Supporting Information

Mitigating concentration polarization for highly-reversible plating/stripping electrochemistry: Li versus Na

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Table S1. The summarized cycling performances of Li|Cu half cells in the literatures.

References	Strategy	Cycling time / h	Efficiency / %	Current / mA cm^{-2}	Capacity / mAh cm^{-2}
Y. Cui et al, Nat. Nanotech. 2014, 9, 618.	A carbon film as the artificial SEI	300	97.5	1	1
Y. Cui et al, Nano lett. 2015, 15, 2910.	Polymer nanofiber current collector	240	97.9	1	1
J.G. Zhang et al, Nat. Commun. 2015, 6, 6362.	4 M LiFSI-DME	1000	98.5	1	1
Y. Cui et al, Nat. Commun. 2015, 6, 7436.	$LiNO_3$ and polysulfide additives	600	98.5	2	2
S. Yu et al, Nano lett. 2016, 16, 4431.	Copper Nanowire Network Current Collector	800	98.6	1	2
Q. Zhang et al, Angew. Chem. Int. Ed. 2017, 56, 7764	N-doped Graphene Current collector	400	98	1	1
Q. Zhang et al, Angew. Chem. Int. Ed. 2017, 56, 14207.	LiF-rich artificial SEI	480	98.7	0.5	1
D. Wang et al, Nat energy 2018, 3, 1076.	porous polyethylenimine sponge current collector	1600	99.1	2	2
Y. Guo et al, Adv. Mater. 2018, 30.	Nitrogen-Doped Graphitic Carbon Foams current collector	600	99.6	2	2
J. Lu et al, Adv. Energy Mater. 2018, 8, 1800266.	3D Copper current collector	400	97.9	1	1
H. Zhang et al, Adv. Funct. Mater. 2018, 28, 1804133.	Au Nanoparticles Pillared rGO current collector	1600	98	0.5	2

B.-W. Mao et al, Nat. Commun. 2018, 9, 1339.	Ultra-smooth ultra-thin SEI	200	99	2	1
Z. Wang et al, Nano Lett. 2019, 19, 494.	Carbon Nanotube Sponge current collector	400	~98.5	1	2
B.-W. Mao et al, Angew. Chem. Int. Ed. 2019, 58, 3092.	Faceted Cu current collector	400	99	2	1

Table S2. The summarized cycling performances of Na|Cu cells in the literatures.

References	Strategy	Cycling time / h	Efficiency / %	Current / mA cm^{-2}	Capacity / mAh cm^{-2}
Y. Cui et al, ACS central science 2015, 1,449.	1 M $NaPF_6$-diglyme	1200	99.9	0.5	1
J.-G. Zhang et al, Nano Energy 2016, 30, 825.	4 M NaFSI-DME	600	99	1	1
C. L. Pint et al, Nano lett. 2017, 17, 1296.	Al@C composite current collector	1000	99.8	0.5	0.25
J. Luo et al, Nano Lett. 2017, 17, 5862.	Porous Al current collector	1000	99.8	1	0.5
S.-A. Freunberger et al, chemsuschem, 2017, 10, 401.	Concentrated NaFSI electrolyte	1250	97.7	0.2	0.2
H. Wang et al, Angew. Chem. Int. Ed. 2018, 57, 9069.	1 M NaOTf-diglyme+ 0.01 M KTFSI	560	98.3	1	1
J.-G. Zhang et al, ACS Energy Lett. 2018,3,315.	Localized high concentration electrolyte(2.1 M NaFSI/DME-BTFE (1:2))	800	98.9	1	1
Y. S. Yun et al, Adv. Energy Mater. 2018, 8, 1701261	Macroporous catalytic carbon nanotemplate current collector	1150	99.9	1	0.5
B.-W. Mao et al, Nano energy, 2018,48,101.	Na-Au alloy-based sodiophilic layer	600	99.8	1	1
S.-L. Chou et al,	Li-Na hybrid	200	99.2	0.2	0.2

