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

Optimization of $LiCoO_2$ Thick Electrodes with Low Tortuosity for Lithium-Ion Batteries by 3D Printing

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Appendix A. Supplementary Data

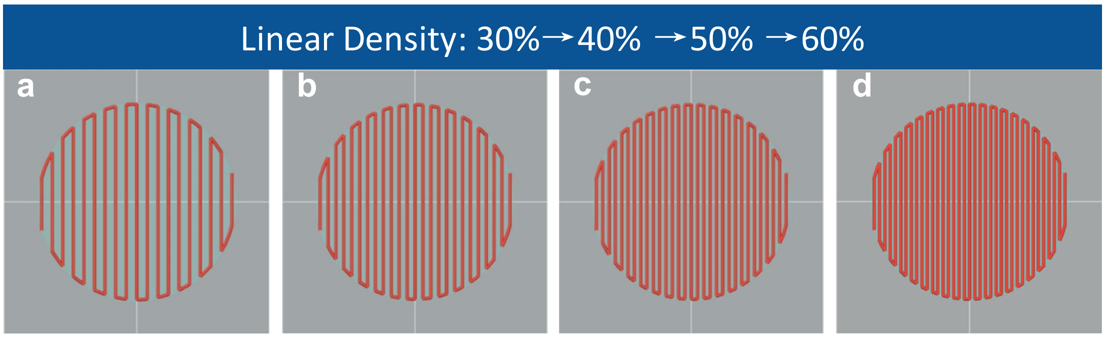

Fig. S1 (a) 30A-LCO, (b) 40A-LCO, (c) 50A-LCO, (d) 60A-LCO electrode printing models

