

## Supporting Information

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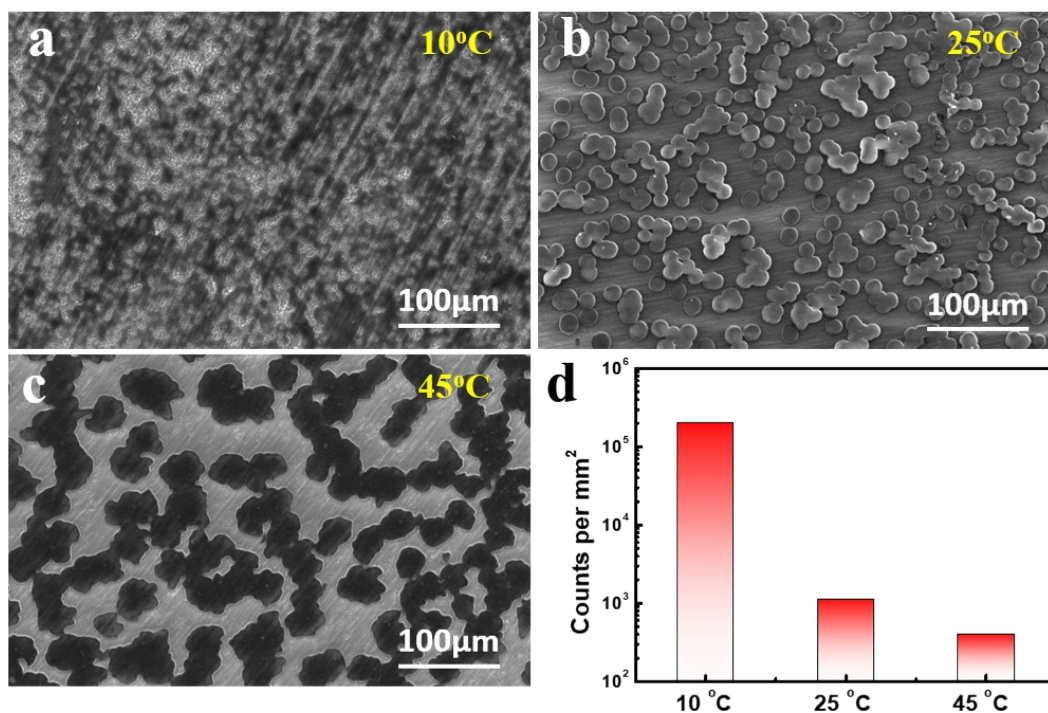
#### 1. Experimental Section

