

## Supplementary information

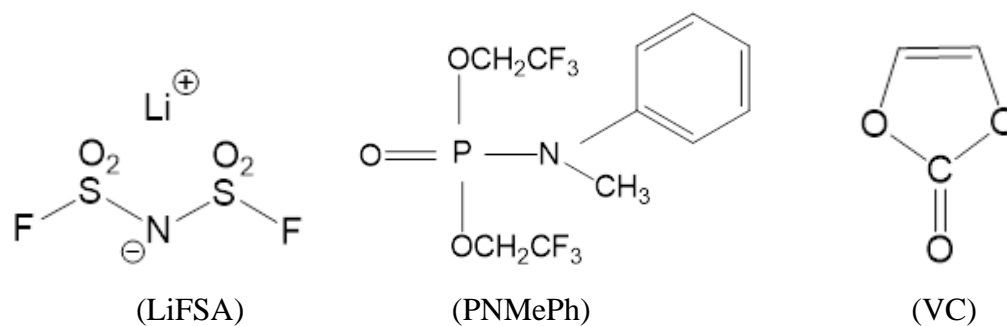
Lithium-ion attack on yttrium oxide in the presence of copper powder during Li plating in a super-concentrated electrolyte

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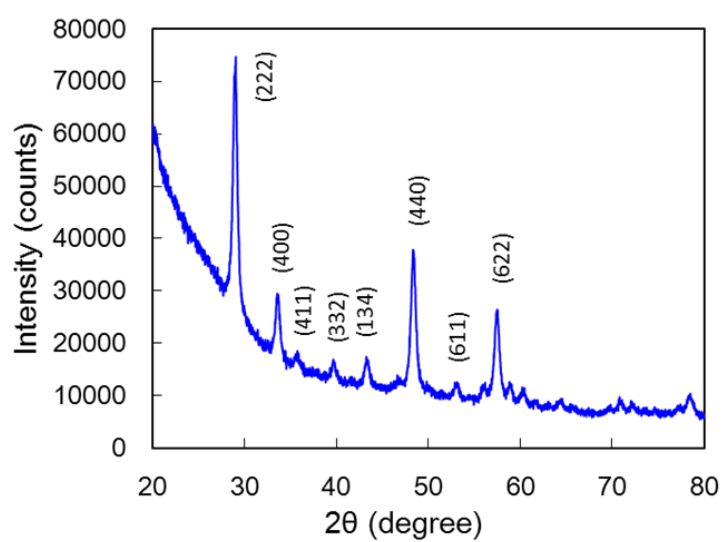
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## 1. Materials



**Figure S1.** Chemical structures of LiFSA, PNMePh, and VC



**Figure S2.** XRD pattern for  $\text{Y}_2\text{O}_3$  powder.

## 2. Experimental

### 2.1. Electrode

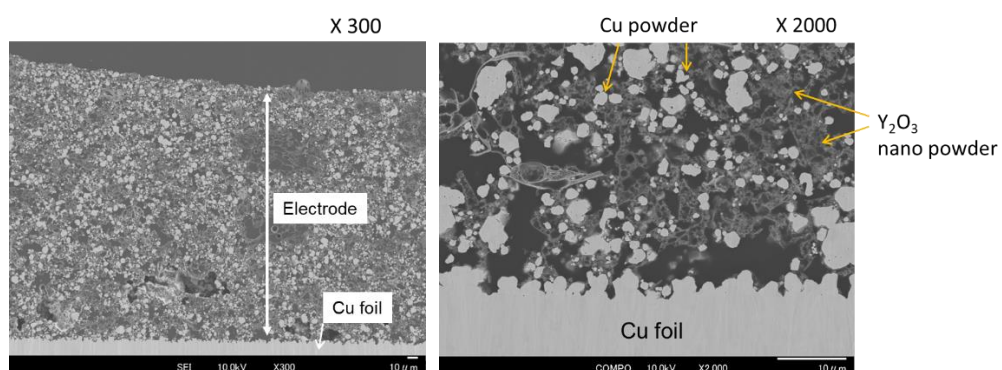


Figure S3. SEM images of the cross section of a Cu+Y<sub>2</sub>O<sub>3</sub> electrode.

