3</sub>Sb, due to  $\gamma_{Li_3Sb-Li_2O} - \gamma_{Li_3Sb-Li} = 0.82 \text{ J} \text{ m}^{-2} > 0$ ,  $\frac{n_{Li_3Sb}}{n_{Li}} < \frac{N_{Li_3Sb}}{N_{Li}}$ , thus Li<sub>3</sub>Sb is

inclined to aggregate in the bulk of Li.





**Figure S1**. Ball-and-stick schematic diagrams of the crystal structures of PAA in different views.



**Figure S2.** XPS spectra of pristine CC and EO-treated CC. (a) XPS survey profiles. High-resolution XPS spectra of (b) C 1s and (c) O 1s.



**Figure S3**. SEM images of PAA crystals grown on EOCC substrates with different anodic oxidation time for (a-c) 3 min, (d-f) 5 min, and (g-i) 10 min.



Figure S4. The size distribution of PAA particles in PAA@EOCC.



Figure S5. Digital images of commercial (a) CC, (b) EOCC, and (c) PAA@EOCC.



Figure S6. SEM images of PAA@CC without EO pretreatment.



Figure S7. High-resolution XPS spectrum of C 1s in PAA@EOCC.



**Figure S8**. (a) TG and DTG curves of PAA@EOCC heated from room temperature to 900 °C. (b) XRD pattern of PAA after calcinating at 900 °C in the ambient atmosphere.

As shown in Supplementary Fig. 8, according to the reactions of (1)–(4) and equations (5)–(7), the value of *n* is 2.1. Besides, the content of PAA in PAA@EOCC is around 14.1%.

$$(H_{3}O)_{2}Sb_{2}O_{6} \cdot nH_{2}O \rightarrow (H_{3}O)_{2}Sb_{2}O_{6} + nH_{2}O$$
(1)

$$(H_3O)_2Sb_2O_6 \rightarrow Sb_2O_{4.5}(OH) + 2.5H_2O$$
 (2)

$$Sb_2O_{4.5}(OH) \rightarrow Sb_2O_5 + 0.5H_2O \tag{3}$$

$$Sb_2O_5 \rightarrow Sb_2O_{4.3} \rightarrow (Sb_6O_{13}) + 0.33O_2$$
 (4)

The mass loss process is accompanied by dehydration(60–450°C), oxygen removal (450–600°C), and carbon fiber consumption (620–860°C). The thermolysis progress of reactions of 1–3 is associated with removing water molecules. In reaction 4, Sb<sup>5+</sup> is reduced to Sb<sup>3+</sup> and accompanied by oxygen escapes.

$$\omega_{H_2O} = 3.47\% - \frac{\omega_{Sb_2O_{4.3}}}{M_{Sb_2O_{4.3}}} \times M_{O_2} \times 0.33$$
<sup>(5)</sup>

$$3+n = \frac{\omega_{H_2O} / M_{H_2O}}{n_{(H_3O)_2 \, Sb_2O_6 \cdot nH_2O}} \tag{6}$$

$$n = 2.1$$
 (7)

$$\omega_{(H_3O)_2 Sb_2 O_6 \cdot 2.1 H_2 O} = \frac{\omega_{Sb_2 O_{4.3}}}{M_{Sb_2 O_{4.3}}} \times M_{(H_3O)_2 Sb_2 O_6 \cdot 2.1 H_2 O}$$
(8)

$$\omega_{(H_3O)_2 Sb_2O_6 \cdot 2.1H_2O} = 14.1\%$$
(9)



**Figure S9.** XRD pattern and XPS spectrum of PAA-w/o@EOCC. (a) XRD pattern. (b) Sb 3d core peak spectrum.



Figure S10. Rietveld refinement patterns of XRD for the (a) PAA and (b)  $Sb_6O_{13}$  powder.



