Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2019

Electronic Supplementary Information

Synthesis and Characterization of a Hierarchically Structured Three-Dimensional Conducting Scaffold for Highly Stable Li Metal Anodes

Ji Young Kim,[ac] Guicheng Liu,*[ad] Minh Xuan Tran,[ab] Ryanda Enggar Anugrah Ardhi,[ab] Hansung Kim,[c] and Joong Kee Lee*[ab]

[a] Center for Energy Storage Research, Clean Energy Institute, Korea Institute of Science and Technology, Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea

[b] Department of Energy and Environment Engineering, KIST School, Korea University of Science and Technology, Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea

[c] Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

[d] Department of Physics, Dongguk University, 30 Pildong-ro 1-gil, Jangchung-dong, Jung-gu, Seoul 04620, Republic of Korea

This file contains Supplementary Figures S1-S12 and Tables S1-S6.

*Corresponding authors: log67@163com, liuguicheng@dongguk.edu (G. Liu);
leejk@kist.re.kr (J. K. Lee)

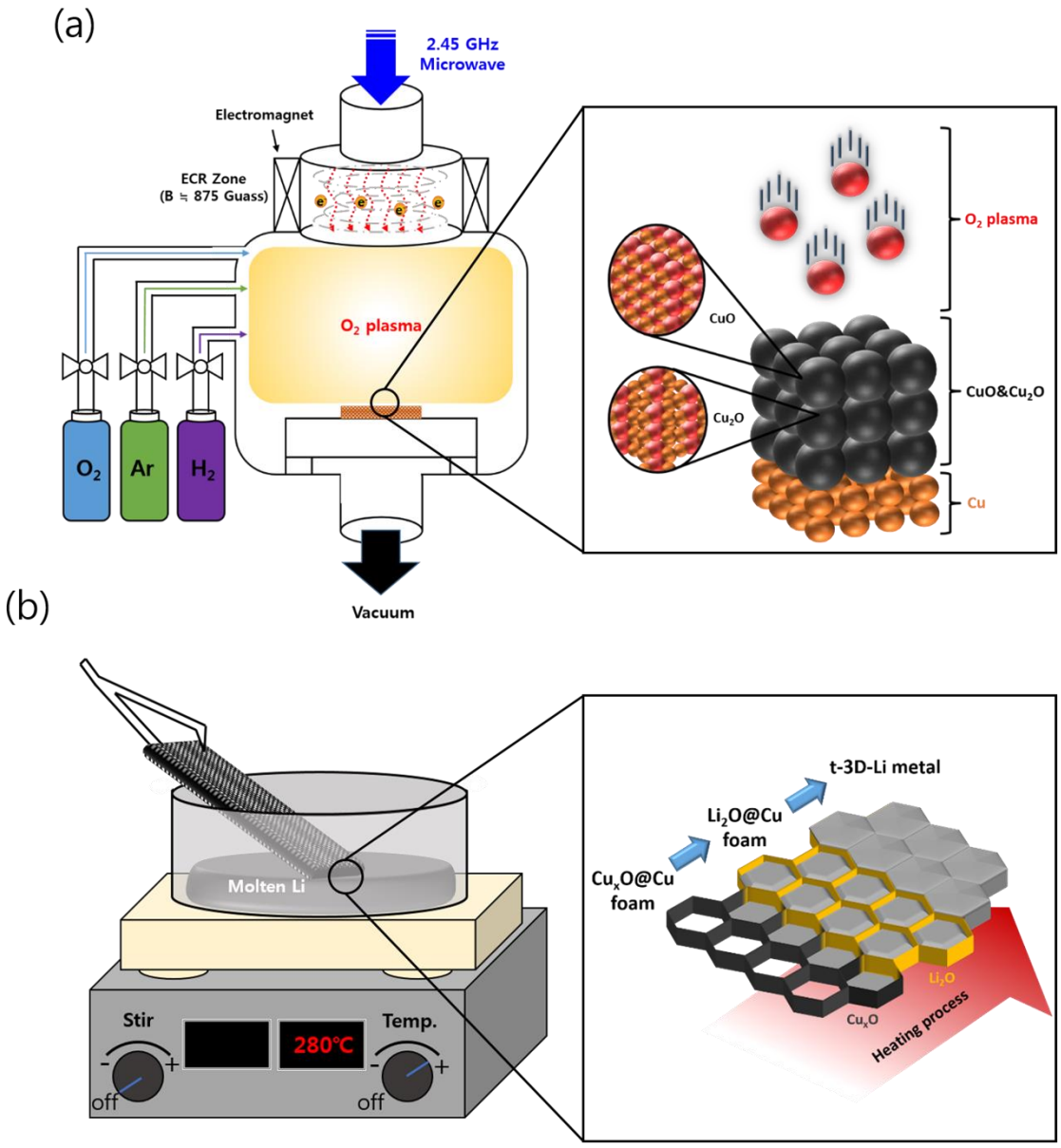

Figure S1. Schematic illustration of (a) ECR plasma oxidation used to prepare Cu_xO@Cu foam and (b) the fabrication of the t-3D-Li metal electrode.