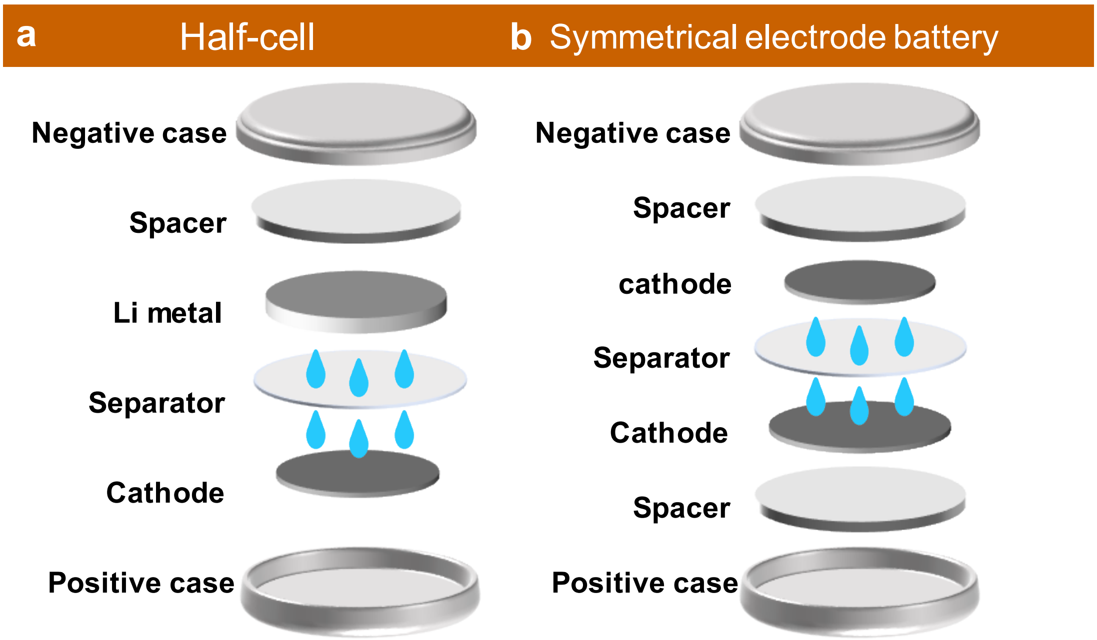

Fig. S2 (a) half battery, (b) symmetrical electrode battery assembly diagram

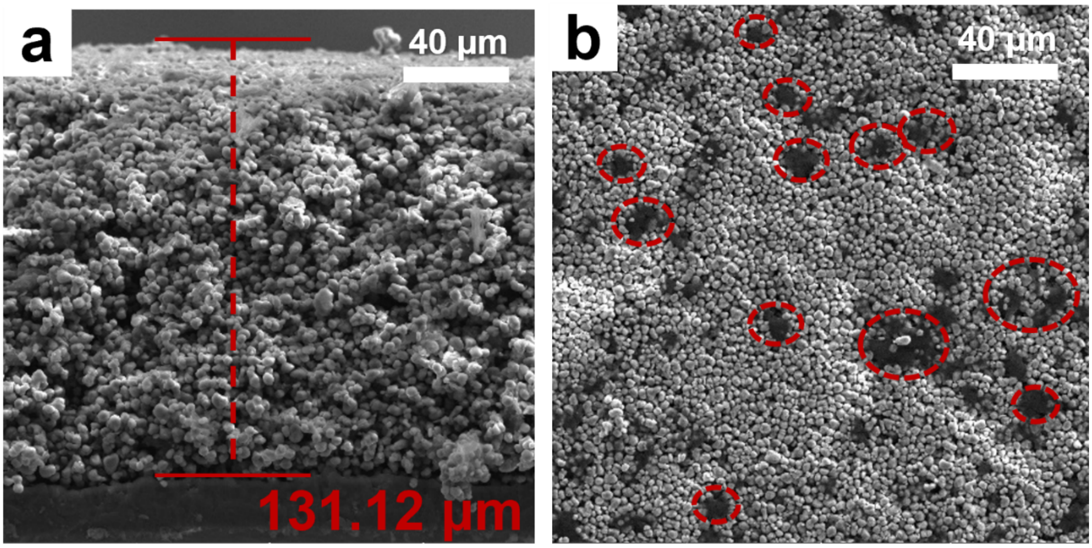

Fig. S3 SEM images of (a) cross-section and (b) surface of the flat electrode (the red circle is where the conductive agents gather)