**Figure S11.** Ball-and-stick schematic diagrams of the crystal structures of  $Sb_6O_{13}$  in different views.



**Figure S12.** Full Li stripping curve of different electrodes to 1 V versus Li<sup>+</sup>/Li: (a) Li-PAA@EOCC and (b) Li-PAA-w/o@EOCC (the insert is the optical photo of Li-PAA@EOCC electrode after full delithiation).



Figure S13. Li-Sb binary phase diagram.<sup>5</sup>



**Figure S14.** High-resolution XPS spectra of O1 1s and Sb 3d spectra for different electrodes: (a) Li-PAA@EOCC and (b) Li-PAA-w/o@EOCC.



Figure S15. Optical images of the bottom and top of Li-PAA@EOCC.



**Figure S16**. Atomic structures for  $Li_2O$  (111), LiOH (001),  $Li_3Sb$  (002),  $Li_2O/Li$  interface, LiOH/Li interface, and  $Li_3Sb/Li$  interface.



**Figure S17**. (a) Atomic structures for Li<sub>3</sub>Sb/Li<sub>2</sub>O and LiOH/Li<sub>2</sub>O interface; (b) The corresponding surface and interfacial energies.



**Figure S18.** (a) The composition distribution of Li<sub>3</sub>Sb and LiOH at the Li/Li<sub>2</sub>O interface. Atomic structures of Li, Li<sub>3</sub>Sb, and Li<sub>2</sub>O and their corresponding interfacial energies. (b) Atomic structures of Li, LiOH, and Li<sub>2</sub>O and their corresponding interfacial energies.



**Figure S19.** Time-lapse images of the reaction progress obtained from Supplementary movie 3 and 4. (a-e) The reaction progress between molten lithium and PAA powder. (f-j) Reaction progress between  $Sb_6O_{13}$  powder and molten Li.

As depicted in Fig. S19, molten Li is placed in stainless-steel containers on a 300 °C hot plate. The entire process is conducted in an Argon-filled glovebox with H<sub>2</sub>O and  $O_2$ <0.1 ppm. Due to the deviation of light and shooting angle, some chromatic aberration may appear on the sample surfaces, but the surface difference can still be compared. Upon the addition of PAA powder, the molten Li surface promptly transitions to a grey hue, followed by a mild chemical reaction and sufficient diffusion progress. These reactions yield products that accumulate as a greyish layer on the Li surface, devoid of metallic luster (insert of Fig. S19e).

However, the situation is quite different after adding  $Sb_6O_{13}$  powder. The molten Li surface adopts a black-purple hue, accompanied by a violent redox reaction. Consequently, the  $Sb_6O_{13}$  sample exhibits a rough and chaotic surface, indicative of the pronounced exothermic chemical reactions leading to an uneven and defect-rich surface (insert of Fig. S19j).



**Figure S20.** SEM images of the above Li-PAA sample and corresponding O and Sb elemental distributions. (a) Top-view and (b) cross-sectional SEM images.



**Figure S21.** SEM images of the above  $\text{Li-Sb}_6O_{13}$  sample and corresponding O and Sb elemental distributions. (a) Top-view and (b) cross-sectional SEM images.

The EDS confirmed that white spots are in the Sb phase. As shown in the bright zone from the top-view SEM images, Sb nanoparticles exist in an agglomerated state. Also, no distinct divider line is observed in the cross-section EDS mapping, wherein O and Sb elements are scattered throughout the mixture.



**Figure S22.** The contact angles measurement of bare Li (a) and the Li-PAA@EOCC electrode (b) with ether-based electrolyte.



**Figure S23.** Measurements of d.c. conductivity of Li-PAA@EOCC, Li-PAAw/o@EOCC, and bare Li using blocking electrodes. The voltage response of bare Li (black curve), Li-PAA-w/o@EOCC (yellow), and Li-PAA@EOCC (pink curve) electrodes to an applied current of 5 mA, from which the resistances are calculated.