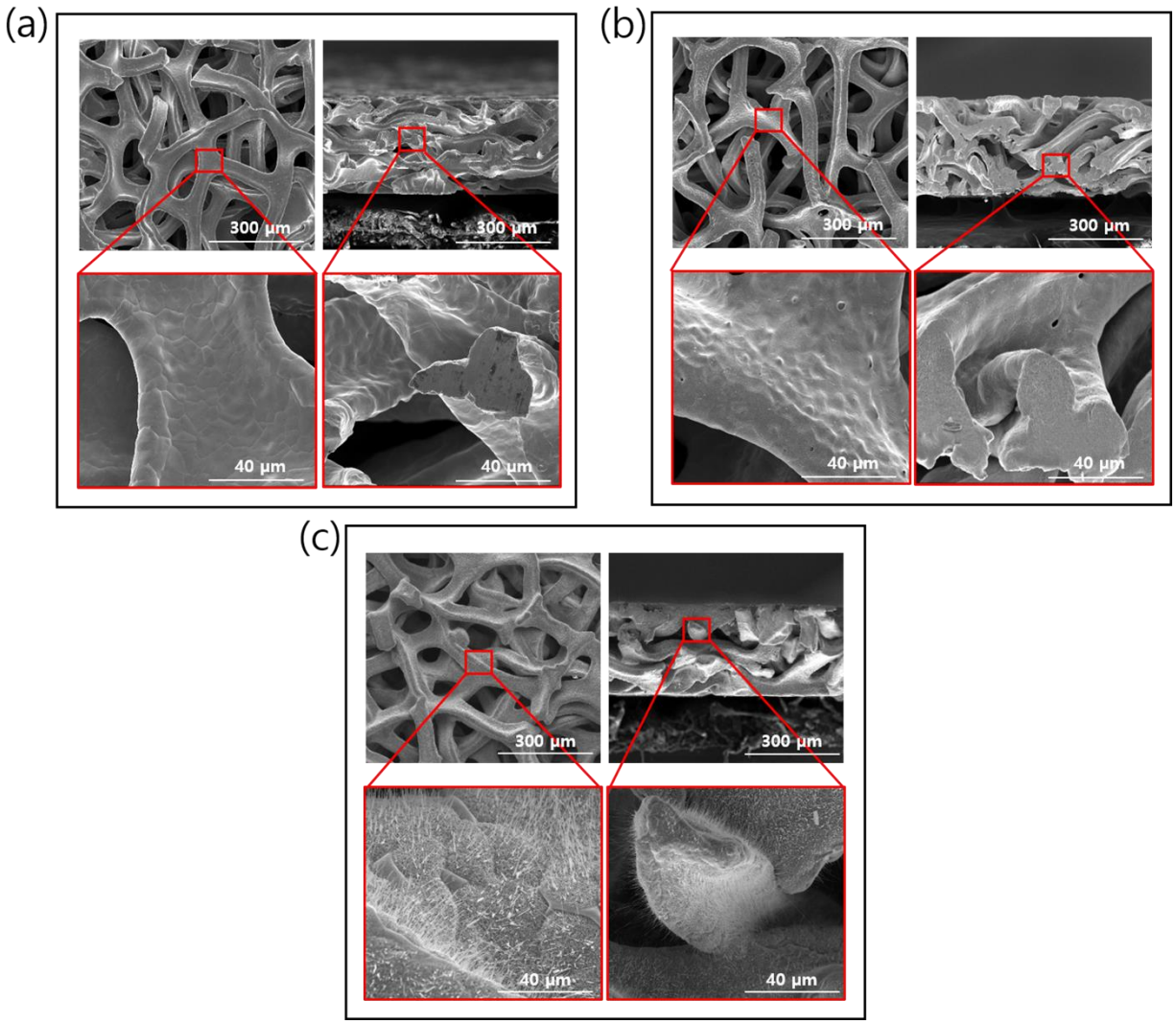

Figure S2. Top-view and cross-sectional images of Cu foam subjected to different surface treatments: (a) pristine Cu foam; Cu_xO@Cu foam prepared by (b) ECR O_2 plasma treatment and (c) heat treatment.

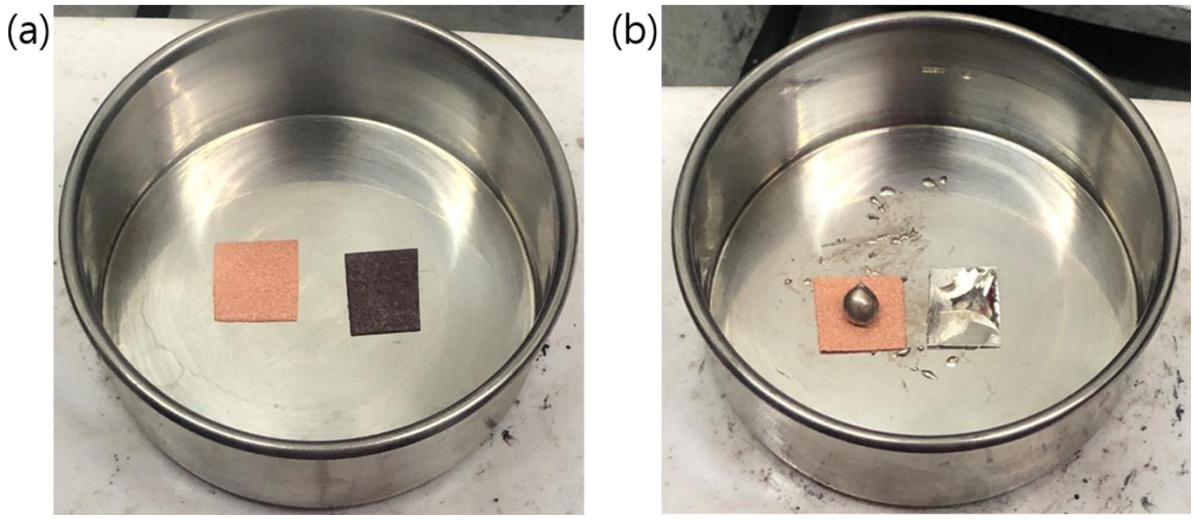

Figure S3. Photographs of Cu foam and Cu_xO@Cu foam (a) before and (b) after Li impregnation at 280 °C.

