Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Micron Zn-Modified Al Current Collector Inducing Uniform Sodium Nucleation for Anode-Free Sodium Batteries

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Experimental section

Material preparation: Micro Zn coating current collector (Zn@Al) was synthesized by chemical deposition. In a one-step process, pure Al foil (99.99%, T=0.2 mm, Co., Ltd., China) was immersed into 200 g/L NaOH solution containing 30 g/L ZnO, and underwent reaction at room temperature with different time of 1.0 min, 2.0 min and 3.0 min, which named Zn@Al-1, Zn@Al-2 and Zn@Al-3, respectively. Then, the Al foil after reaction was washed with deionized water three times and dried at 60 °C for 12 h to obtain Zn@Al.

Characterizations: The morphology of the electrode materials was characterized by scanning electron microscopy (SEM, Jeol JSM-IT700HR) operated at 15 kV and transmission electron microscopy (TEM, Oxford FEI Tecnai G2 F20) operated at 200 kV, and the corresponding elemental distribution was analyzed by the energy dispersive spectrometer (EDS, Oxford Xplore 30). The structural features of the electrode materials were measured by X-ray diffraction spectroscopy (XRD, MiniFlex600). The elemental composition of the samples was determined by X-ray photoelectron spectroscopy (XPS, PHI VersaProbe 4). An optical microscope (Phenix, BMC100-UA510CA) was used to in situ directly observe the deposition process of Na metal on different substrates in a home-made transparent cell.

Electrochemical measurements: CR2032 coin cells (Canrd Technology Co., Ltd., China) assembled in an Ar-filled glove box (Mikrouna) were used for electrochemical tests. The electrolyte was obtained by dissolving 0.9 M $NaPF_6$ (Macklin, battery grade) and 0.1 M $NaBF_4$ (Macklin, 99.99% metals basis) in diglyme (DoDoChem, battery grade). Celgard 2400 (PP) membrane was utilized as the separator. The half-cell was fabricated to investigate the behavior of the Na plating and stripping, using Zn@Al or Al foil (19 mm) and Na foil (16 mm, Canrd Technology Co. Ltd., China) as the working electrode and the counter/reference electrode, respectively with 90 μL of electrolyte. Cyclic voltammetry (CV) curves were test using a CHI660e electrochemical workstation at 0.1 mV/s from –0.05 to 0.20 V. $Na_3V_2(PO_4)_3$ (NVP, Neware Co., Ltd., China) electrode was prepared by coating the uniform slurry (80 wt% NVP, 10 wt% super P and 10 wt% PVDF in NMP) on the carbon coated Al foil, which was subsequently dried at 90 °C for 12 h in a vacuum oven and finally punched into disks with 12 mm in diameter. The mass loading of NVP electrode was about 10.0 mg cm^{-2}. For the full-cells, NVP electrode served as cathode and zero amount of Na deposited on the Zn@Al or Al foil electrode as anode. All cells were evaluated using a LAND battery test system (CT2001A) at 25°C.

Calculations: All the calculations were carried out with the Vienna Ab initio Simulation Package (VASP) which is based on the density functional theory (DFT) and the projector augmented wave (PAW) method [1]. The Grimme (DFT-D3) was used to consider the van der Waal interaction [2]. The convergence criteria of energy and force were set to 10^{-5} eV, and 0.02 eV $Å^{-1}$ per atom. The cut-off energy and degree of vacuum were set to 500 eV and 15 Å. The Na adsorption energy E_{ad} was denoted as $E_{ad} = E_{composite} - (E_{Na} + E_{substrate})$, where $E_{composite}$, E_{Na}, and $E_{substrate}$ represent the energies of the composite state, the Na ion, and different substrates, respectively.