### 2.2. Electrochemical cell

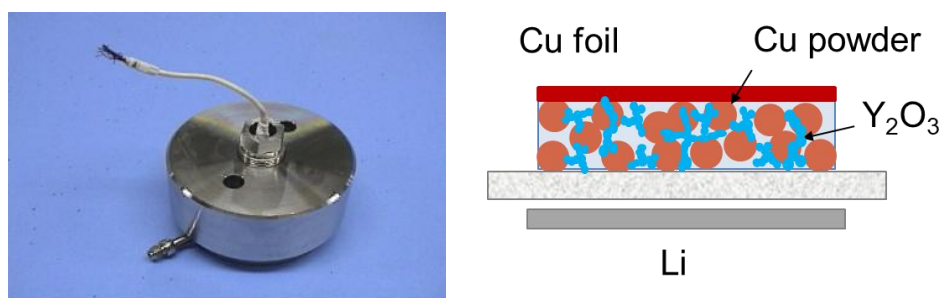
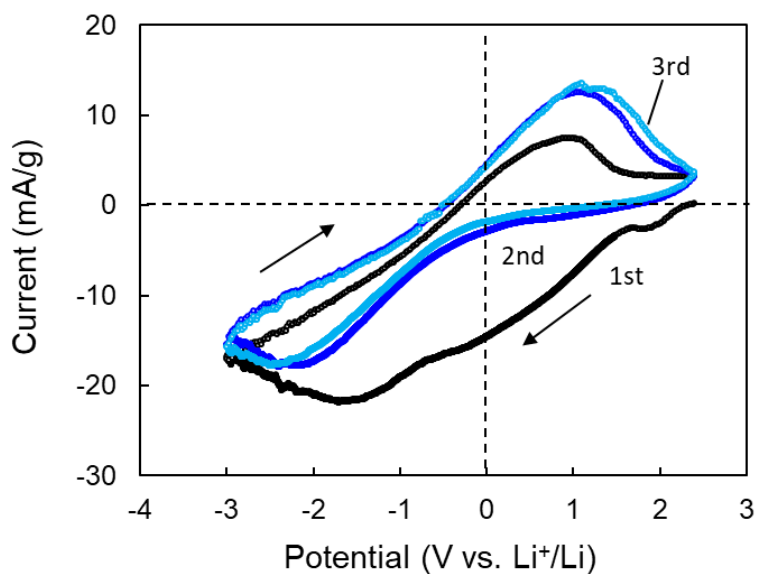


Figure S4. Photograph and schematic of an electrochemical cell.



**Figure S5.** The 1<sup>st</sup> through 3<sup>rd</sup> cyclic voltammograms for LiFSA/PNMePh super-concentrated electrolyte. The sweep rate was 1 mV/sec.

**Table S1.** <sup>7</sup>Li-NMR measurement parameters

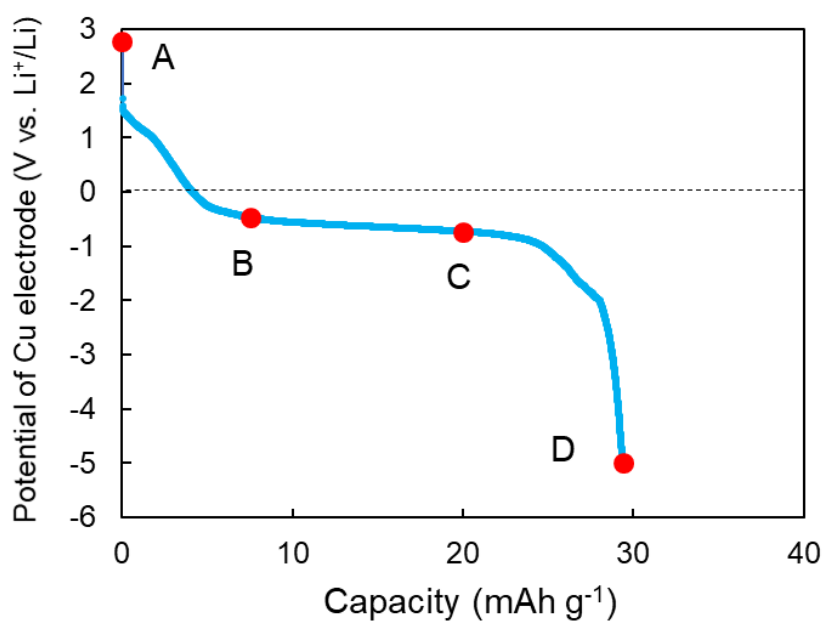
Measurement frequency	155.5080156 MHz
Spectral width	100 kHz
Pulse width	1.0 $\mu$ m (30° pulse)
Pulse repetition time	12 sec
Observation point	8192 points
Reference material	1M LiCl aqueous solution
Temperature	Room temperature
Rotational frequency	0 Hz, 15 Hz
Sample tube	ZrO <sub>2</sub> , inner diameter 1 mm Length 2.5 mm