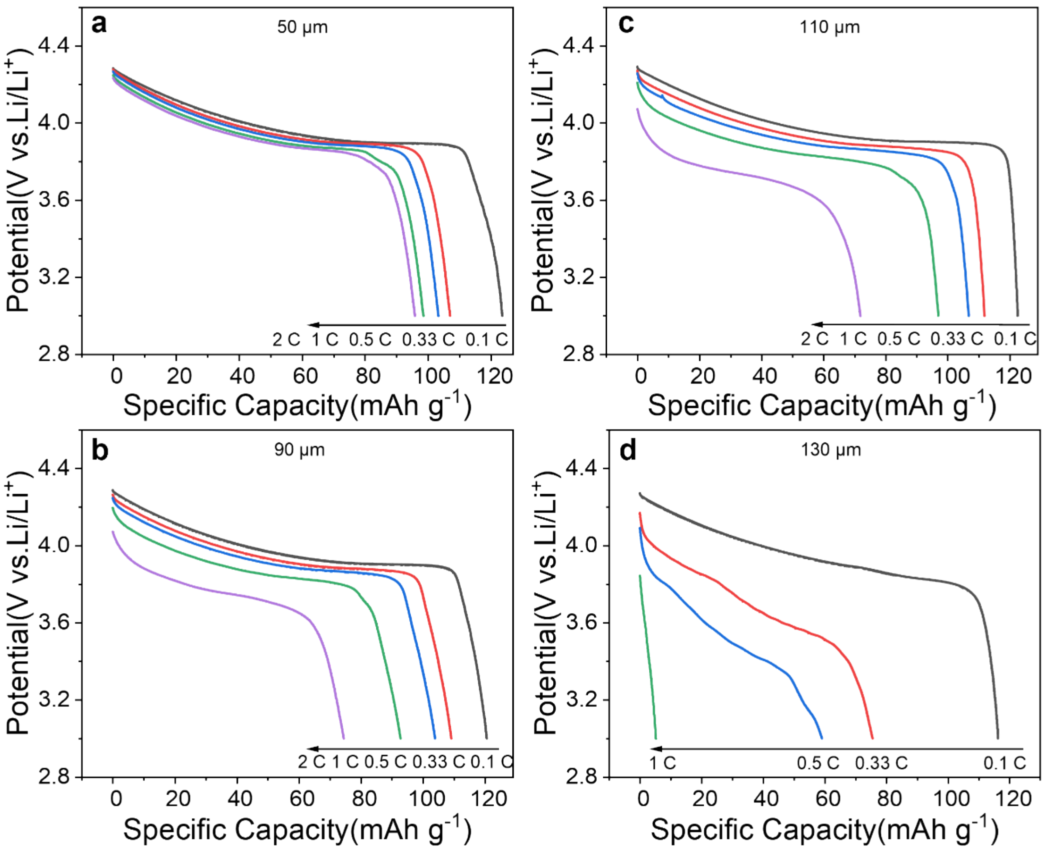

Fig S4 The rate performance of the flat-plate structure electrodes of different thickness (a) 50, (b) 90, (c) 110, (d) 130 μm. (1 C= 140 mAh g^{-1})

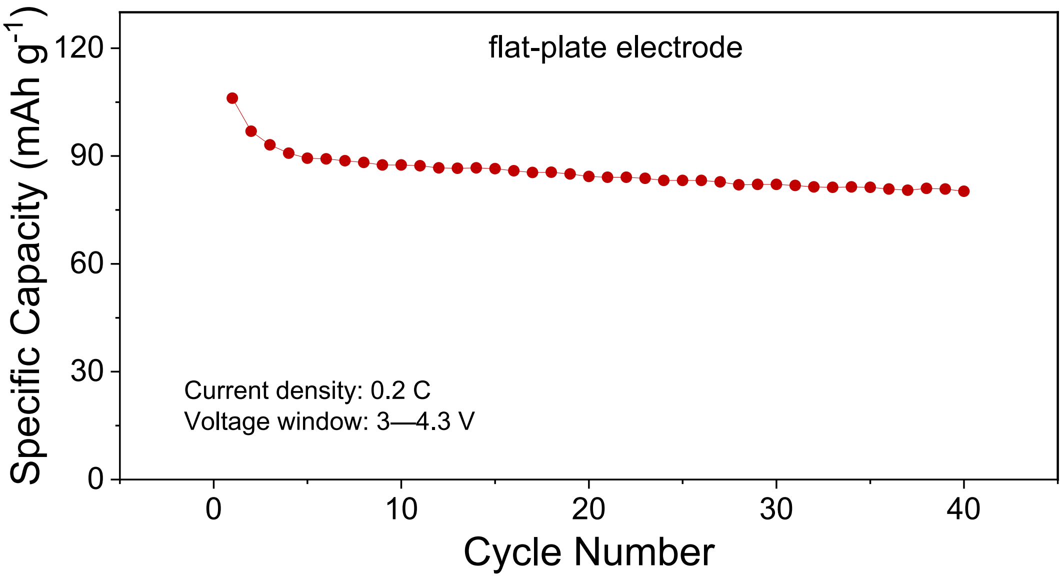

Fig S5 The cycle performance of the flat-plate structure electrodes (1 C= 140 mAh g^{-1})

The impedance of the symmetric electrode battery system follows the equation given in Formula 1.1:

$$Z_{\omega} = \sqrt{\frac{R_{ion,L}}{j\omega C_{dl,A}2\pi r}} coth\sqrt{R_{ion,L} \cdot j\omega C_{dl,A}2\pi r}L \# \text{ (1.1)}$$