- Figure S1.** Low-magnified SEM images of Li nuclei in ether electrolytes at different temperatures. (a) 10 °C, (b) 25 °C, (c) 45 °C and (d) corresponding counted nucleation density.
- Figure S2.** SEM images of Li nucleates over Copper foil in ester electrolyte at (a-b) -20°C and (c-d) 45°C with different deposition capacity. Current density: 0.05 mA cm<sup>-2</sup>.
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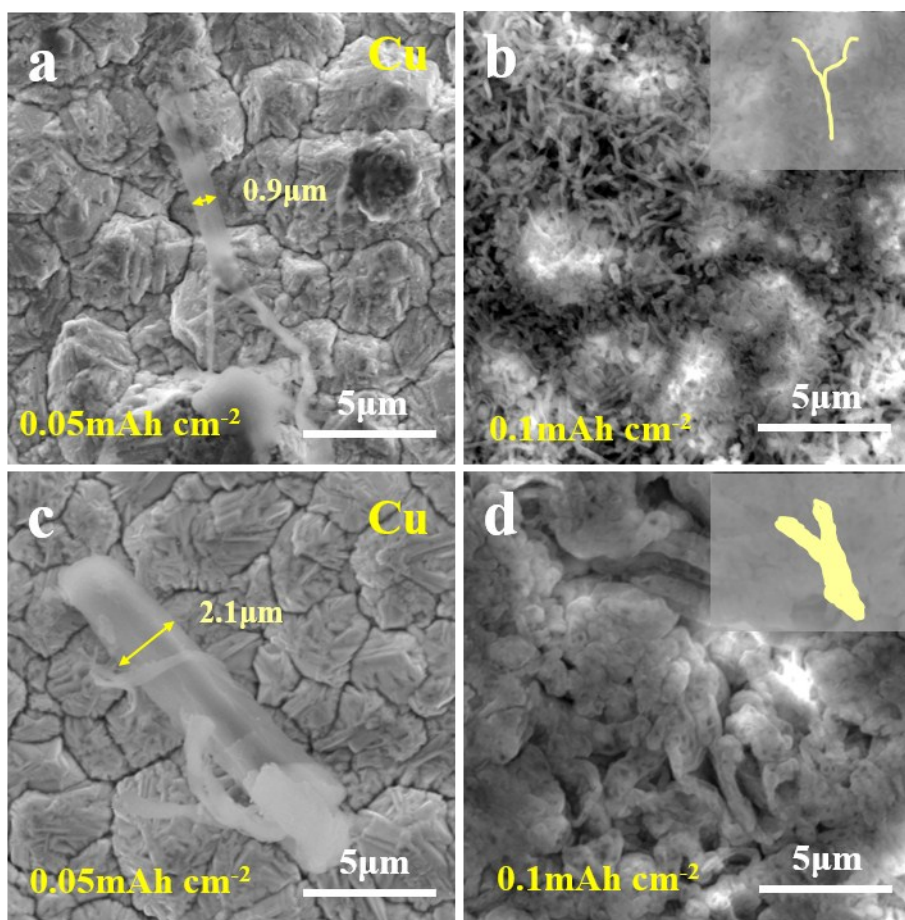
## Experimental Section

**Electrochemical Measurements.** Commercialized Cu foil was punched into disks of 14 mm in diameter and then washed by ethanol for three times to eliminate contamination followed by natural drying. CR2032-type Li-Cu half-cells, Li-Li symmetric cells and Li-LiCoO<sub>2</sub> cells (commercialized LiCoO<sub>2</sub>, Shenzhen Kejing Star Technology Co., LTD) were assembled inside an argon-filled glove box with 12.5 mm Li disks as both the reference and counter electrodes. 1 M LiPF<sub>6</sub> in EC/DMC/EMC (v:v:v=1:1:1) and 1 M LiTFSI in DOL/DME (v:v=1:1) with 1 wt% LiNO<sub>3</sub> were selected as electrolytes (Jiangsu Guotai Chaowei New Materials Co., Ltd.). Separator is PP-based celgard 2500. 60 $\mu$ L electrolyte is used per cell. Li plating/stripping measurements were performed using LAND battery testing system. The cells were initially stabilized at a current density of 50  $\mu$ A with a cut-off potential between 0.01V and 3V and then cycled at set current densities and capacities under different temperatures. Cyclic voltammetry (CV) studies were carried out at different temperatures using CHI760e electrochemical workstation. The electrochemical impedance spectroscopy (EIS) tests were conducted on Solartron Electrochemical Interface SI 1287 and SI 1260 from 0.01 to 100000 Hz with the amplitude of 5 mV.

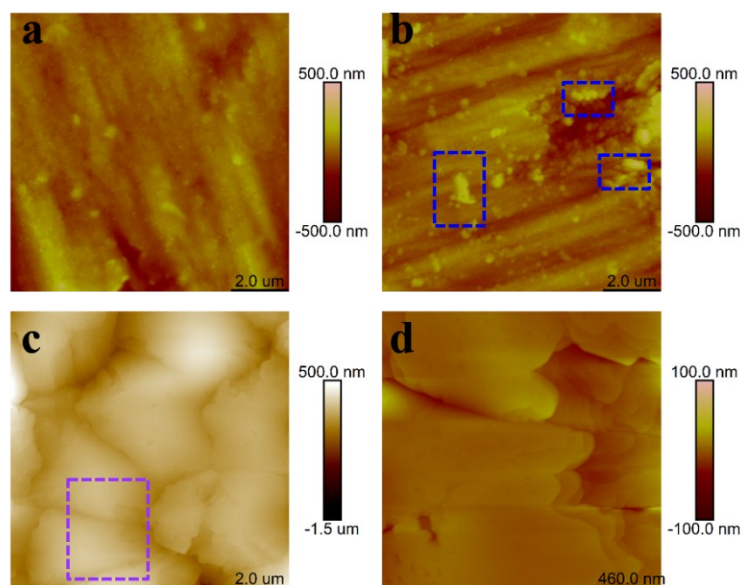
**Materials Characterizations.** The morphology and chemical compositions were characterized using SEM (FEI Sirion 200) and XPS (Thermo Fisher ESCALab250 with monochromatic 150 W AlK $\alpha$  radiation).