**Table S2.** XAFS measurement parameters

Experimental facility	Aichi Synchrotron Radiation Center in Japan
Experimental station	BL11S2
Split	Si(111)2Crystal spectroscopy
Absorption end	Y-K absorption end (17038.0 eV)
Detection method	Through the law
Detectors	Ion chambers

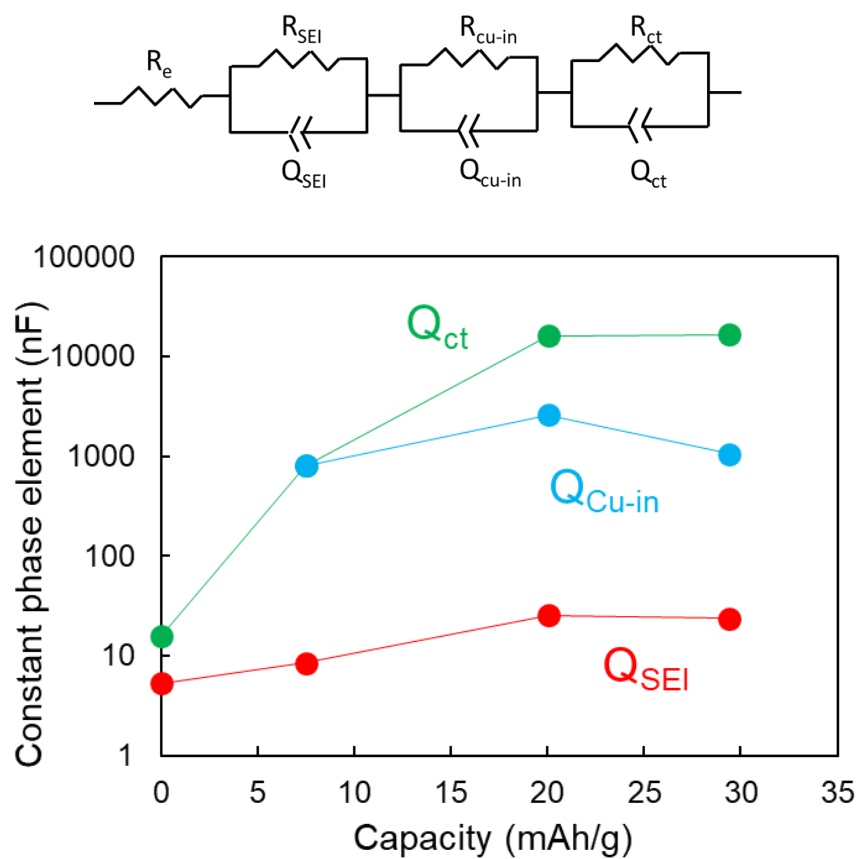
### 3. Results

#### 3.1. Li plating behavior for the cell fabricated using only Cu powder

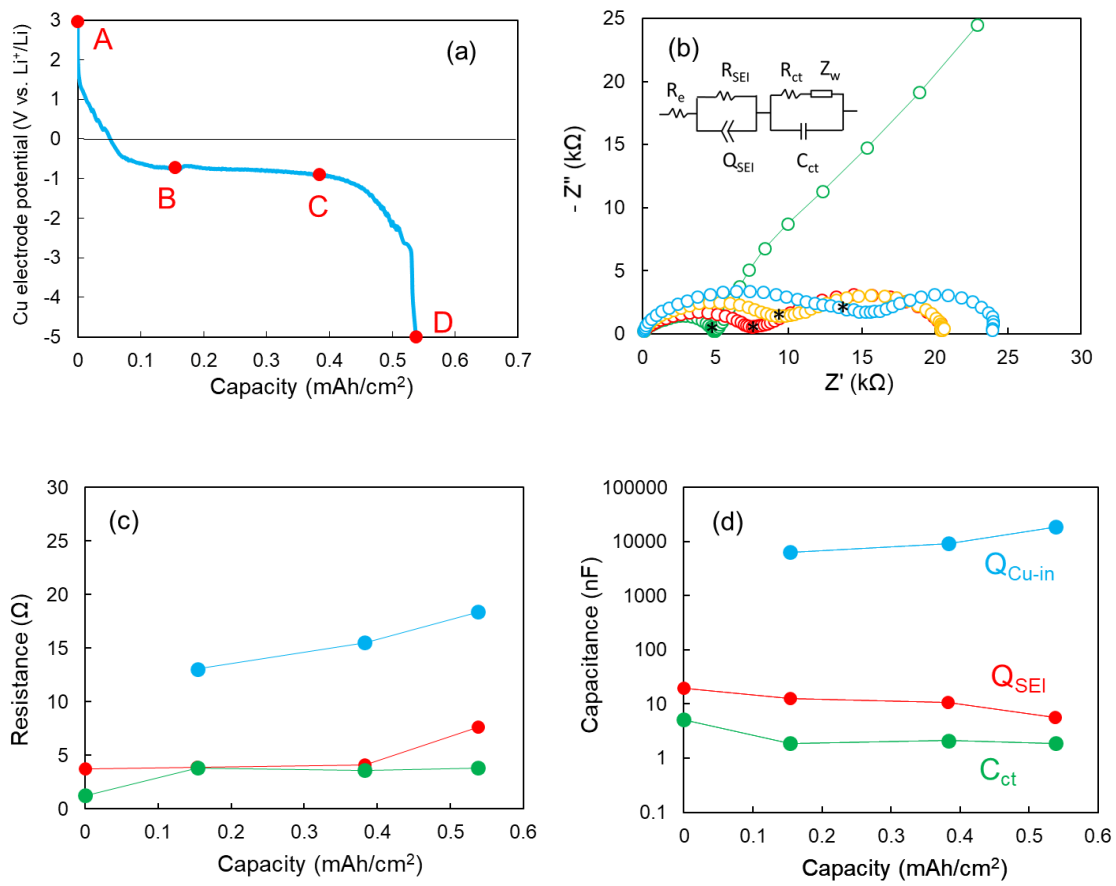