Angew. Chem. Int. Ed. 2018, 57, 14796.	batteries				
G.-X. Wang et al, Adv. Mater. 2018, 30, 1801334.	N and S co-doped CNT paper current collector	800	99.8	1	1
Z. Wang et al, ACS Appl. Mater. Interfaces. 2018, 10, 30417.	N and O Co-doped Graphitized Carbon Fibers current collector	960	99.8	1	8
Y.-S. Yun et al, ACS applied energy mater. 2018, 1, 1846	Sulfur-doped carbon Current collector	2400	99.8	2	1
B.-W. Mao et al, Adv. Mater. 2019, 31, e1807495.	In-situ alloy reaction formed sodiophilic interphase	2000	99.9	2	1

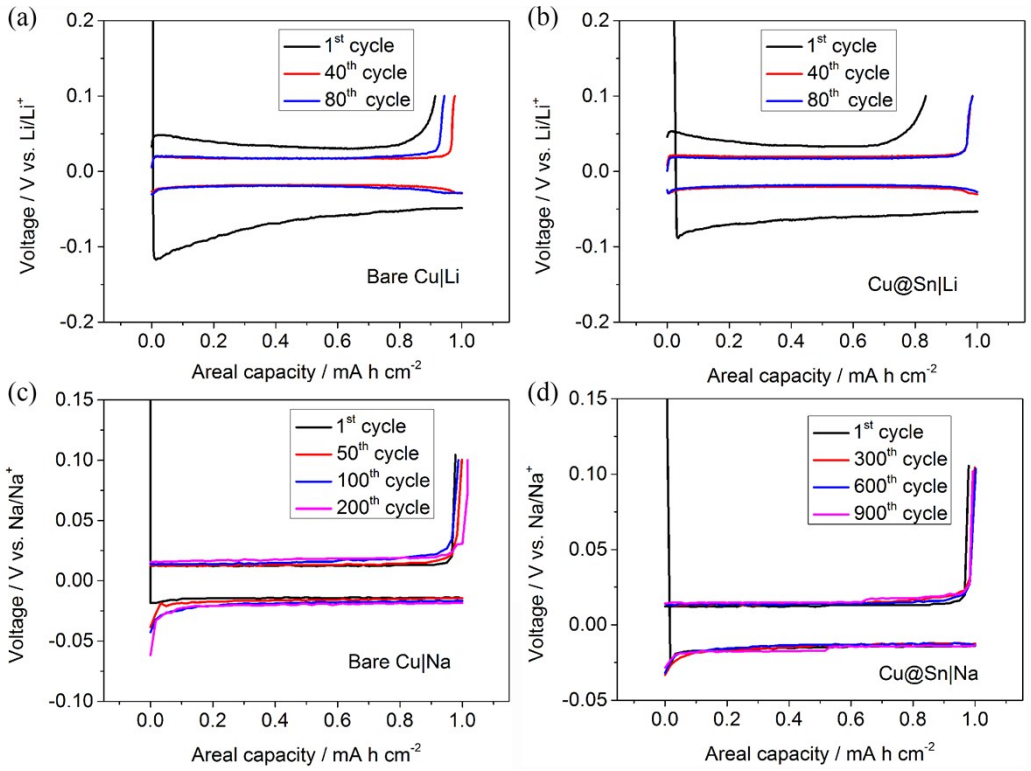

Figure S1. The voltage profiles of Li (a, b) and Na (c, d) plating/stripping cycles on Cu and Cu@Sn respectively. The electrolyte added was 25 μL for each cell.

Table S3. The elemental composition of the surface layer after 30 plating/stripping cycles of Li.

Elements	Weight ratio (%)	Atomic ratio (%)
C	7.30	10.21
N	16.18	19.40
O	48.86	51.29
F	16.92	14.95
S	5.66	2.96
Cu	3.76	0.99
Sn	1.33	0.19
Sum	100.00	100

Table S4. The elemental composition of the surface layer after 30 plating/stripping cycles of Na.

