## Electronic Supplementary Information

## Interconnected LiCuVO<sub>4</sub> Networks with *In-Situ* Cu Generation

## as High-Performance Lithium-Ion Battery Anode

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Fig. S1 Schematic illustration for the fabrication of interconnected LiCuVO<sub>4</sub> networks.



Fig. S2 TG curve of I-LCVO after calcination.



Fig. S3 SEM images of (a) I-LCVO, (b) A-LCVO before calcination.



Fig. S4 (a, b) SEM images, (c) TEM image, (d) HRTEM image of A-LCVO.



Fig. S5  $N_2$  adsorption/desorption isotherms and pore size distributions of (a) I-LCVO, (b) A-LCVO.



Fig. S6 SEM images of LiCuVO<sub>4</sub> with different amounts of CTAB: (a) 0.1 g, (b) 0.2 g, (c) 0.4 g and (d) 0.8 g.



Fig. S7 (a) CV curves of A-LCVO obtained in a voltage range of 0.01 to 3.0 V (*vs.* Li<sup>+</sup>/Li) at a scan rate of 0.1 mV s<sup>-1</sup>. (b) Representative galvanostatic charge/discharge profiles of A-LCVO at 0.1 A g<sup>-1</sup>.



Fig. S8 Cycling performances of I-LCVO and A-LCVO at (a) 0.5 A g<sup>-1</sup>, (b) 1 A g<sup>-1</sup>.



**Fig. S9** (a) The cycling performance and its corresponding Coulombic efficiency of I-LCVO in an I-LCVO/LiFePO<sub>4</sub> full cell; (b) galvanostatic charge/discharge curves of an I-LCVO/LiFePO<sub>4</sub> full cell.



**Fig. S10** TEM images of (a) the pristine I-LCVO, (b) discharged to 0.01 V, (c) recharged to 3.0 V. SAED patterns of I-LCVO (d) discharged to 0.01 V, (e) recharged to 3.0 V.



**Fig. S11** (a-b) *Ex-situ* SEM images, (c-d) *ex-situ* TEM images of I-LCVO collected after 10 cycles at 0.1 A  $g^{-1}$ . (e-h) EDS mapping images of the Cu, V and O elements for the electrode after 5000 cycles at a current density of 5 A  $g^{-1}$ .



Fig. S12 CV curves of A-LCVO at various scan rates from (a) 0.1 to 1 mV s<sup>-1</sup>. (b) 2 to 20 mV s<sup>-1</sup>.

Sample	Mass	Element	Molar ratio
1	0.262g	Cu	1.02
		V	1
2	0.254g	Cu	1.03
		V	1

Table S1 The molar ratios of Cu and V in I-LCVO and A-LCVO.