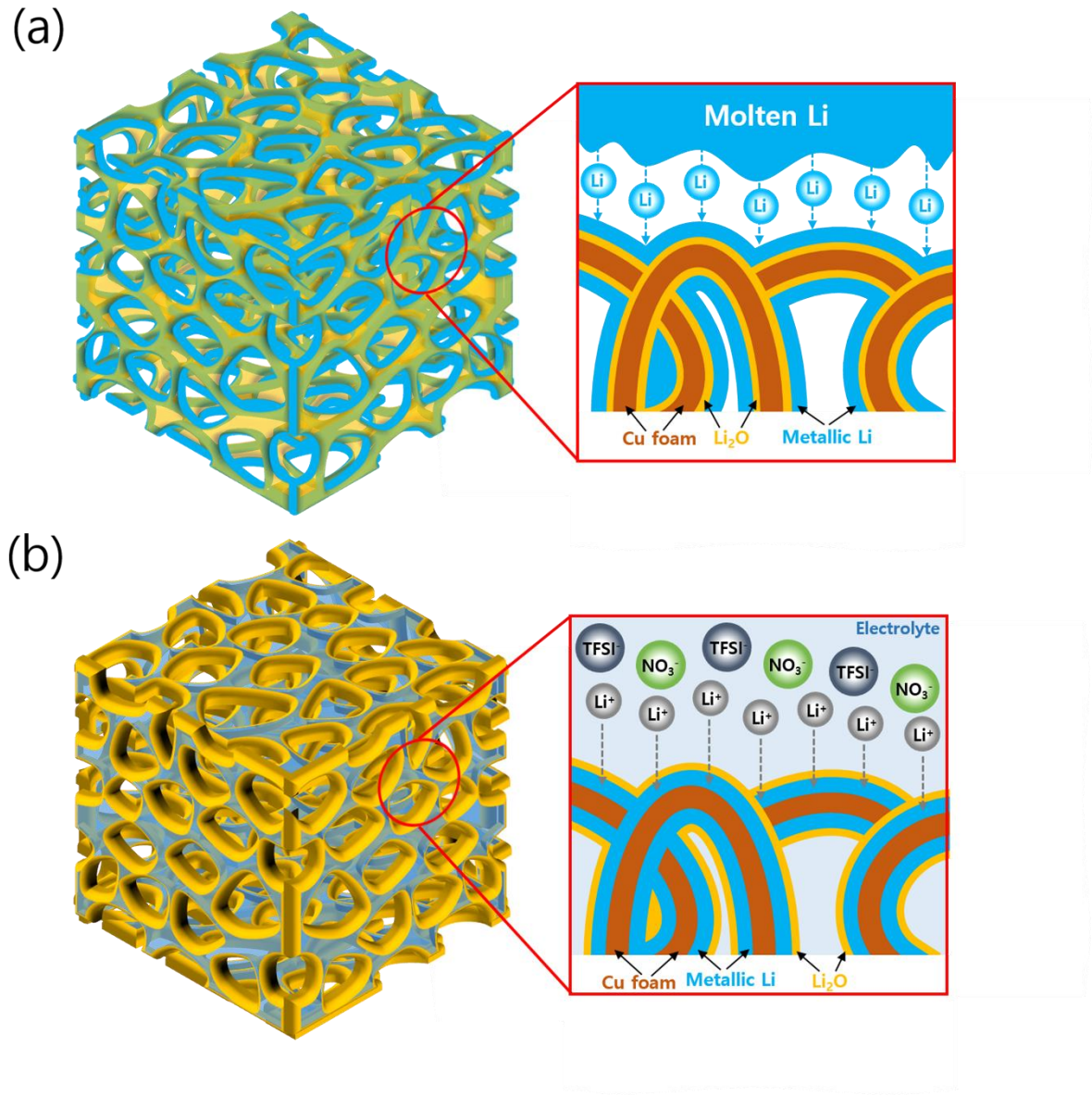

Figure S4. Detailed hierarchical structures of (a) t-3D-Li metal and (b) e-3D-Li metal anodes.

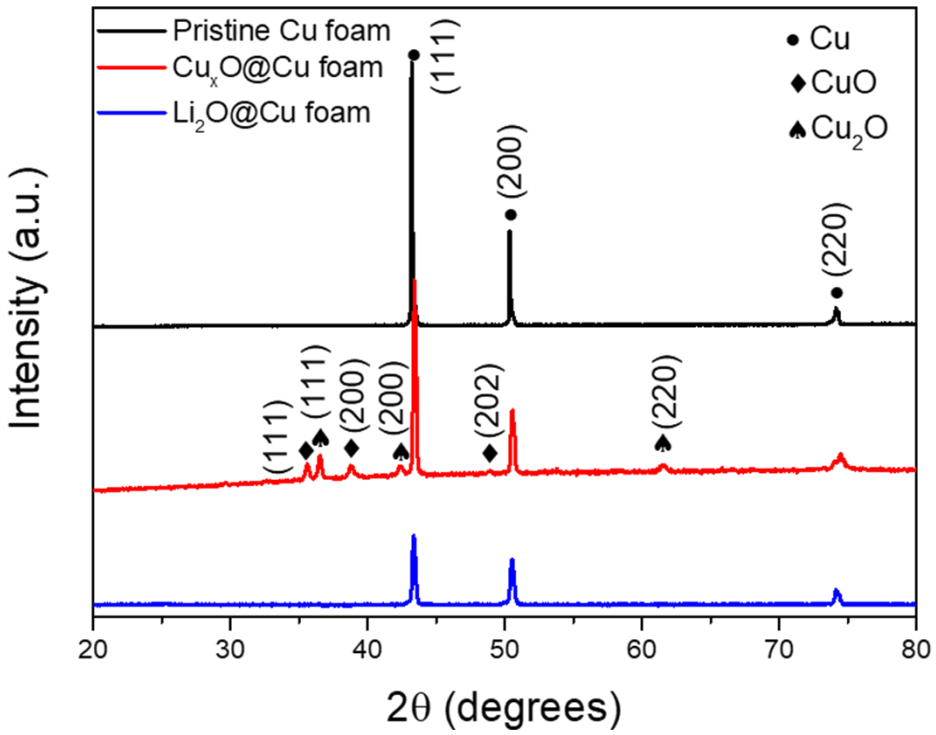

Figure S5. XRD patterns of pristine Cu foam, Cu_xO@Cu foam, and Li_2O@Cu foam.