**Figure S6.** Cu electrode potential-capacity curve for the electrode fabricated using only Cu powder. The samples A,B,C, and D were applied to the EIS measurement.

### 3.2. EIS results

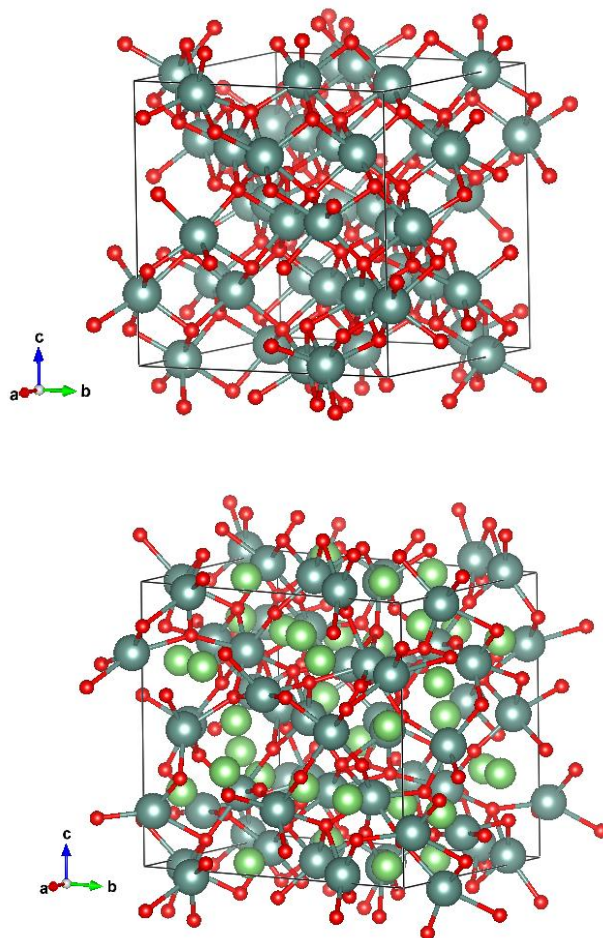


**Figure S7.** Equivalent circuit (top) and constant phase elements (bottom) for the three components of the cell using Cu powder electrode.