As ω approaches 0, the limiting values of the real and imaginary parts satisfy the equations given in Formula 1.2 and Formula 1.3, respectively:

$$Z_{\omega \to 0}^{'} = \frac{R_{ion}}{3} \# \text{ (1.2)}$$

$$Z_{\omega \to 0}^{''} = \frac{1}{\omega C_{dl}} \# \text{ (1.3)}$$

where R_{ion} represents the resistance for lithium-ion transport in the liquid phase, and the relationship between R_{ion} and tortuosity is described by Equation 1.4:

$$\tau = \frac{R_{ion} A \varepsilon \kappa}{2d} \# \text{ (1.4)}$$

where A is the electrode surface area,，k is the ionic conductivity of the electrolyte, and d is the electrode thickness.

The electrode porosity ε satisfies the following equation (1.5):

$$\varepsilon = 1 - \frac{m_{areal}}{d}\left(\frac{\omega_{AM}}{\rho_{AM}} + \frac{\omega_{B}}{\rho_{B}} + \frac{\omega_{CA}}{\rho_{CA}}\right) \# \text{ (1.5)}$$

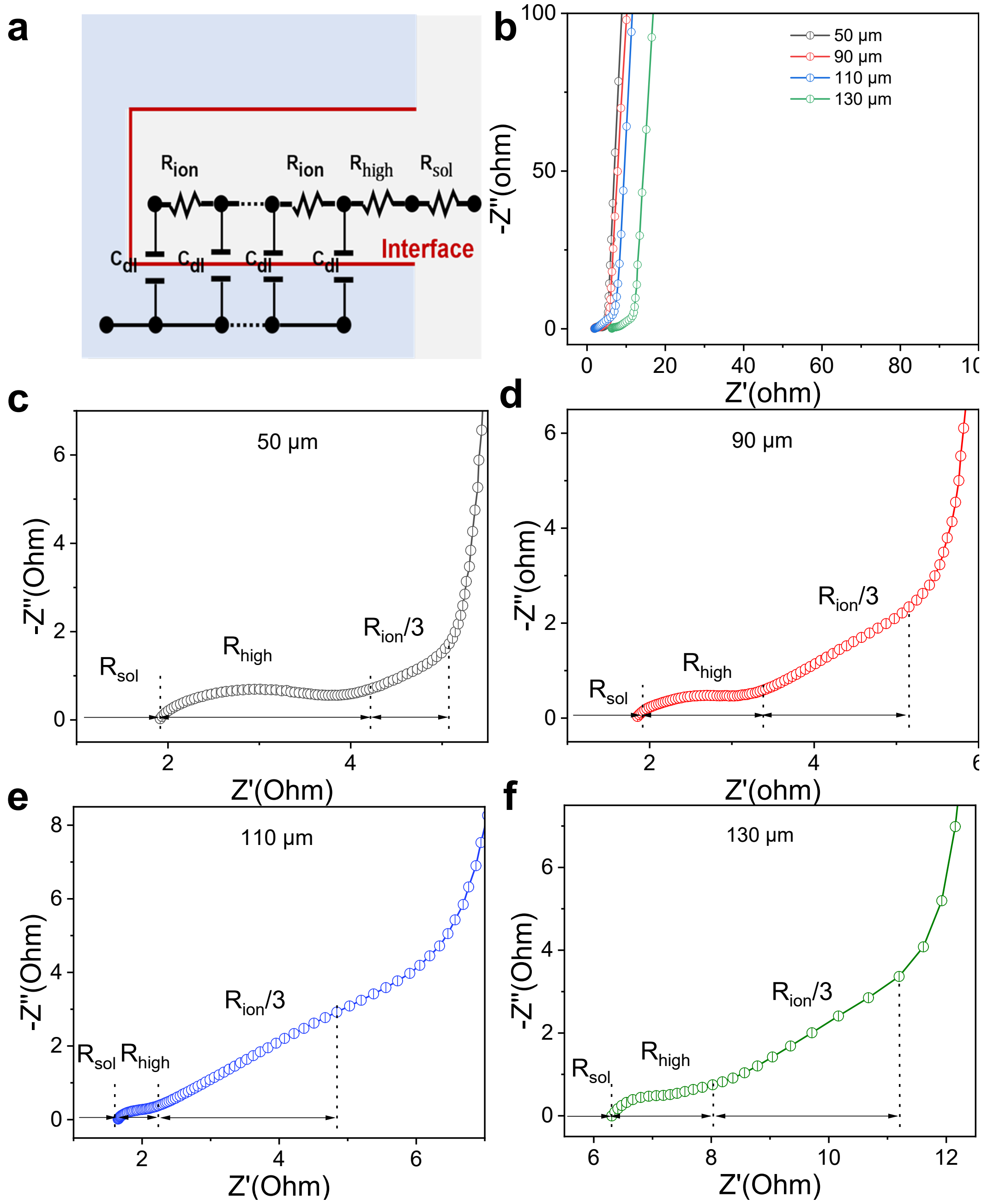

Fig. S6 (a)The transmission line model schematic diagram. EIS diagram of electrodes of different thickness: (b) general EIS of all thickness electrodes and (c) 50, (d) 90 (e) 110 (f) 130 μm.