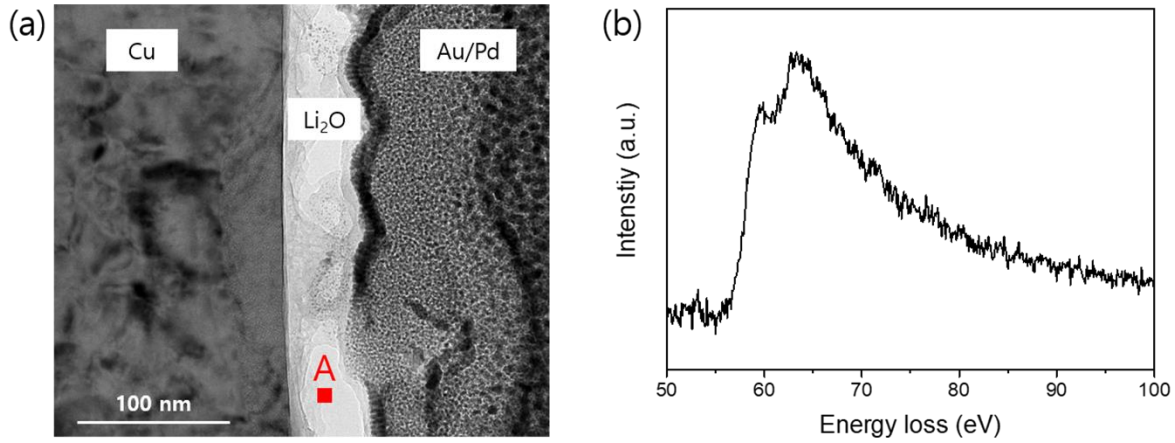

Figure S6. (a) HAADF-STEM images of Li_2O@Cu and (b) EELS analysis of the Li-K edge. (Note: The specimen was sputter-coated with Au/Pd to avoid damage and surface charge under the Ga^+ ion beam.)

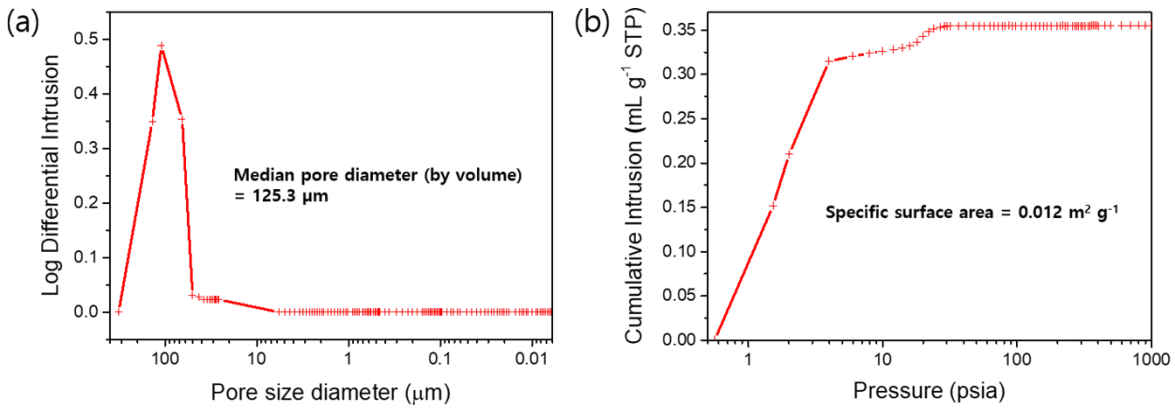

Figure S7. (a) Pore size distribution and (b) intrusion curve of Cu foam determined by Hg porosimetry.