Elements	Weight ratio	Atomic ratio
C	2.88	9.37
N	3.50	9.77
O	5.52	13.51
F	1.80	3.72
Na	10.03	17.08
S	0.39	0.48
Cu	73.46	45.27
Sn	2.42	0.80
Sum	100.00	100

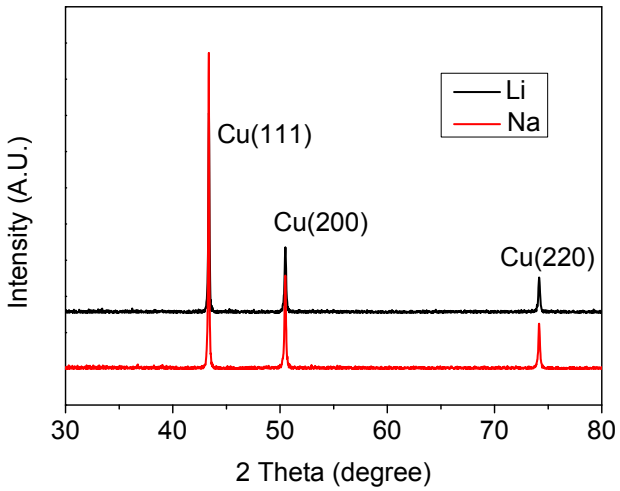

Figure S2. XRD patterns of the Cu@Sn electrodes in the stripped state after 30 cycles of Li and Na plating/stripping, respectively.

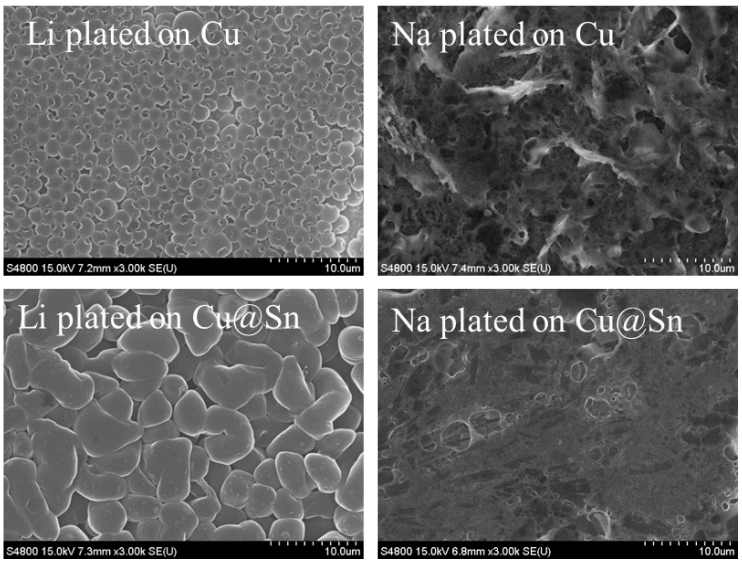

Figure S3. The 1st plated Li and Na on Cu and Cu@Sn electrodes, respectively. The current density is 1 mA cm^{-2} and the loading is 1 mA h cm^{-2}.