For the electronic resistivity of the protective film, the voltage response to a direct current of 5 mA was measured for bare Li, Li-PAA-w/o@EOCC, and Li-PAA@EOCC via using blocking electrodes, which are all sandwiched between two stainless sheets of steel. The voltage response to a direct current of 5 mA is applied to calculate the electronic resistivity as follows:

$$\rho = \frac{R \times S}{L} = \frac{U \times S}{I \times L}$$

L-thickness of the Li<sub>2</sub>O-rich layer;

I-applied current;

S-area of the contact between the stainless and the protective layer;

U-average voltage increase;

The calculated values of electronic resistivity for the Li<sub>2</sub>O-rich layer is around

7.424×10<sup>3</sup>  $\Omega$  cm (that is,  $\sigma$ =1.35×10<sup>-4</sup> S cm<sup>-1</sup>).



**Figure S24.** Nyquist plots of Li-PAA@EOCC symmetrical cells at the fresh condition and corresponding equivalent circuit model. The first semi-circle (on the left) corresponds to the protective layer resistance, and the second (on the right) corresponds to the charge transfer resistance.

For the ionic conductivity of the protective layer of the composite film, EIS measurement of symmetrical cells assembled with Li-PAA@EOCC electrodes is conducted. Ionic conductivity is calculated as follows:

$$\sigma = \frac{2L}{R \times S}$$

L- the thickness of the composite protection layer;

R-the resistance;

S-the area of the protection layer.

The ionic conductivity of the oxygen-rich film is calculated to be  $1.21 \times 10^{-4}$  S cm<sup>-1</sup>, much higher than that of Li<sub>2</sub>O (~(0.8-0.5)×10<sup>-12</sup> S cm<sup>-1</sup> at 25°C).<sup>6</sup> This ionic conductivity value for the Li<sub>2</sub>O-rich layer is large enough to diffuse Li<sup>+</sup>.



**Figure S25.** Schematic representations of Li nucleation and growth mechanisms of (a) Li-PAA-w/o@EOCC and (b) Li-PAA@EOCC electrodes after cycling.



Figure S26. Electrostatic potential profiles of Li<sub>3</sub>Sb (002)/LiOH (001) interface.



**Figure S27.** (a) The calculated energy profile of Li along the diffusion path at (b) the interface of  $Li_3Sb$  (002)/ $Li_2O$  (111).



**Figure S28.** GITT curves of the Li-PAA@EOCC and Li-PAA-w/o@EOCC applied for calculating the lithium-ion diffusion coefficient.



**Figure S29.** (a) Time-voltage profiles of Li plating/stripping in Li-PAA@EOCC, Li-PAA-w/o@EOCC, and bare Li symmetrical cells at 5 mA cm<sup>-2</sup> with a Li deposition capacity of 1 mAh cm<sup>-2</sup>. (b) Time-voltage profiles of Li plating/stripping in Li-PAA@EOCC symmetrical cell at 20 mA cm<sup>-2</sup> with a Li deposition capacity of 10 mAh cm<sup>-2</sup>.



**Figure S30.** Comparison of voltage plateau. Voltage profiles during charging and discharging processes of (a-b) bare Li foil, (c-d) Li-PAA-w/o@EOCC, and (e-f) Li-PAA@EOCC are compared under a current density of 1 mA cm<sup>-2</sup> and 5 mA cm<sup>-2</sup>, with areal capacity fixed at 1 mAh cm<sup>-2</sup>.



**Figure S31.** Temperature-dependent Nyquist plots. (a) Bare Li, (b) Li-PAA@EOCC, and (c) Li-PAA-w/o@EOCC symmetrical cells. (d)  $E_{a,ct}$  and (e)  $E_{a,sei}$  derived from the temperature-dependent Nyquist plots of the bare Li, Li-PAA@EOCC, and Li-PAA-w/o@EOCC symmetrical cells.



**Figure S32.** Tafel plots of symmetrical cells with the Li-PAA@EOCC, Li-PAA-w/o@EOCC, and bare Li to derive the exchange current densities ( $j_0$ ).