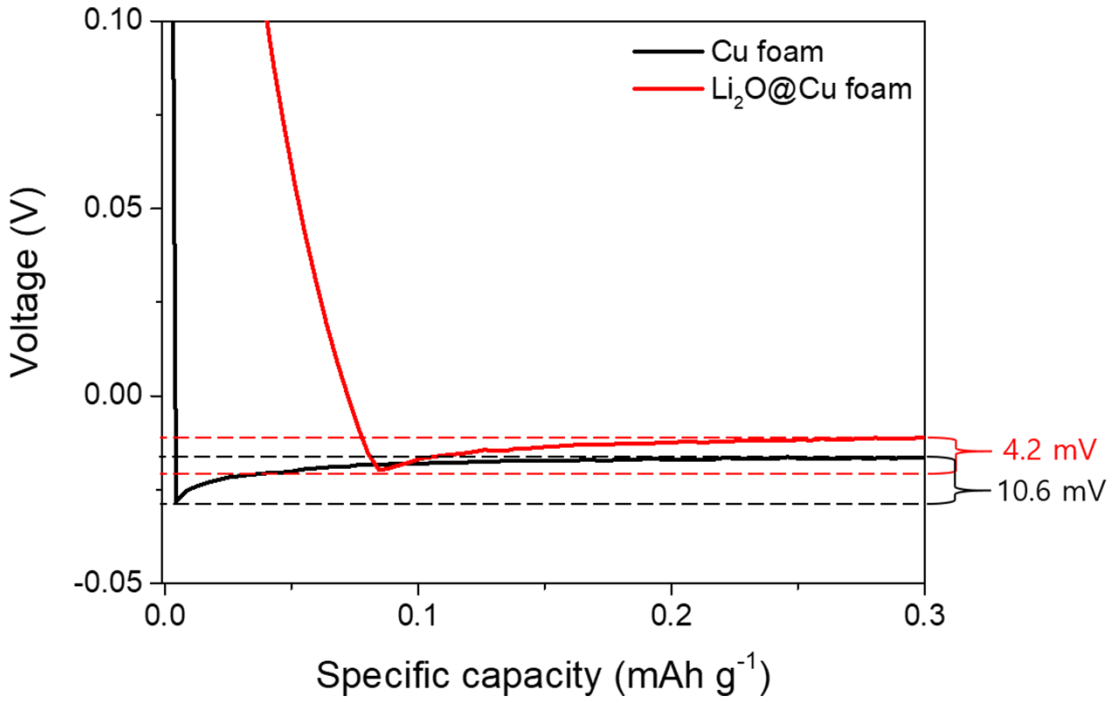

Figure S8. Voltage profiles of Cu foam and Li_2O@Cu foam recorded at a current density of 0.5 mA cm^{-2}.

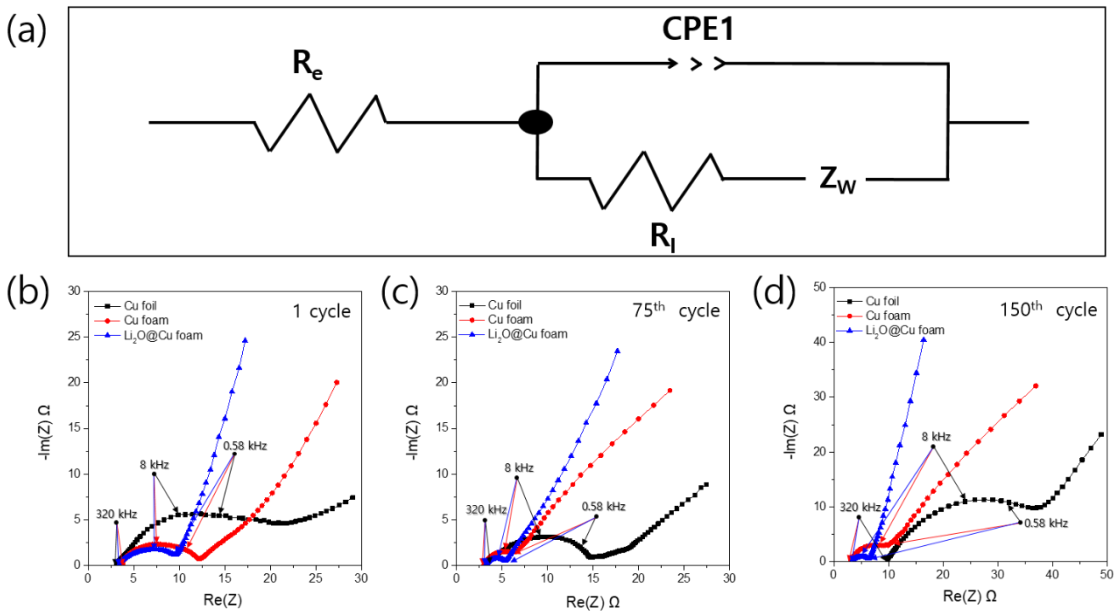

Figure S9. (a) Equivalent circuit curve for Nyquist plots of Li/Cu cells. (b, c, d) The corresponding Nyquist plots with frequency information at different cycle.