**Figure S8.** EIS results for the cell using Cu foil electrode.

### 3.3. Calculation results



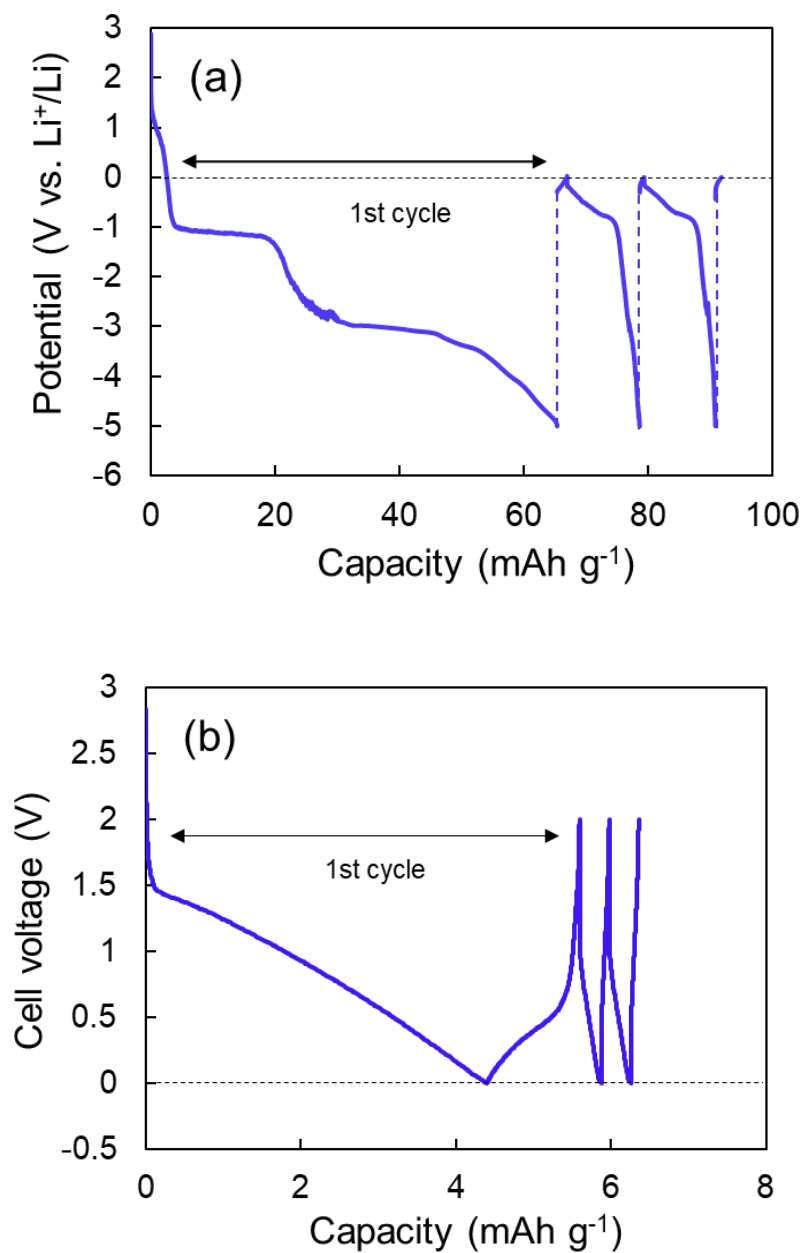
**Figure S9.** Crystal structure of bulk  $\text{Y}_2\text{O}_3$  (upper) and  $\text{Li}_{1.5}\text{Y}_2\text{O}_3$  (bottom). The dark and light green, and red circles represent yttrium, lithium, and oxygen elements in turn.

**Table S3.** Bader charge ( $e$ ) for each element in  $\text{Y}_2\text{O}_3$  and  $\text{Li}_{1.5}\text{Y}_2\text{O}_3$