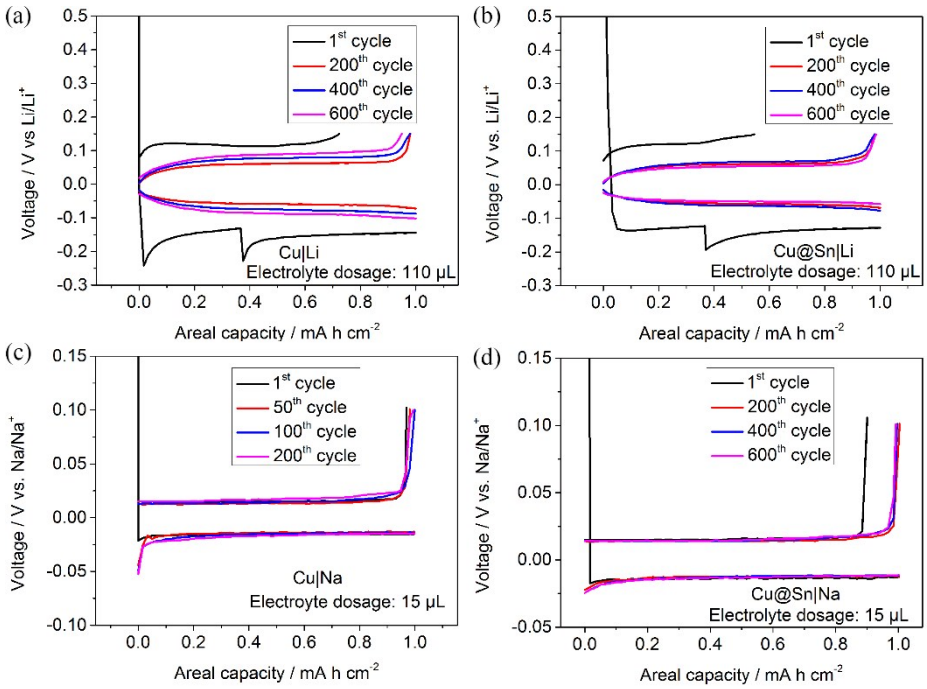

Figure S4. The voltage profiles of Li and Na plating/stripping cycles on Cu and Cu@Sn, respectively, with different electrolyte dosages.

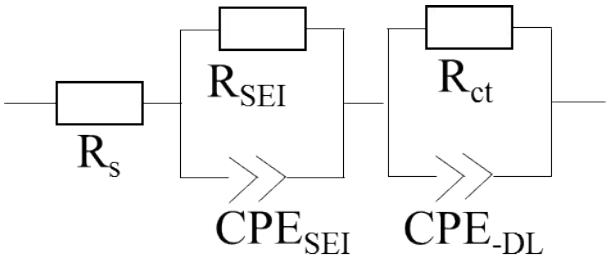

Figure S5. The equivalent circuit for the impedance spectra for the Cu@Sn|Li and Cu@Sn|Na cell with the working electrode plated with Li or Na metal of 1 mA h cm^{-2}.

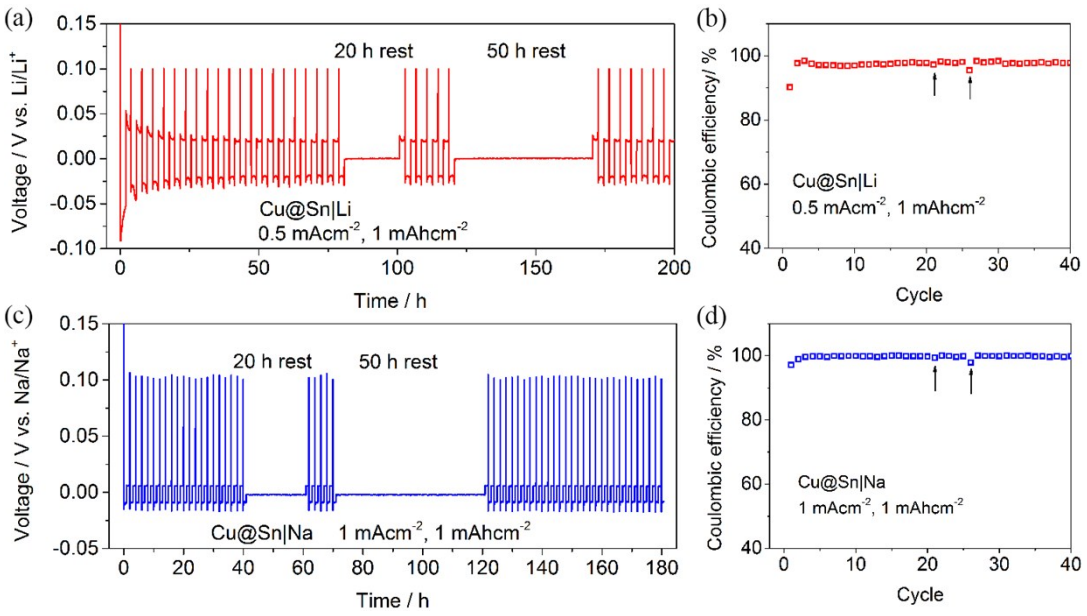

Figure S6. The voltage profiles (a, c) and Coulombic efficiencies (b, d) of Li and Na plating/stripping cycles with resting for 20 and 50 hours, respectively.