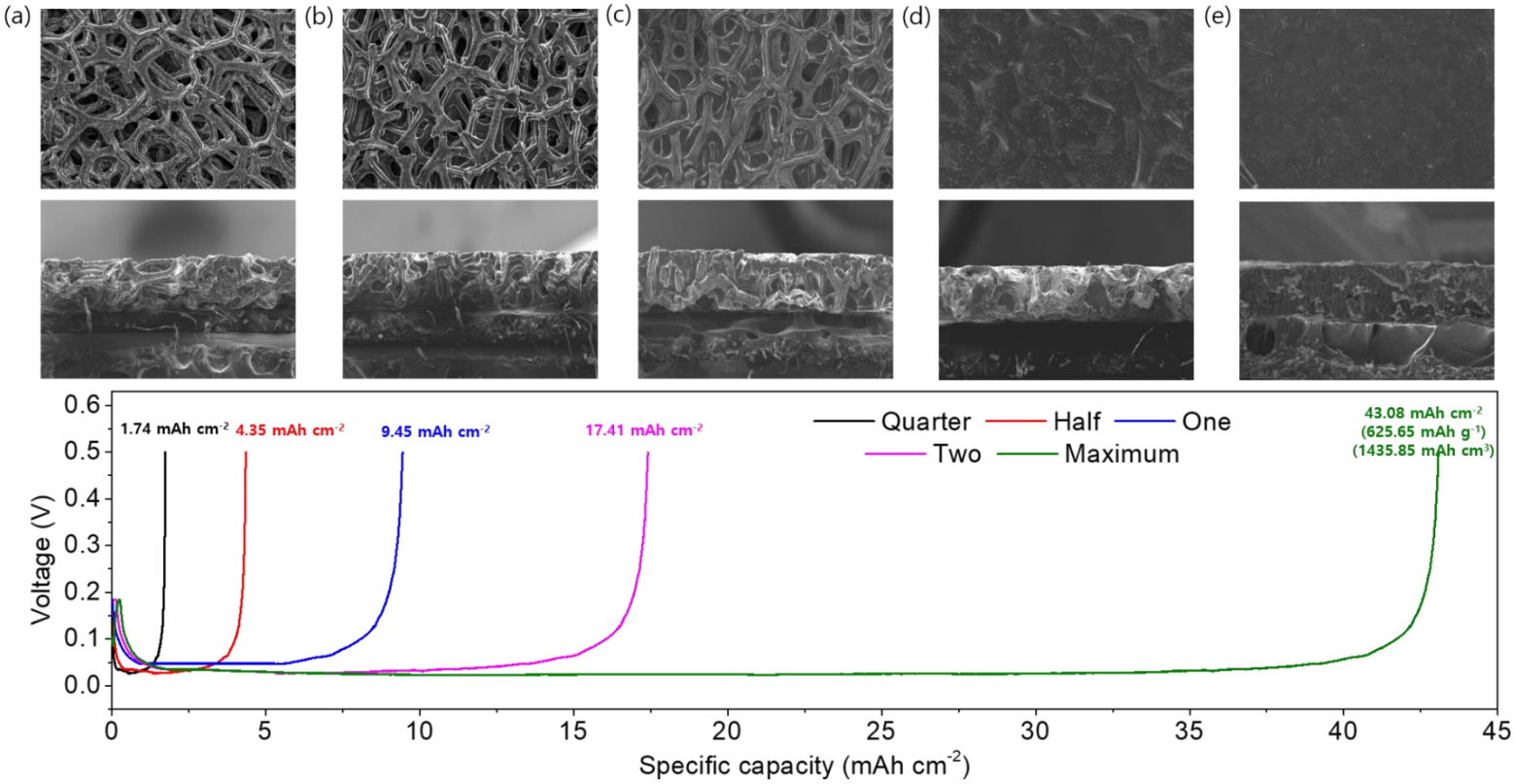

Figure S10. Top-view and cross-sectional images of t-3D-Li metal electrodes with different amounts of impregnated molten Li (measured in multiples/fractions of one bare Li foil with a diameter of 12 mm (0.03 g)). Images of Li_2O@Cu foam impregnated using (a) one quarter, (b) one half, (c) one, (d) two Li foils and (e) excess Li. The Cu_xO@Cu foam sample had a width and length of 2 cm and a thickness of 300 µm. The cutoff voltage was set at 0.5 V. (Note: The gravimetric and volumetric capacity calculated by total weight and volume of t-3D-Li metal including the Cu foam exhibit specific capacities of 625.65 mAh g^{-1} and 1,435.85 mAh cm^{-3}, respectively, shown in the green curve. Comparing theoretical capacity of pristine Li metal (2,061 mAh cm^{-3}) with the volumetric capacity of the excessive Li impregnated t-3D-Li metal (1,435.85 mAh cm^{-3}), we can know that the porosity of the Cu foam is 69.6%. As a standard areal capacity for electrochemial test, The areal capacity of 1.0 mAh cm^{-2} is corresponding to volumetric capacity of 33.33 mAh cm^{-3} owing to the thickness of Cu foam (here, i.e. 300 µm). Therefore, the volumetric capacity of 33.33 mAh cm^{-3} matches with pore occupation of 2.32% of the t-3D-Li metal.)

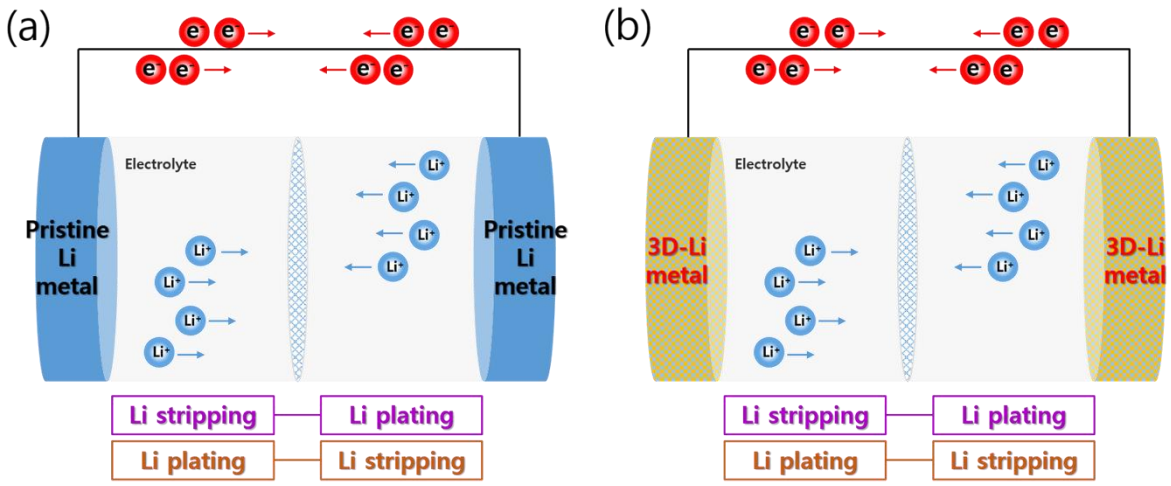

Figure S11. Configuration of the symmetric cell with (a) pristine Li and (b) 3D-Li metal for galvanostatic cycling.