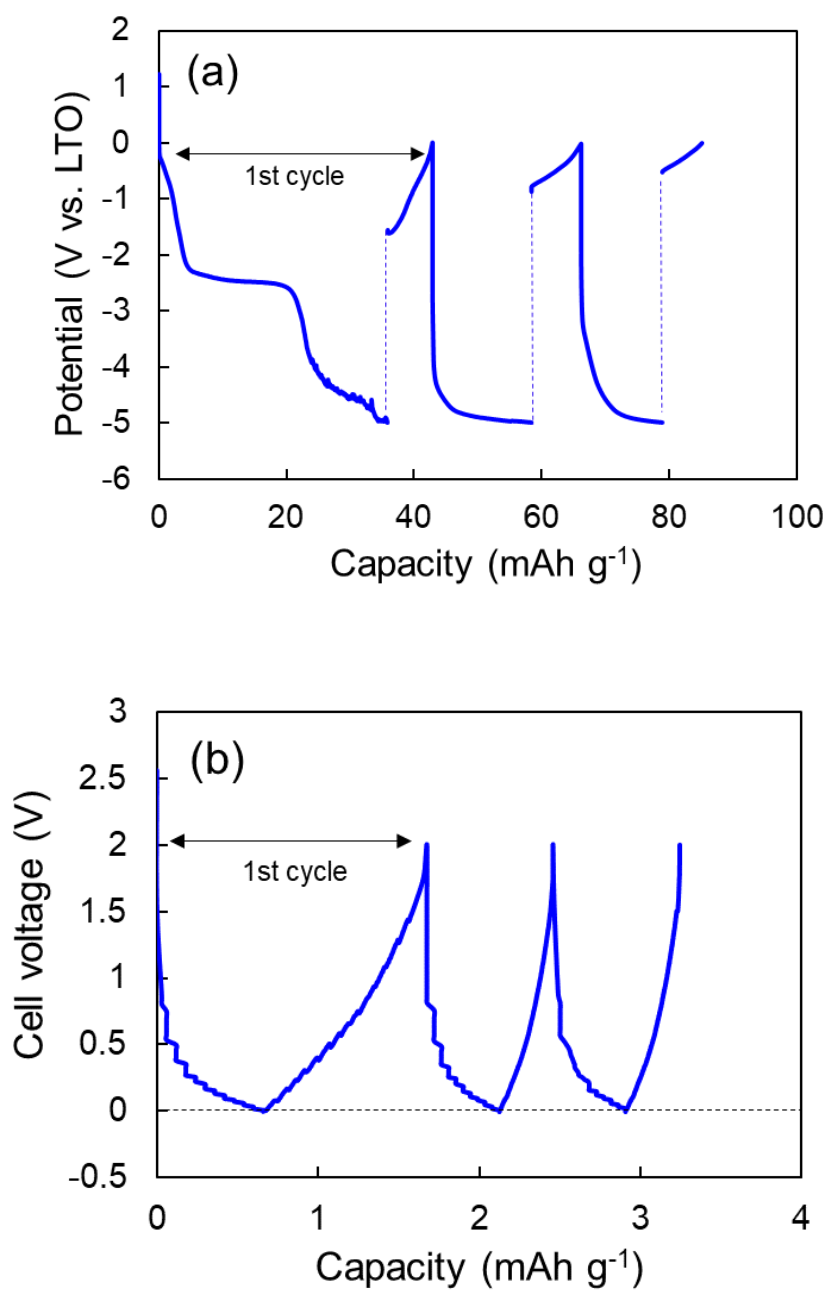
	$\text{Y}_2\text{O}_3$	$\text{Li}_{1.5}\text{Y}_2\text{O}_3$
Y	2.14	1.62
O	-1.43	-1.52
Li	—	0.85