**Figure S33. EIS results of symmetric cells after cycling.** EIS spectra of (a) Li-PAA@EOCC, (b) bare Li, and (c) Li-PAA-w/o@EOCC in symmetrical cells after cycling under 1 mA cm<sup>-2</sup>, with a fixed capacity of 1 mAh cm<sup>-2</sup>. The equivalent circuit for fitting EIS spectra  $R_1$ ,  $R_2$ ,  $R_3$ , CPE, and  $Z_w$  refers to the internal resistance, SEI resistance, charge transfer resistance, constant phase elements, and Warburg impedance of symmetric cells, respectively.



**Figure S34.** Top-view and cross-sectional SEM images of different electrodes after 50 cycles at the plated state under the current density of 1 mA cm<sup>-2</sup> for 1 mAh cm<sup>-2</sup>. (a, d) bare Li, (b, e) Li-PAAA-w/o@EOCC, and (c, f) Li-PAA@EOCC.



**Figure S35.** Top-view SEM images of the pit formation on different electrodes after 50 cycles at the stripped state under the current density of 1 mA cm<sup>-2</sup> for 1 mAh cm<sup>-2</sup>. (a-b) Bare Li, (c-d) Li-PAA-w/o@EOC , and (e-f) Li-PAA@EOCC.



Figure S36. XPS depth profiles of the symmetrical cells with bare Li electrodes after 20 cycles at the plated state under the current density of 0.5 mA cm<sup>-2</sup> for 1 mAh cm<sup>-2</sup>.



**Figure S37**. COMSOL simulation for distribution of current density. (a) Bare Li and (b) Li-PAA@EOCC. The current density through the entire cell was fixed at 2 mA cm<sup>-2</sup>.



**Figure S38.** Charge/discharge profiles of LFP||Li-PAA@EOCC (a) and LFP|| bare Li full cells (b) at various rates from 0.2 to 20C (1 C=170 mAh  $g^{-1}$ ).



**Figure S39.** The Nyquist plots of the LFP full batteries with the Li-PAA@EOCC and bare Li electrodes before cycling.



**Figure S40**. (a) Cycling performance of LFP||Li-PAA@EOCC and LFP||Li full cell with LFP-loading of 12 mg cm<sup>-2</sup>, and corresponding voltage profiles of (b) LFP||Li-PAA@EOCC and (c) LFP||Li for selected cycles at 1 C.



**Figure S41**. (a) Cycling performance of LFP||Li-PAA@EOCC full cell with LFP-loading of 14 mg cm<sup>-2</sup>, and (b) corresponding voltage profiles of LFP||Li-PAA@EOCC for selected cycles at 0.5 C.



**Figure S42.** Voltage vs. capacity profiles of the LCO||Li-PAA@EOCC and LCO||Bare Li full cells.



**Figure S43**. (a) Cycling performance of full cell with LCO-loading of 25.3 mg cm<sup>-2</sup> (areal capacity: 4.5 mAh cm<sup>-2</sup>), and corresponding voltage profiles of (b) LCO||Li-PAA@EOCC and (c) LCO||Li full cell.



**Figure S44.** LLZO pellet. (a) Digital photo, (b) thickness measurement, (c) XRD pattern, (d) top-view SEM images, and (e) cross-sectional SEM image.



**Figure S45**. Voltage vs. capacity profiles of (a) Li-PAA@EOCC||LLZO||LFP and (b) Li||LLZO||LFP at the rate of 0.1 C.



**Figure S46.** Voltage vs. capacity profiles of Li-PAA@EOCC||PVdF-HFP||NCM811 pouch cell.



**Figure S47**. Schematic illustration of interface issues within different cell system, (a) liquid electrolyte, (b) solid inorganic electrolytes, and (c) solid-state polymer electrolytes.

# Part III. Supplementary Tables

**Table S1.** Structural analysis results were obtained from XRD Rietveld refinement of the PAA and  $Sb_6O_{13}$  powder.