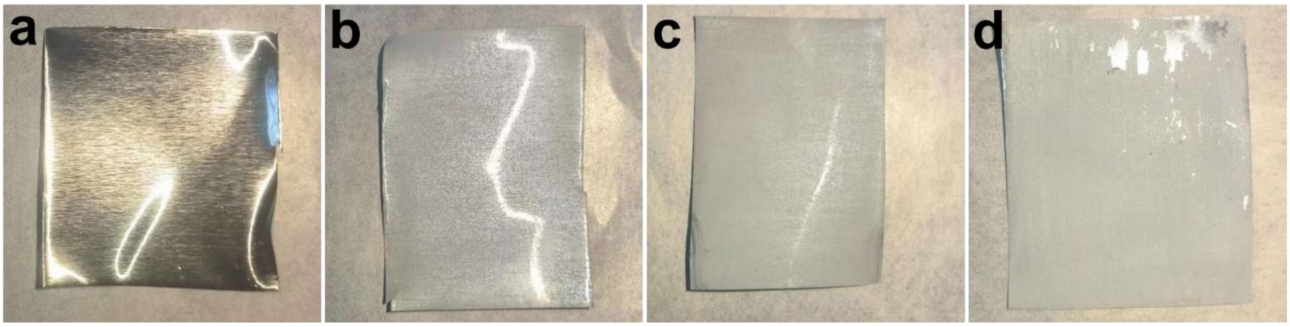

Figure S1. Optical image of (a) Al foil; Optical image of Zn@Al via reaction time of (b) 1.0 min, (c) 2.0 min and (d) 3.0 min.

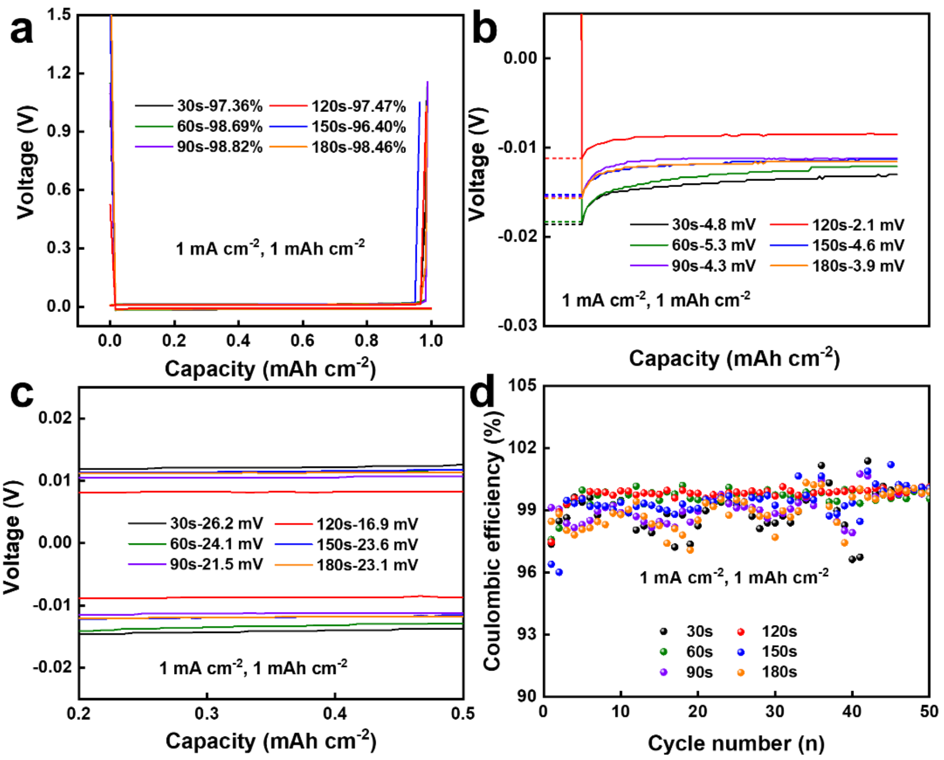

Figure S2. The electrochemical performance of Zn@Al with different reaction time. (a) initial coulombic efficiency. (b) nucleation overpotential. (c) voltage hysteresis. (d) cycle life.