### 3.4. Charge-discharge curves for the Cu+Y<sub>2</sub>O<sub>3</sub> cells

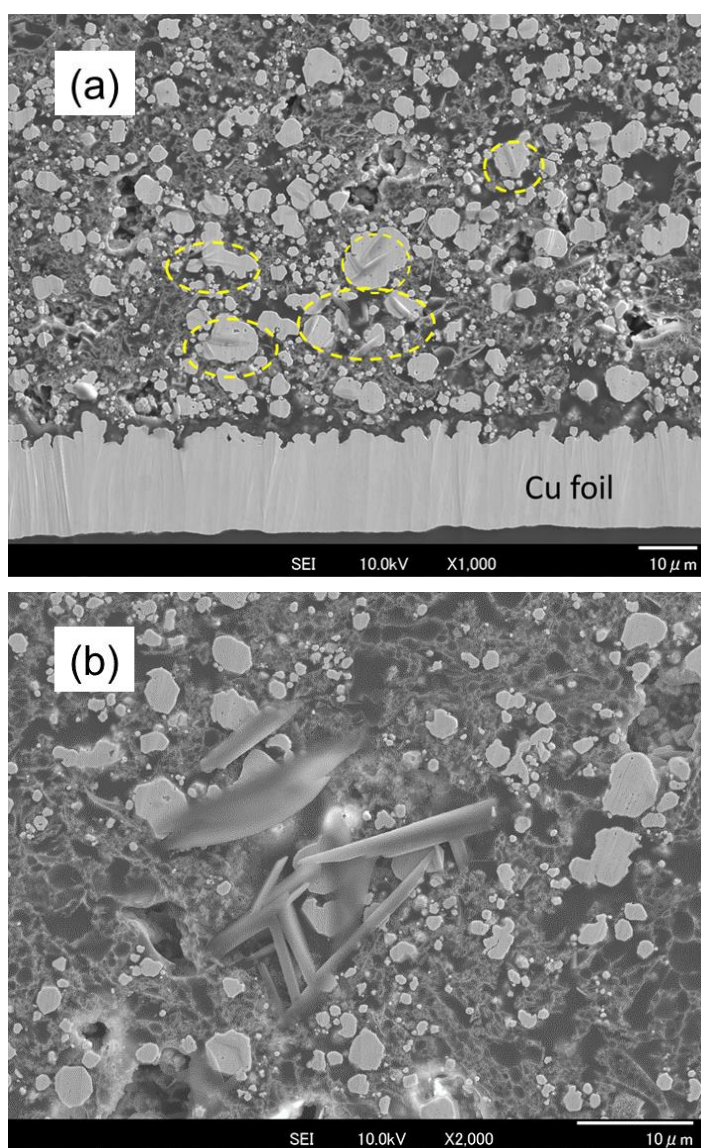


**Figure S10.** Charge/discharge curves for Cu+Y<sub>2</sub>O<sub>3</sub> cells using Li metal electrode between (a) -5 V - 0V, and (b) 0 V - +2 V.



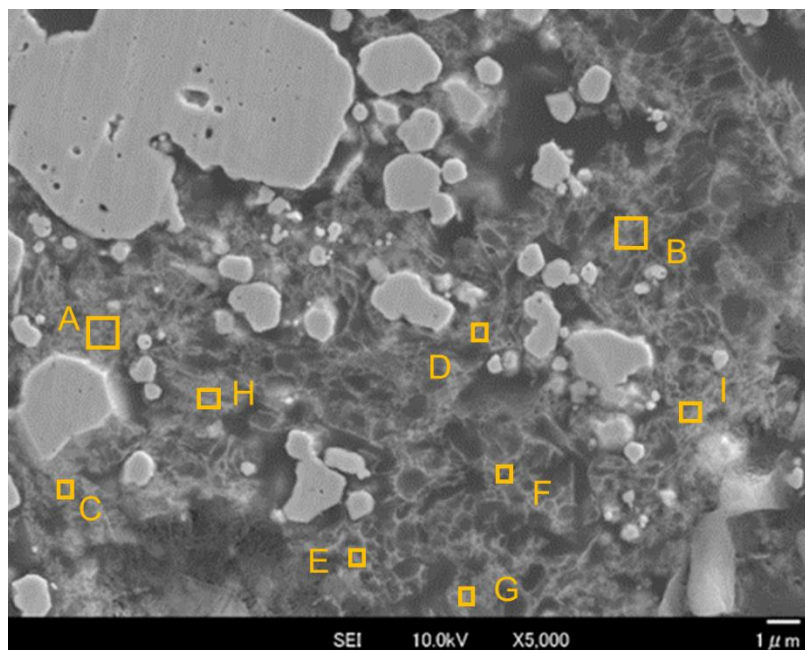
**Figure S11.** Charge/discharge curves for Cu+Y<sub>2</sub>O<sub>3</sub> cells using Li-doped LTO (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) electrode between (a) -5 V - 0V, and (b) 0 V - +2V.

### 3.5. FE-SEM images



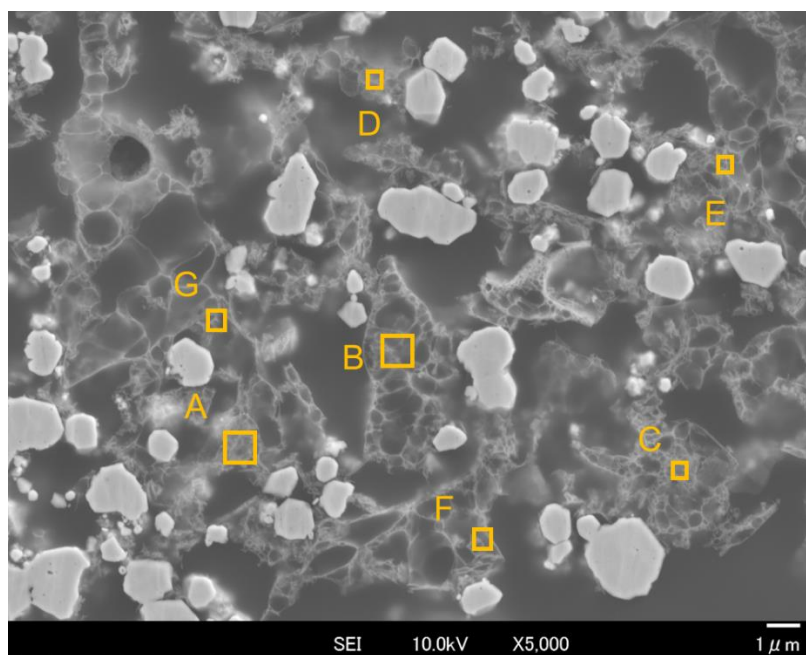
**Figure S12.** FE-SEM images of electrodeposited metallic lithium at (a) 1000x, and (b) 2000x magnification.