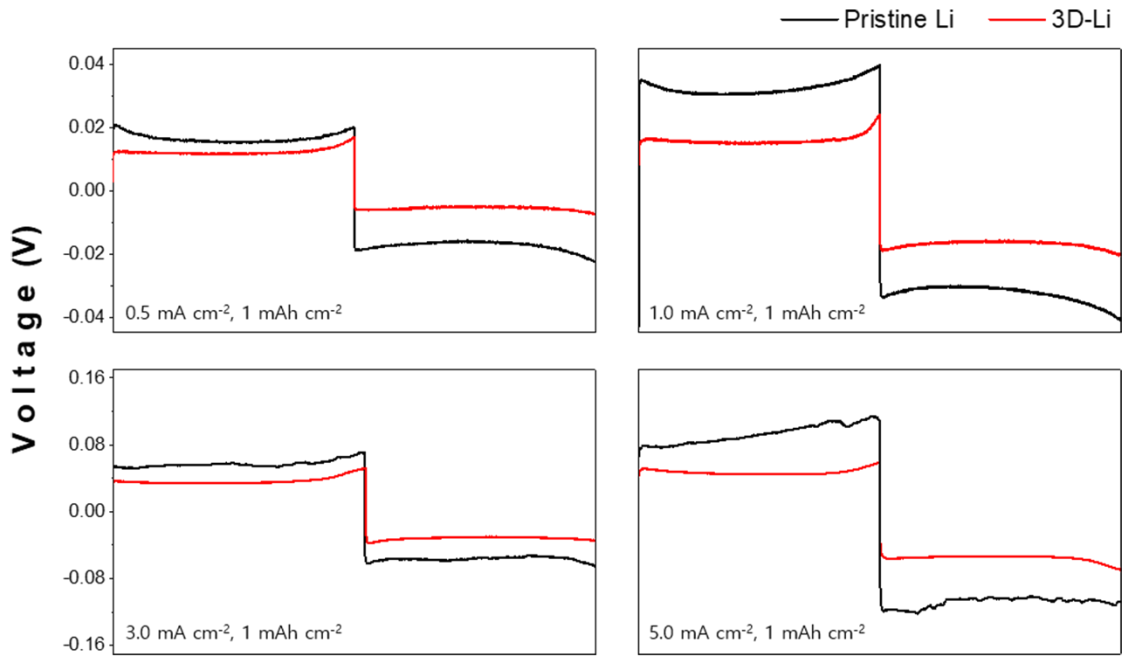

Figure S12. Expanded voltage profiles (corresponding to blue dashed rectangles in Fig. 7) of symmetric cells comprising pristine Li and 3D-Li metal electrodes.

Table S1. Inherent coefficients of each materials for Shomate equation.

(550K)	Cu	Li_2O	Cu_2O	CuO	Molten Li
A	17.72891	68.6971	59.42033	48.56494	32.46972
B	28.0987	5.467149	37.84767	7.498607	-2.635975
C	-31.25289	23.18308	-26.45083	-0.05598	-6.327128
D	13.97243	-9.495631	11.07609	0.013851	4.230359
E	0.068611	-1.60244	-0.54218	-0.760082	0.005686
F	-6.056591	-625.0352	-191.7109	-173.4272	-7.117319
G	47.89592	109.3928	151.0177	94.85128	74.29361
H	0	-598.7304	-170.7072	-156.0632	2.380002

Table S2. Thermodynamic parameters of each materials calculated by Shomate equation.

	Enthalpy (H, kJ/mol)	Entropy (S, J/mol·K)	Gibbs free energy (G_{550K}, kJ/mol)
Cu	6.4059	48.9125	-20.4960
Li_2O	-544.4125	71.6612	-583.8268
O_2	7.6507	223.6550	-115.3596
Cu_2O	-151.4258	132.0277	-224.0410
CuO	-145.4399	68.6776	-183.2126
Liquid Li	7.6979	52.7193	-21.2977

Table S3. The determination of the spontaneity of the three kinds of chemical reactions based on difference of difference of Gibbs free energy.

	Formula	$\triangle G_{Rxn} = \sum G_{550K}(products) - \sum G_{550K}(reactants)$	Value of $\triangle G_{Rxn}$
Rxn ①	$CuO + 2Liquid\ Li \rightarrow Cu + Li_2O$	$\triangle G_{Rxn} = [G(Cu)+G(Li_2O)]-[G(CuO)+2G(Liquid\ Li)]$	-378.5141
Rxn ②	$Cu_2O + 2Liquid\ Li \rightarrow 2Cu + Li_2O$	$\triangle G_{Rxn} = [2G(Cu)+G(Li_2O)]-[G(Cu_2O)+2G(Liquid\ Li)]$	-358.1817

The spontaneity of a chemical reaction can be generally determined from the corresponding change of Gibbs free energy. In turn, Gibbs free energy is defined as *H(T)* − *T* × *S(T)*, where *H* is enthalpy, *T* is absolute temperature, and *S* is entropy. The second law of thermodynamics implies that spontaneous phenomena are characterized by an increase of overall entropy (Δ*S* > 0), i.e., spontaneous reaction should feature negative changes of Gibbs free energy (Δ*G* < 0). To determine the Gibbs free energy of a certain material, one needs to know the corresponding enthalpy and entropy, which were herein calculated using the Shomate equation:[1]

① Enthalpy (*H*, kJ mol^{-1}): $\boldsymbol{H^{o}_{298.15} + A * t + \frac{Bt^2}{2} + \frac{Ct^3}{3} + \frac{Dt^4}{4} - \frac{E}{t} + F - H}$,

② Entropy (*S*, J mol^{-1} K^{-1}): $\boldsymbol{A * \ln t + Bt + \frac{Ct^2}{2} + \frac{Ct^3}{3} + \frac{E}{2t^2} + G}$,

where *t* is temperature (K) divided by 1000, the shomate parameters are listed in Table S1 using a symbol of *A, B, C, D, E, F, G and H.* The calculated thermodynamic parameters are listed in Table S2. The Δ*G* values under our experimental conditions (*T* = 550 K) were determined from the standard Gibbs free energies of each material. As shown in Table S3, Δ*G* for a chemical reaction was defined as the difference between the sum of Gibbs free energies of all products and that of all reactants. Both the reduction of Cu_xO (*x* = 1, 2) and the oxidation of molten Li were characterized by negative Δ*G* values and were therefore spontaneous.

Table S4. Electrochemical impedances simulated from equivalent circuit curve of Cu foil, Cu foam and Li_2O@Cu foam.