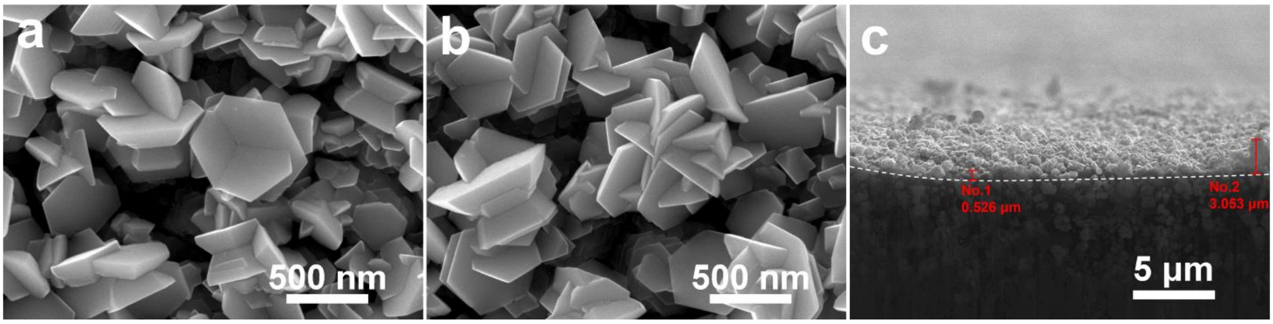

Figure S3. (a-b) Top view and (c) Cross-sectional SEM images of Zn@Al after 2.0 min reaction time.

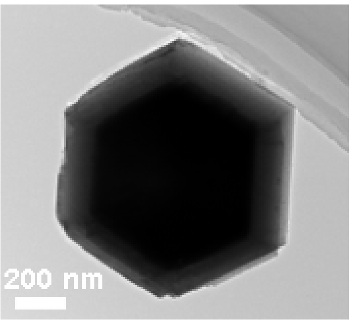

Figure S4. HR-TEM image of Zn@Al.

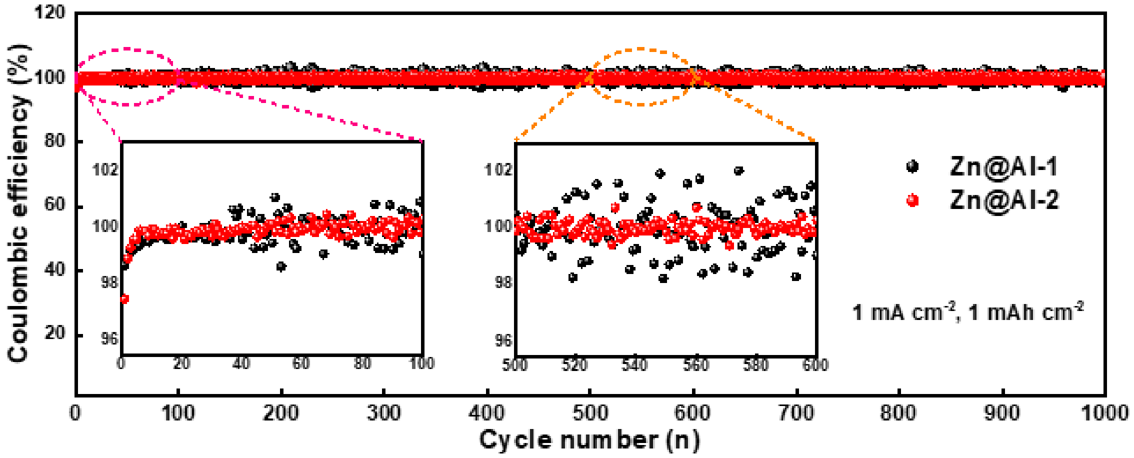

Figure S5. Cycling properties of the Na‖Zn@Al-1 and Na‖Zn@Al-2 half-cells at 1 mA cm^{-2} and 1 mAh cm^{-2}