Table S5. The Binding energies between Li(Na) and different crystal facets of Cu.

Facet	E_b with Li (eV)	E_b with Na (eV)
Cu(100)	-1.872	-1.402
Cu(111)	-1.746	-1.379
Cu(110) (bridge site)	-1.720	-1.298
Cu(110) (hollow site)	-2.302	-1.706

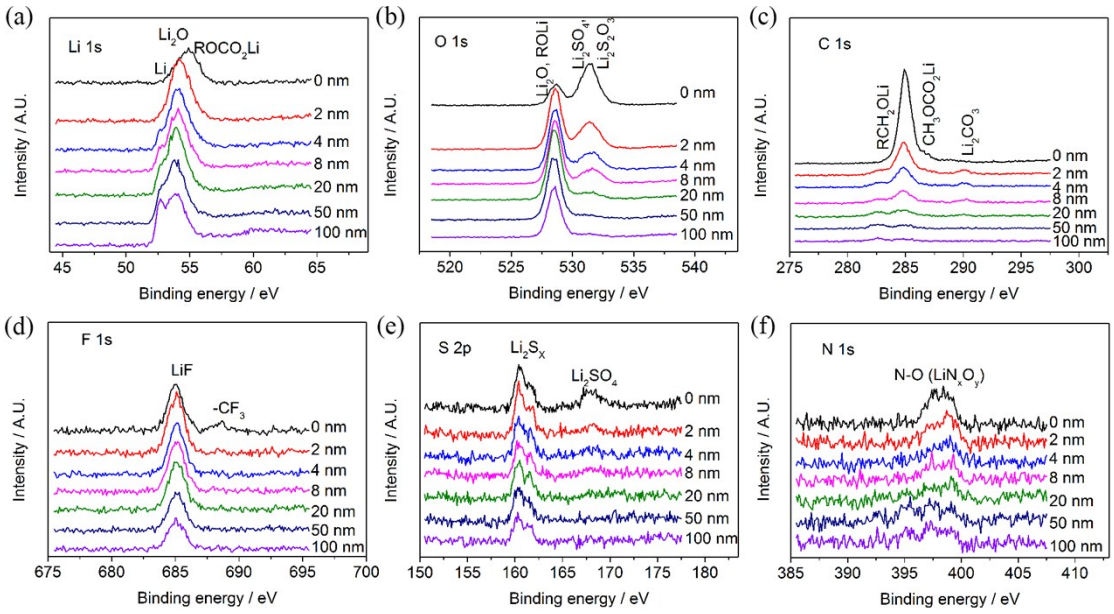

Figure S7. The XPS spectra of the SEI on the plated Li metal anode after 5 cycles.