	Cu foil		Cu foam		Li_2O@Cu foam	
	R_e	R_l	R_e	R_l	R_e	R_l
1st	3.077	17.983	3.214	6.439	3.232	7.326
75th	3.328	11.17	3.183	3.295	3.016	2.272
150th	19.14	21.6	3.200	5.364	3.044	2.878

Table S5. The specific values of Coulombic efficiency for each Cu substrates at higher current density of 1.0, 3.0 and 5.0 mA cm^{-2}.

Cycle		1st	10th	20th	30th	40th	50th	60th	70th	80th	90th	100th
1.0 mA/cm^2	Cu foil	91.7 %	90.6 %	92.0 %	89.3 %	77.3 %	-	-	-	-	-	-
	Cu foam	94.0 %	97.4 %	98.7 %	98.3 %	98.8 %	98.6 %	98.4 %	96.8 %	81.5 %	-	-
	Li_2O @Cu foam	94.0 %	98.3%	99.4 %	99.6 %	99.3 %	99.1 %	99.2 %	99.2 %	99.0 %	98.8 %	99.0%

Cycle		1st	10th	20th	30th	40th	50th	60th	70th	80th	90th	100th
3.0 mA/cm^2	Cu foil	86.8 %	83.7 %	84.3 %	84.4 %	81.3 %	73.5 %	-	-	-	-	-
	Cu foam	84.1 %	96.6 %	97.3 %	97.4 %	97.4 %	96.9 %	93.2 %	86.9 %	77.1 %	-	-
	Li_2O @Cu foam	88.4 %	96.0%	98.2 %	97.5 %	97.5 %	98.2 %	97.5 %	97.0 %	96.6 %	97.5 %	97.5%

Cycle		1st	10th	20th	30th	40th	50th	60th	70th	80th	90th	100th
5.0 mA/cm^2	Cu foil	85.9 %	80.4 %	85.7 %	92.7 %	92.0 %	77.4 %	-	-	-	-	-
	Cu foam	85.0 %	96.8 %	93.3 %	89.3 %	91.3 %	96.3 %	96.9 %	94.9 %	84.4 %	-	-
	Li_2O @Cu foam	87.1 %	96.2 %	98.0 %	96.8 %	96.0 %	96.7 %	97.2 %	97.4 %	95.7 %	97.5 %	97.5%

Table S6. The comparison of Coulombic efficiency of porous current collector for Li metal anode with previous literatures

Porous scaffold	Lithiophilic agent	Current density (mA cm^{-2})	Capacity (mAh cm^{-2})	CE	Cycle	Reference
Cu foam	Li_2O	0.5	1.0	99.0 %	150	This work
		1.0		99.0 %	100	
		3.0		97.5 %	100	
		5.0		97.5 %	100	
Cu foam	- (Mechanical pressing)	0.5	1.0	93.8 %	100	[2]
Porous Cu foil	X (Not Li impregnated)	0.5	1.0	98.5 %	50	[3]
Porous Cu foil	X (Not Li impregnated)	0.5	1.0	97.0 %	250	[4]
		1.0			140	
Graphene flake	X (Not Li impregnated)	0.5	0.5	93.0 %	50	[5]
		2.0	1.0	90.0 %		
Cu nanowire film	X (Not Li impregnated)	1.0	2.0	98.6 %	200	[6]
Cu-CuO-Ni hybrid structure	CuO	3.0	0.5	90.0 %	100	[7]
Ni foam	- (Mechanical pressing)	1.0	1.0	85.0 %	100	[8]
Graphene@Ni foam	X (Not Li impregnated)	0.5	1.0	98.0 %	100	[9]
		1.0		92.0 %		
CuO nanosheets on Cu foil	CuO	0.5	1.0	94.0 %	180	[10]
		1.0				

References:

1 NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 2005, **20899** (http://webbook.nist.gov).

2 Q. Li, S. Zhu, Y. Lu, *Adv. Funct. Mater.* 2017, **27**, 1606422-1606429.

3 C.-P. Yang, Y.-X. Yin, S.-F. Zhang, N.-W. Li, Y.-G. Guo, *Nat. Commun.* 2015, **6**, 8058-8065.

4 Q. Yun, Y.-B. He, W. Lv, Y. Zhao, B. Li, F. Kang, Q.-H. Yang, *Adv. Mater.* 2016, **28**, 6932-6939.

5 R. Zhang, X.-B. Cheng, C.-Z. Zhao, H.-J. Peng, J.-L. Shi, J.-Q. Huang, J. Wang, F. Wei, Q. Zhang, *Adv. Mater.* 2016, **28**, 2155-2162.

6 L.-L. Lu, J. Ge, J.-N. Yang, S.-M. Chen, H.-B. Yao, F. Zhou, S.-H. Yu, *Nano Lett.* 2016, **16**, 4431-4437.

7 S. Wu, Z. Zhang, M. Lan, S. Yang, J. Cheng, J. Cai, J. Shen, Y. Zhu, K. Zhang, W. Zhang, *Adv. Mater.* 2018, **30**, 1705830-1705836.

8 S. S. Chi, Y. Liu, W. L. Song, L. Z. Fan, Q. Zhang, *Adv. Funct. Mater.* 2017, **27**, 1700348-1700357.

9 K. Xie, W. Wei, K. Yuan, W. Lu, M. Guo, Z. Li, Q. Song, X. Liu, J.-G. Wang, C. Shen, *ACS Appl. Mater. Interfaces* 2016, **8**, 26091-26097.

10 C. Zhang, W. Lv, G. Zhou, Z. Huang, Y. Zhang, R. Lyu, H. Wu, Q. Yun, F. Kang, Q.-H. Yang, *Adv. Energy Mater.* 2018, **8**, 1703404-1703411.