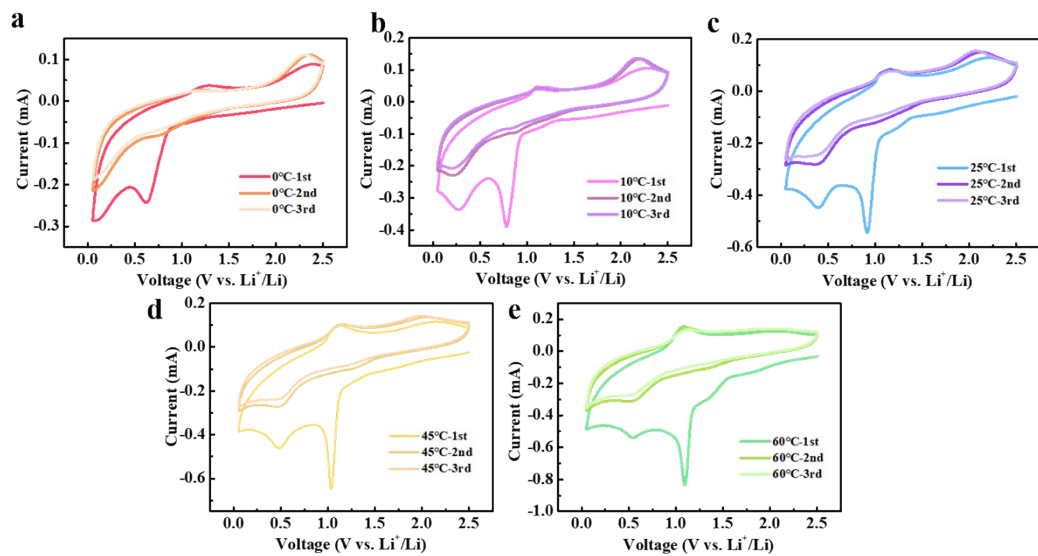
**Fig. S1.** Low-magnified SEM images of Li nuclei in ether electrolytes at different temperatures. (a) 10 °C, (b) 25 °C, (c) 45 °C and (d) corresponding counted nucleation density.



**Fig. S2.** SEM images of Li nucleates over Copper foil in ester electrolyte at (a-b) -20°C and (c-d) 45°C with different deposition capacity. Current density: 0.05 mA cm<sup>-2</sup>.



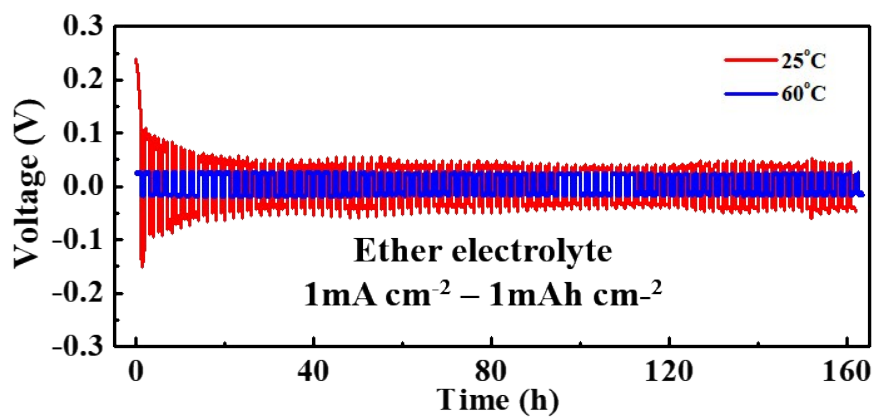
**Fig. S3.** Typical AFM images of (a) pristine Cu electrode and Cu electrode after cycled at (b) 0 °C and (c) 60 °C. (d) AFM images of a locally magnified area as marked in (c).