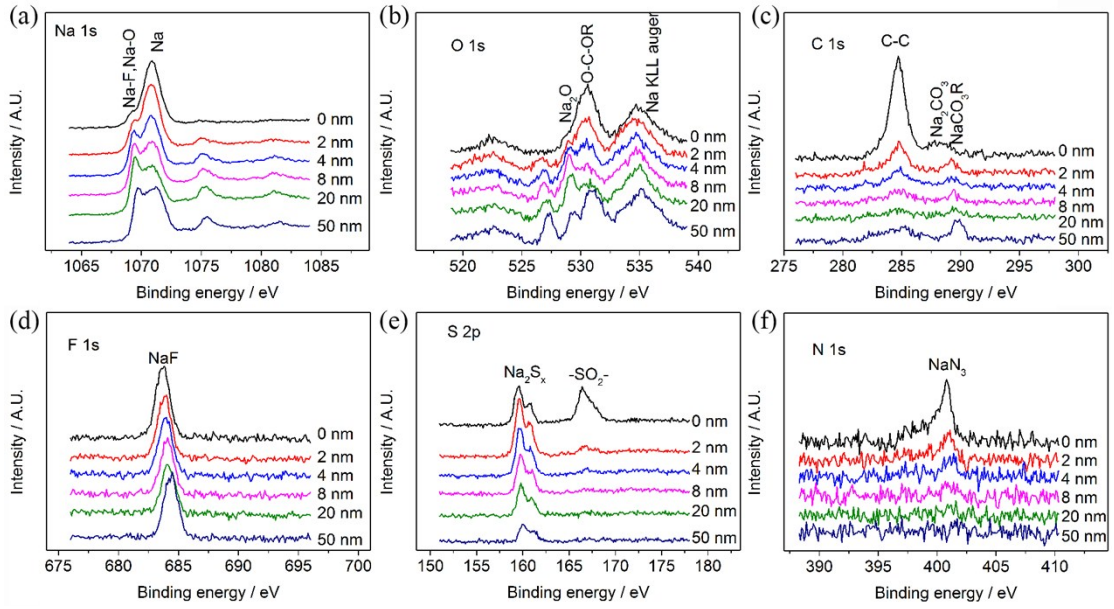

Figure S8. The XPS spectra of the SEI on the plated Na metal anode after 5 cycles.

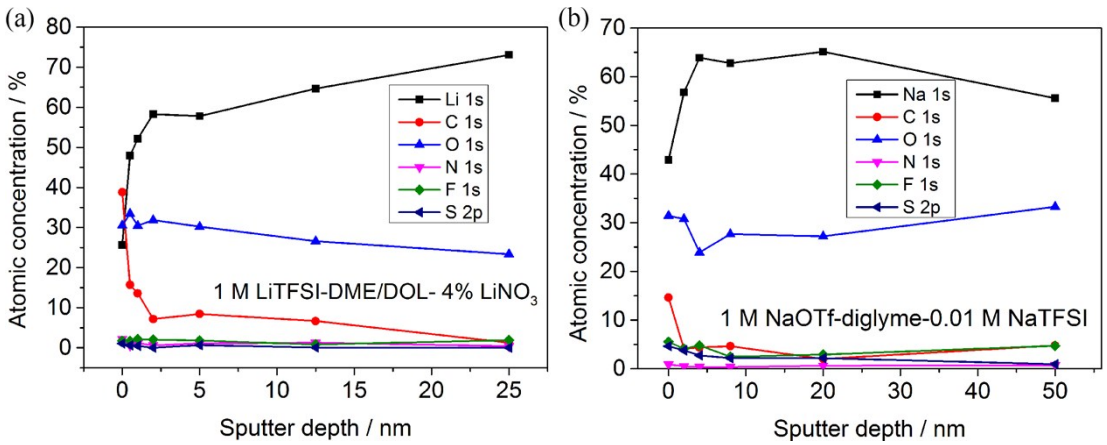

Figure S9. The elemental ratios at different depths of the SEI on Li (a) and Na (b). The depth is estimated according to the calibrated sputtering rate of 4 nm/min in SiO_2.