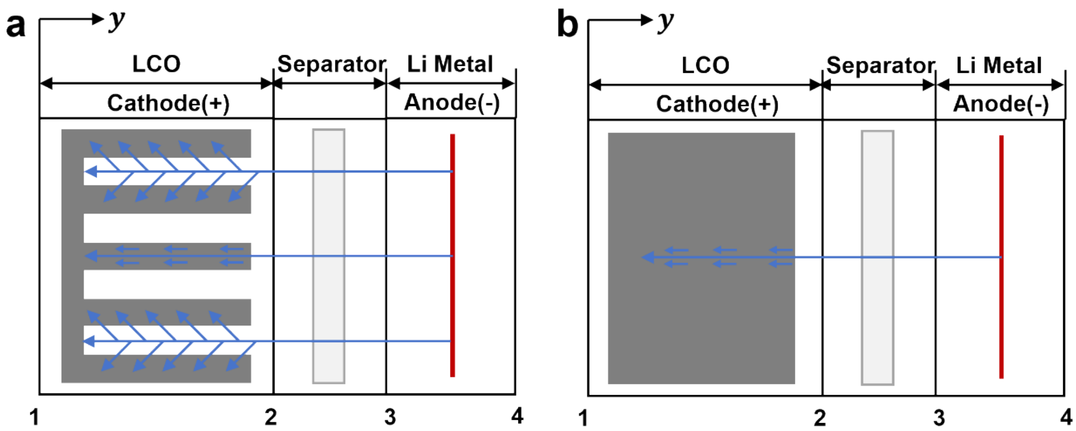

Fig. S7. Schematic of the finite element model: (a) ordered structure electrode, (b) flat structure electrode.

Model Description:

A two-dimensional half-cell model based on the framework proposed by J. Newman et al. was developed to calculate lithium-ion concentration distribution in the electrolyte and the cathode ($LiCoO_2$) to investigate ion transport challenges in thick electrodes. For simplification, a 2D model was constructed based on the cross-section of the battery. The model incorporates the following five fundamental assumptions:

1. The effects of thermal phenomena are neglected, and an isothermal model is established.

2. The electrode material consists of uniformly distributed spherical particles of equal size.

3. Conductive agents and binders are homogeneously distributed within the electrode, forming a continuous conductive network. Ion diffusion within the electrode follows Fick's law, with tortuosity derived from experimental data.