**Fig. S4** Cyclic voltammograms of Li-Cu cells with initial 3 cycles between 0.01-3V in ether electrolyte at (a) 0 °C, (b) 10 °C, (c) 25 °C, (d) 45 °C and (e) 60 °C. Scan rate: 5 mV s<sup>-1</sup>.

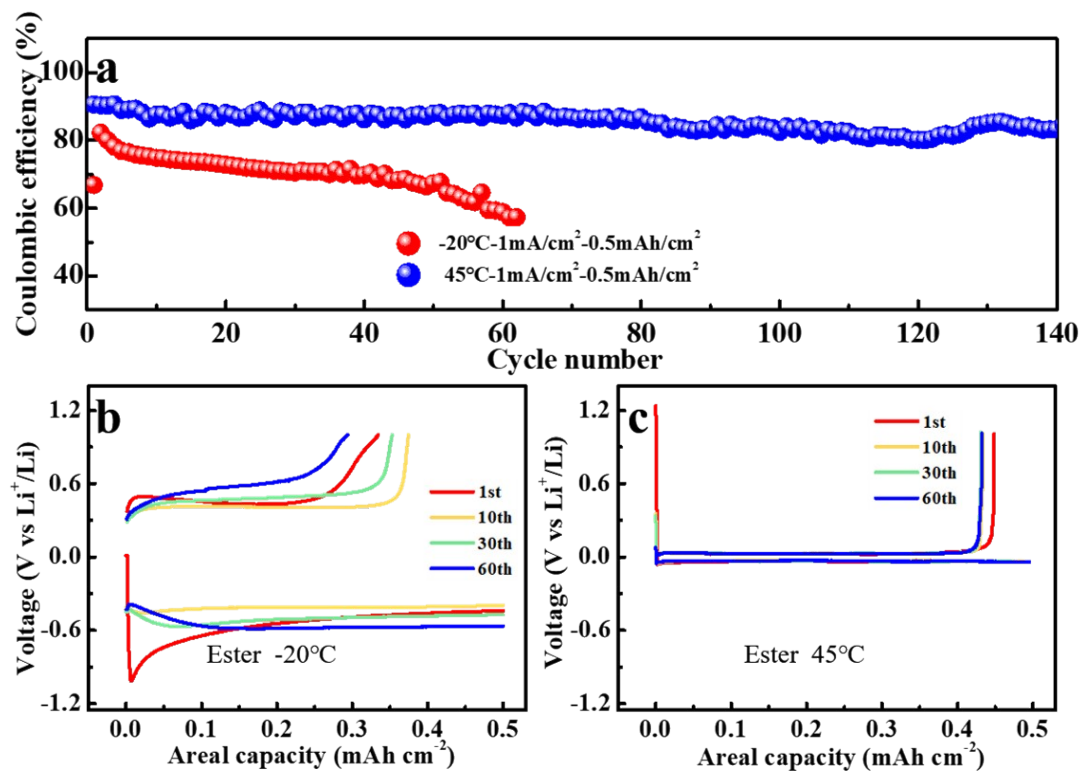
Temperature	Spectra	Binding energy	Compositions	Peak area
0°C	N1s	404.23	R-NO <sub>2</sub>	56.93549
		399.9	Li <sub>3</sub> N	481.4097
		399.05	LiN <sub>x</sub> O <sub>y</sub>	178.4166
60°C	N1s	404.07	R-NO <sub>2</sub>	160.621
		399.56	Li <sub>3</sub> N	509.9226
		398.53	LiN <sub>x</sub> O <sub>y</sub>	176.5701
0°C	S2p	170.5	Li <sub>2</sub> SO <sub>4</sub>	306.6817
		169.45	SO <sub>4</sub> <sup>2-</sup>	666.9973
		167.5	Li <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	55.31921
60°C	S2p	170.31	Li <sub>2</sub> SO <sub>4</sub>	237.9653
		169.2	SO <sub>4</sub> <sup>2-</sup>	509.8306
		167.8	Li <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	144.6707
0°C	F1s	689.06	Li <sub>x</sub> C <sub>2</sub> F <sub>y</sub>	8508.244
		684.9	LiF	745.0798
60°C	F1s	688.65	Li <sub>x</sub> C <sub>2</sub> F <sub>y</sub>	8907.233
		684.85	LiF	1352.6