### 3.6. EDX results



	C	O	F	Cu	Y	Y/O
A	63.7	9.6	4.1	6.4	16.2	1.688
B	79.1	6.1	4.1	0.9	9.8	1.606
C	52.3	11.3	4	8	24.4	2.159
D	70.2	6.6	4.7	2.2	16.3	2.469
E	76.8	5.7	4.3	0.2	13	2.281
F	81.5	5.7	3.3	0.1	9.3	1.632
G	70.6	7	5.1	0.3	17	2.429
H	71.8	6.8	5	0.3	16	2.353
I	1	7.1	5.2	65.7	21	2.958

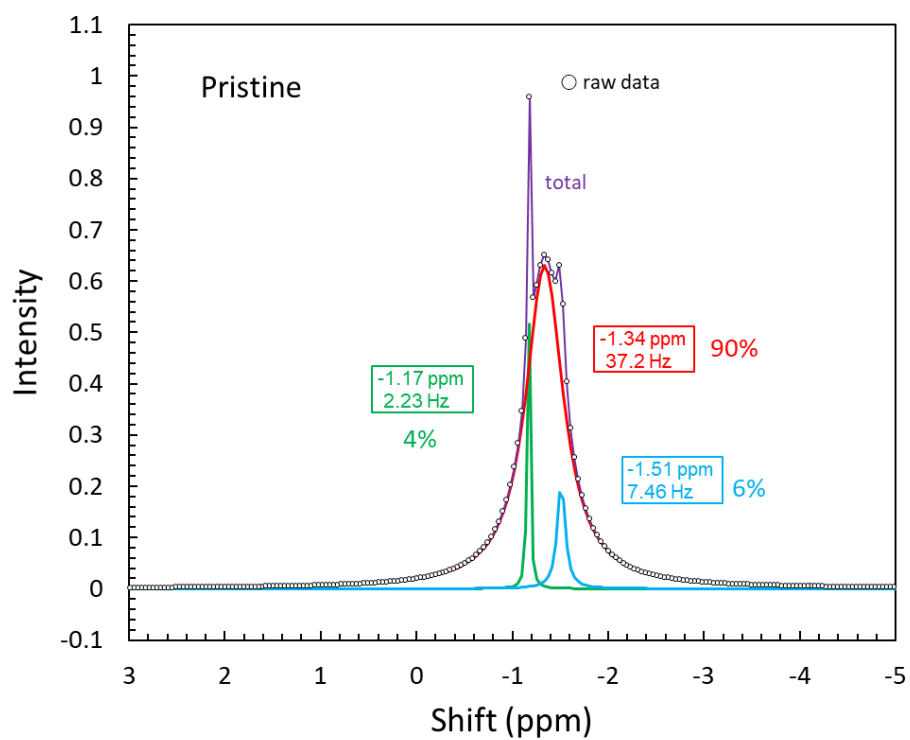
**Figure S13.** EDX measurement points on the Cu+Y<sub>2</sub>O<sub>3</sub> electrode after Li plating (top) and the EDX results (bottom).



	C	O	F	Cu	Y	Y/O
A	73.8	7.1	2.4	8.1	8.7	1.225
B	83.7	6.4	1.4	3.5	5	0.781
C	84.9	5.8	1.8	0.1	7.5	1.293
D	43.9	5.3	2.6	40.1	8	1.509
E	37.7	4	1.9	51.4	4.9	1.225
F	59.5	9.5	3.4	9.6	17	1.789
G	72.1	7.6	1.7	5.8	12.8	1.684

**Figure S14.** EDX measurement points on the Cu+Y<sub>2</sub>O<sub>3</sub> electrode before Li plating (top) and the EDX results (bottom).

### 3.7. $^7\text{Li}$ -NMR results



**Figure S15.** Waveform separation results for the region near 0 ppm in the  $^7\text{Li}$ -NMR spectrum of a  $\text{Cu}+\text{Y}_2\text{O}_3$  electrode before Li plating.