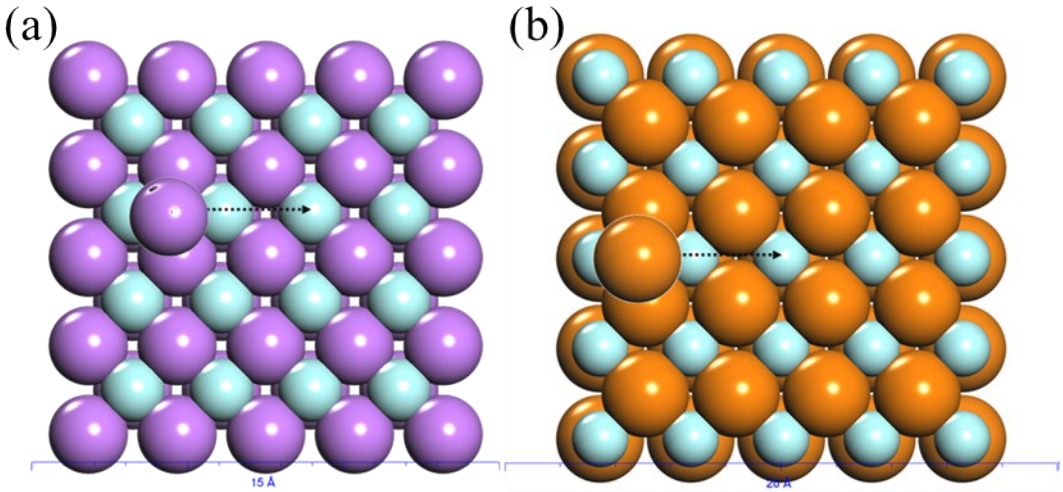

Figure S10. The calculated diffusion barriers for the Li (a) and Na (b) adatoms on LiF and NaF, respectively.

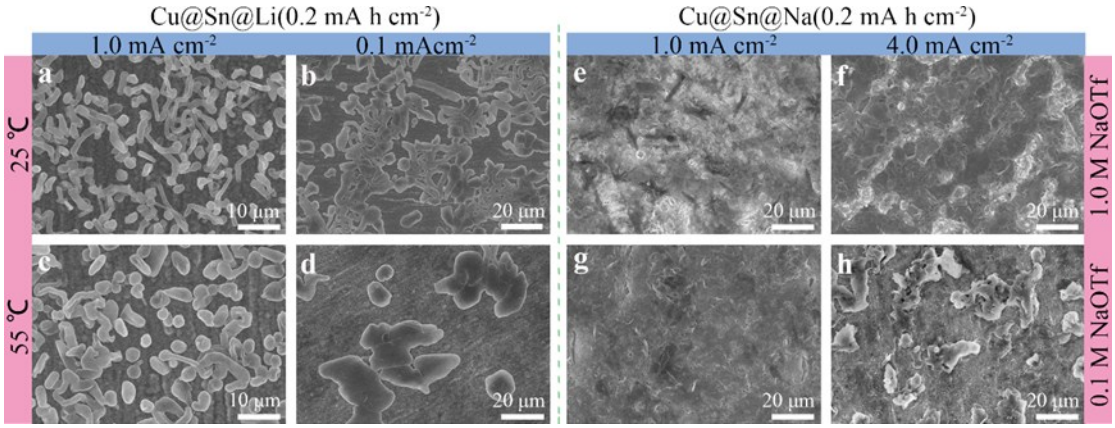

Figure S11. The SEM photos of plated Li (a~ d) on Cu@Sn at different temperatures and Na (e~ h) on Cu@Sn at different concentrations with various current densities and constant areal loading of 0.2 mA h cm^{-2}.

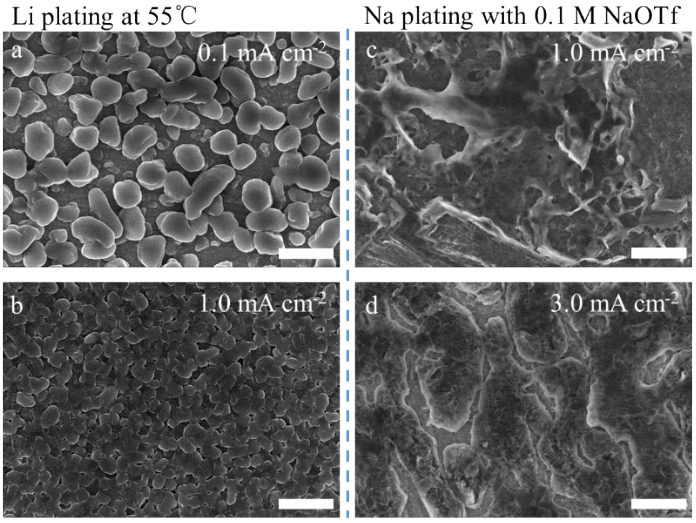

Fig. S12. The morphologies of plated Li and Na metals on the Cu@Sn electrodes with different conditions. The active loading of Li and Na metal on Cu@Sn electrodes is 1 mA h cm^{-2}. Scale bar: 20 μm.