**Table. S1** The compositions and peak areas extracted from XPS spectra.

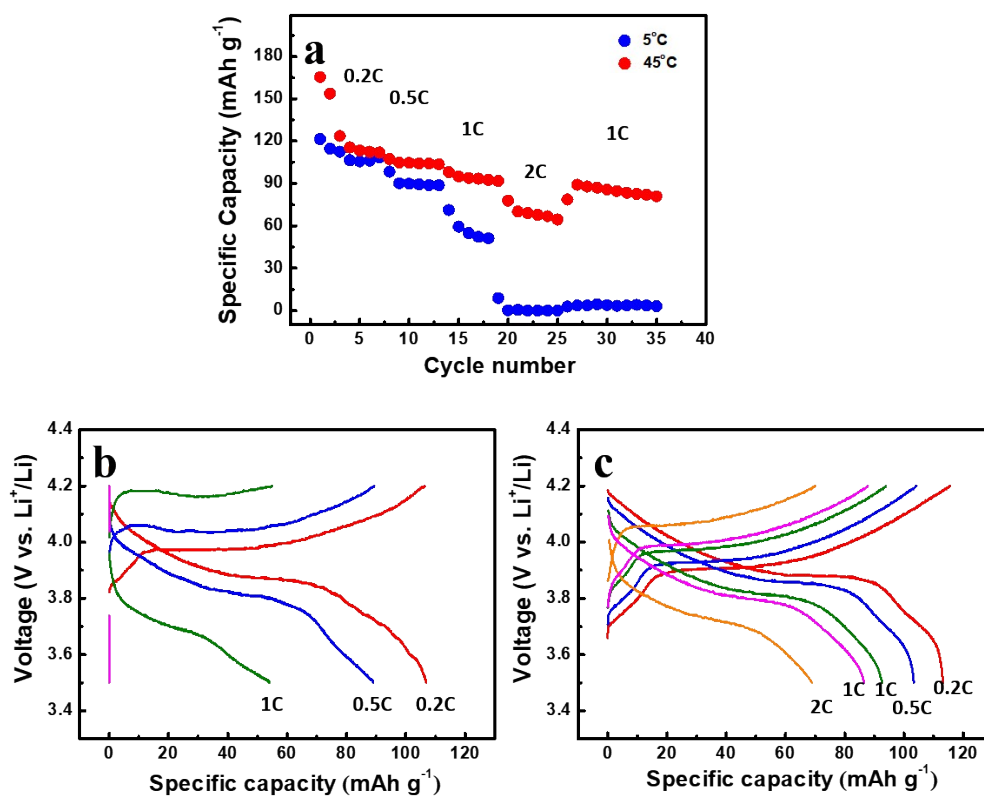


**Fig. S5.** The voltage-time curves of Li-Li symmetric cells cycled in ether electrolyte at 25 °C and 60 °C using a current density of  $1\text{mA cm}^{-2}$  with capacity of  $1\text{mAh cm}^{-2}$ .





**Fig. S6.** (a) Coulombic efficiency of Li-Cu cells cycled at low T and high T in ester electrolyte and (b-c) corresponding plating/stripping curves.



**Fig. S7.** (a) Rate performances of Li-LiCoO<sub>2</sub> cells under both high and low T and corresponding charging-discharging curves at (b) 5°C and (c) 45 °C.