Sample	Reference PAA	ΡΑΑ	Sb <sub>6</sub> O <sub>13</sub>
Space group	Fd-3m	Fd-3m	Fd-3m
a (=b=c) (Å)	10.363	10.333	10.298
α (=β=γ) (°)	90	90	90
Z	8	8	8
V(ų)	1112.9	1103.3	1092.0
16c	Sb <sup>5+</sup> (0, 0, 0)	Sb <sup>5+</sup> (0, 0, 0)	Sb <sup>5+</sup> (0, 0, 0)
48f	O <sup>2-</sup>	O <sup>2-</sup>	O <sup>2-</sup>
	(0.332, 0.125, 0.125)	(0.332, 0.125, 0.125)	(0.419, 0.419, 0.419)
8b	H <sub>2</sub> O	H <sub>2</sub> O	O <sup>2-</sup>
	(0.375,0.375, 0.375)	(0.375,0.375, 0.375)	(0.125, 0.125, 0.125)
16d	H <sub>3</sub> O <sup>+</sup>	H <sub>3</sub> O <sup>+</sup>	Sb <sup>3+</sup>
	(0.5, 0.5, 0.5)	(0.5, 0.5, 0.5)	(0, 0, 0)
R <sub>wp</sub> (%)	/	8.13	6.34
R <sub>p</sub> (%)	/	5.88	4.64

Materials	Average weight/mg
CC	13.57
PAA@EOCC	16.81
Li-PAA@EOCC	37.2
Li in Li-PAA@EOCC	20.39

 Table S2.
 Weight of CC, PAA@EOCC, and Li-PAA@EOCC electrode.

The specific capacity of Li-PAA@EOCC electrode

=Theoretical specific capacity of Li  $\times$  Weight percentage of Li in the Li-PAA@EOCC electrodes

 $= \frac{3860 \times 20.39}{37.2} \approx 2115.7$  mAh g<sup>-1</sup>

**Table S3.** Summary of the calculated interfacial energies  $\gamma$  with Li metal, bulk modulus *E* from MP (The Materials Project, https://materialsproject.org/) (N.B. 1 meV/Å<sup>2</sup>=16.02 mJ/m<sup>2</sup>).

Configuration	Y	Y	Ε	γΕ
	J m <sup>-2</sup>	meV/Ų	(GPa)	(eV/Ų MPa)
Li <sub>2</sub> O	1.00	62.42	78	4868.8
Li₃Sb	0.33	20.60	28	576.8
LiOH	0.49	30.59	18	550.6
Li <sub>2</sub> CO <sub>3</sub> <sup>7</sup>	0.95	59.30	63	3735.9
Li <sub>2</sub> S <sup>7</sup>	0.31	19.35	40 <sup>7</sup>	774.0

**Table S4.** Comparison of the cyclic stability in symmetric cells of our work with thereported Li anodes based on interface engineering.

Lianada	Current	Capacity	Cycle	Pof
Li anode	(mA cm <sup>-2</sup> )	(mAh cm <sup>-2</sup> )	numbers	Rel.
x-PCMS-g- PEGMA/LN	10	10	1400	8
CS/DF-PEG-DF@Li	10 50	10 50	1600 300	9
LiF/Li₃Sb	20	2	1360	10
LS@A-Li	5	10	150	11
rAGA-Li	1	1	1000	12
DRS	5	40	60	13
CNT sponge	20	10	300	14
G-LiF-Li	10	1	165	15
GZCNT	5	1	325	16
PRC	2	1	800	17
Li/Al <sub>4</sub> Li <sub>9</sub> -LiF	20	1	100	18
Li/Li <sub>22</sub> Sn <sub>5</sub>	30	5	200	19
PA-LiOH/Li	20	20	500	20
PrGOLi	1	1	400	21
Li <sub>13</sub> In <sub>3</sub> or LiZn	2	2	600	22
Li-Sr	30	1	180	23
Li <sub>20</sub> Ag	1	2	300	24
NAR-CC	12	12	100	25
LiZrO(NO <sub>3</sub> ) <sub>2</sub> @Li	10	10	275	26
Li-Ni/Li₃N-NS@CC	60	60	500	27
	1	1	1000	
LI-DAV@EOCC	5	1	1075	This
LIFFAA@LUCC	20	10	500	work
	50	25	1280	

