Supporting information

Metal-organic framework derived electrical insulating-conductive double-layer structure for stable lithium metal anode

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Fig. S1 XRD patterns of ZIF-67 and simulated ZIF-67.

Fig. S2 XRD pattern of Co@NPC.
Fig. S3 Raman spectrum of Co@NPC

Fig. S4 N₂ adsorption-desorption isotherms of (a) ZIF-67 and (c) Co@NPC, pore size distribution of (b) ZIF-67 and (d) Co@NPC.
Fig. S5 (a) The XPS survey spectrum of Co@NPC. (b-d) high-resolution of XPS spectrums of C 1s, N 1s and Co 2p.
As shown in Fig. S6, the broad absorption band at 3450 cm$^{-1}$ is characteristic of the stretching vibration of N-H bonds. The band at 2820 cm$^{-1}$ is ascribed to the C-H stretching vibration. The band at 1590 cm$^{-1}$ is attributed to the C=N bond stretching vibration, which indicates the presence of N in the porous carbon. Besides, the two bands at 1340-1400 cm$^{-1}$ are related to C-N stretching and the O-H bonds bending vibration.
Fig. S7 Cross-section view of (a) ZIF-67/Cu and (b) ICDL/Cu electrodes before cycling.

Fig. S8 (a) The thickness changes of planar Cu, ZIF-67/Cu, and ICDL/Cu after plating Li 0 mAh cm$^{-2}$, 1 mAh cm$^{-2}$, 2 mAh cm$^{-2}$, and 5 mAh cm$^{-2}$, (b) the thickness expansion ratio of planar Cu, ZIF-67/Cu, and ICDL/Cu after plating Li 0 mAh cm$^{-2}$, 1 mAh cm$^{-2}$, 2 mAh cm$^{-2}$, and 5 mAh cm$^{-2}$. 

Fig. S9 Optical images of Li deposition on planar Cu, ZIF-67/Cu, and ICDL/Cu-Li for different time at the current density of 3 mA cm$^{-2}$. 
Fig. S10 SEM images of (a) ZIF-67 and (b) carbonized ZIF-67 after Li deposition with a capacity of 1 mAh cm$^{-1}$.

As shown in Fig. S10a, b, the polyhedral morphology of ZIF-67 is kept well, and the size of ZIF-67 nanoparticles does not change after plating Li, which proves the ZIF-67 coating layer is not involved in Li deposition. After Li deposition, the morphology of Co@NPC nanoparticles is changed significantly, and the Co@NPC is dispersive (Fig. S10c, d), suggesting that Li is firstly deposited on the Co@NPC in the initial Li plating stage due to the strong Li affinity of Co metal nanoparticles and N doped porous carbon.
Fig. S11 Comparison of Li nucleation overpotential on the planar Cu, ZIF-67/Cu, and ICDL/Cu at the current density of (a) 0.5 mA cm\(^{-2}\) and (b) 3 mA cm\(^{-2}\).

Fig. S12 Voltage profiles of Li plating/stripping of the (a) planar Cu, (b) ZIF-67/Cu, and (c) ICDL/Cu at the current density of 1 mA cm\(^{-2}\) for 1 mAh cm\(^{-2}\).
Fig. S13 Comparison of voltage profiles of symmetrical cells at the current density of 1 mA cm\(^{-1}\) with the plating/stripping capacity of 5 mAh cm\(^{-1}\).

Fig. S14 The equivalent circuit of cells.
Fig. 15 Nyquist plots of impedance of symmetrical cells after (a) 50 cycles and (b) 100 cycles.

After 50 and 100 cycles, the ICDL/Cu-Li\textbar|ICDL/Cu-Li symmetrical cell exhibits the smallest values of $R_{SEI}$ and $R_{ct}$ than that of ZIF-67/Cu-Li\textbar|ZIF-67/Cu-Li and Cu-Li\textbar|Cu-Li. The impedances of ZIF-67/Cu-Li\textbar|ZIF-67/Cu-Li and Cu-Li\textbar|Cu-Li are gradually increased from 50 cycles to 100 cycles.
Table S1 Comparison of symmetrical cell cycling performance between this work and reported literature with the similar electrode configuration.

<table>
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<th>Composite Li metal</th>
<th>Current density-capacity</th>
<th>Hysteresis voltage (mV)</th>
<th>Cycling time (h)</th>
<th>Reference</th>
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<td>Li$_2$CO$_3$/PVDF</td>
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coated Li

ZnO-based 0.5-0.5 ~ 100 500 2

inorganic/organic double-layer structure

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<th>R_{SEI}</th>
<th>R_{ct}</th>
<th>Rs</th>
<th>R_{SEI}</th>
<th>R_{ct}</th>
<th>Rs</th>
<th>R_{SEI}</th>
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<td>MOF-HCF@Li</td>
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<td>~ 20</td>
<td>1000</td>
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<td>1100</td>
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Table S2 The simulated parameters of impedance.
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References