4. Side reactions and gas generation within the cell are ignored.

5. Lithium-ion transport behavior is limited to diffusion and electromigration, while convection effects are neglected.

The 2D LCO/Li model is shown in Figure S7, where Figure S7(a) represents the schematic of the 3D-printed ordered structure electrode, and Figure S7(b) illustrates the conventional flat structure electrode. The blue arrows indicate the direction of lithium-ion transport. Region 12 corresponds to the cathode, and region 23 corresponds to the separator, while the lithium metal anode is defined as the boundary. The electrolyte consists of 1 M $LiPF_6$, distributed across all regions of the model. The related parameters and definitions are provided in Table S3.

In this model, the current density in the electrolyte is described using the electrolyte potential node, with the governing equation as:

$$i_l = -\sigma_l \nabla \phi_l + \frac{2RT\sigma_l}{F}\left(1 + \frac{\partial \ln f}{\partial \ln C_l}\right)(1 + t_+)\nabla \ln C_l \# \ (1.6)$$

where i_l represents the current density, σ_l is the ion conducitivity, ϕ_l is the electrolyte potential, R is universal gas content, T is the temperature, F is the Faraday content, $f_\pm$ is the mean molar activity coefficient of the electrolyte, t_+ is the transference number of lithium ions, and C_l is the lithium ion concentration in the electrolyte.

The diffusion and migration of lithium ions in the electrolyte follow Fick's law:

$$\frac{\partial C_l}{\partial t} + \nabla \cdot J_l = 0 \# \ (1.7)$$

$$J_l = -D_l \nabla C_l + \frac{i_l t_+}{F} \# \ (1.8)$$

where J_l and D_l represent the lithium ion flux and the diffusion coefficient in the electrolyte, respectively. Equation (1.7) and (1.8) describe the diffusion and migration process of lithium ion in the electrolyte.

The reaction at the solid-liquid interface is governed by the Butler-Volmer kinetic equation:

$$i_{int} = i_0\left\{exp\left(\frac{\alpha_n F}{RT}\eta\right) - exp\left(-\frac{\alpha_p F}{RT}\eta\right)\right\} \# \ (1.9)$$

where i_{int} represents the local current density, i_0 is the exchange current density, α_n and α_p are the charge transfer coefficients for the anode and cathode, respectively, and η is the overpotential of the cell.

The diffusion of lithium ions within the solid-phase particles of the electrode also follows Fick's law：

$$\frac{\partial C_s}{\partial t} + \nabla \cdot J_s = 0 \# \quad (1.10)$$

$$J_s = -D_s \nabla C_s \# \quad (1.11)$$

where C_s and J_s represent the lithium-ion concentration and flux within the electrode particles, respectively, and D_s is the lithium-ion diffusion coefficient in the electrode particles.

Table S1: 3D print parameters

Parameter	Value/description
Sparse density (%)	30/40/50/60
Printing speed (mm s^{-1})	30
Air pressure (MPa)	0.5
Layer height (mm)	0.3
Line width (mm)	0.34
Pattern	Aligned rectilinear
Heating platform temperature (°C)	80

Table S2: Impedance spectrum data and tortuosity calculation of symmetric cells

Thickness (μm)	**R_{sol} (Ω)**	**R_{high} (Ω)**	**R_{ion} (Ω)**	**ε (%)**	**τ**
50	1.91	2.28	3.10	41.74	15.56
90	1.85	1.46	5.44	48.14	16.81
110	1.65	2.51	10.21	41.92	21.98
130	6.36	/	/	/	/

Table S3 LCO/Li half cell model parameters and definitions

Abbreviation	Expression/value	Description
epss_pos	0.6	Electrode phase volume fraction, cathode
epsl_pos	0.4	Electrolyte phase volume fraction, cathode
rp_pos	1.44 [μm]	Particle radius, cathode materials
cl_0	2000 [mol/m^3]	Initial electrolyte salt concentration
Ecell_up	4.45 [V]	Upper cut-off voltage
Ecell_low	3.0 [V]	Cutoff voltage lower limit
C	0.1、2	C-rate factor for the parametric study
T	298.15 [K]	Temperature