Electrode	Cycles	<i>R</i> s (Ω)	R <sub>sei</sub> (Ω)	R <sub>ct</sub> (Ω)
Bare Li	1	3.288	59.2	22.44
	5	5.22	20.67	26.68
	10	5.83	17.36	9.256
	20	4.138	3.048	9.079
	30	2.81	1.075	1.381
	50	1.671	6.649	10.65
Li-PAA@EOCC	1	3.497	16.43	3.021
	5	3.985	7.219	9.650
	10	6.171	7.440	4.834
	20	3.439	1.601	3.889
	30	4.65	1.85	3.83
	50	6.01	1.21	6.33
Li-PAA-	1	3.14	57.45	6.97
w/o@EOCC	5	3.2	9.79	11.06
	10	3.54	3.74	18.97
	20	5.02	2.15	5.14
	30	4.39	1.67	4.52
	50	3.72	1.56	14.6

**Table S5.** The corresponding fitting values are based on the equivalent circuit.

**Table S6**. Corresponding values of  $R_{ct}$  and  $R_{SEI}$  under various temperatures for bare Li||Li cells in temperature-dependent Nyquist plots getting from the equivalent circuit.

<i>Т</i> (К)	1000/ <i>T</i>	<i>R</i> <sub>ct</sub> (Ω)	ln(T/R <sub>ct</sub> )	<i>R</i> <sub>SEI</sub> (Ω)	ln( <i>T/R</i> <sub>SEI</sub> )
288	3.47	178.9	0.48	31.74	2.21
293	3.41	137.1	0.76	23.26	2.53
298	3.36	79.27	1.32	9.20	3.48
303	3.30	53.28	1.74	5.65	3.98
308	3.25	26.95	2.44	3.16	4.58
313	3.19	20.54	2.72	2.43	4.86

**Table S7**. Corresponding values of  $R_{ct}$  and  $R_{SEI}$  under various temperatures for Li-PAA@EOCC||Li-PAA@EOCC cells in temperature-dependent Nyquist plots getting from the equivalent circuit.

<i>Т</i> (К)	1000/ <i>T</i>	R <sub>ct</sub> (Ω)	ln(T/ <i>R<sub>ct</sub></i> )	<i>R</i> <sub>SEI</sub> (Ω)	ln( <i>T/R</i> <sub>SEI</sub> )
288	3.47	23.13	2.52	147.4	0.67
293	3.41	21	2.64	101	1.07
298	3.36	16.35	2.90	66.12	1.51
303	3.30	13.29	3.13	44.92	1.91
308	3.25	10.68	3.36	29.76	2.34
313	3.19	7.35	3.75	20.13	2.74

**Table S8.** Corresponding values of  $R_{ct}$  and  $R_{SEI}$  under various temperatures for Li-PAAw/o@EOCC||Li-PAA-w/o@EOCC symmetrical cells in temperature-dependent Nyquist plots getting from the equivalent circuit.

<i>Т</i> (К)	1000/T	<i>R</i> <sub>ct</sub> (Ω)	ln(T/ <i>R<sub>ct</sub></i> )	<i>R</i> <sub>SEI</sub> (Ω)	ln( <i>T/R</i> <sub>SEI</sub> )
288	3.47	55.26	1.65	175.3	0.50
293	3.41	29.28	2.30	126.5	0.84
298	3.36	24.5	2.50	85.75	1.25
303	3.30	18.45	2.80	56.52	1.68
308	3.25	10.11	3.42	24.46	2.53

313	3.19	8.26	3.63	16.44	2.95

#### Part IV. Supplementary References

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