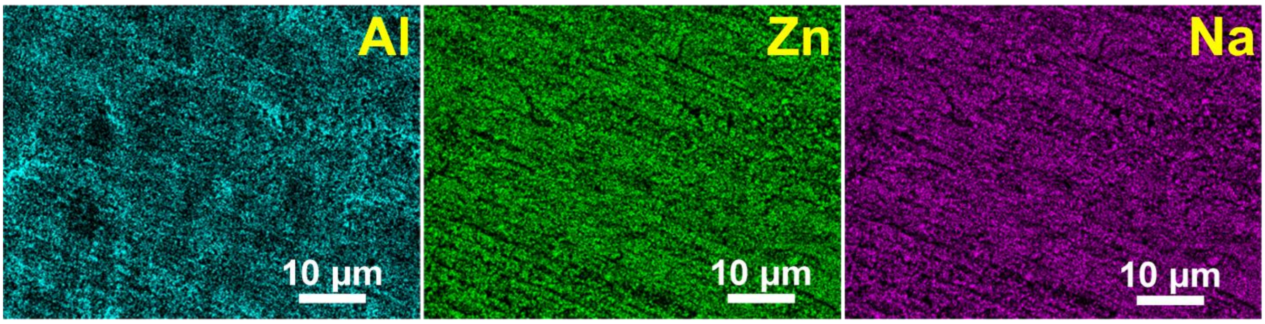

Figure S6. SEM-EDS images Zn@Al anode after 10 cycles at 1 mA cm^{-2} and 1 mAh cm^{-2}

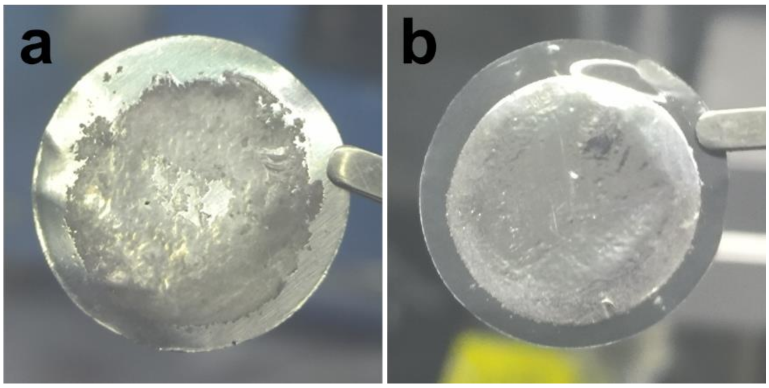

Figure S7. The optical image of (a) Al foil and (b) Zn@Al anode with a nucleation capacity of 1.0 mAh cm^{-2}.

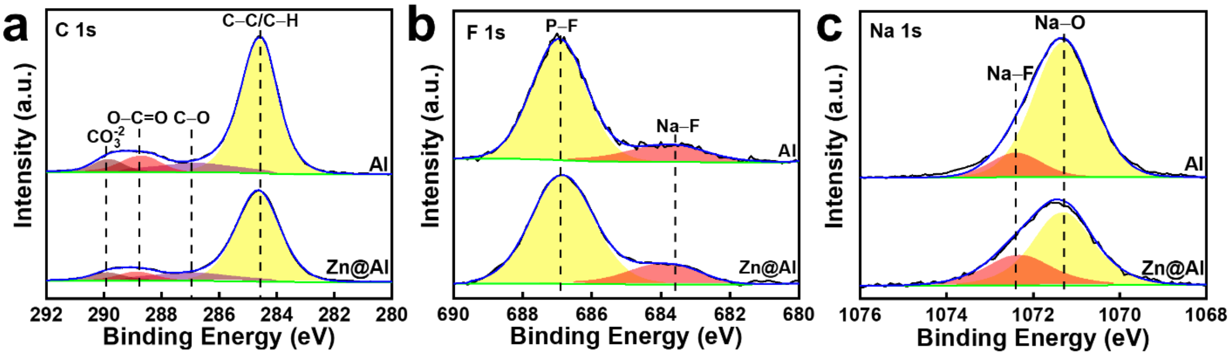

Figure S8. High-resolution XPS: (a) C 1s; (b) F 1s and (c) Na 1s profiles of the Al and Zn@Al electrodes after 10 cycles at 1 mA cm^{-2} with 1 mAh cm^{-2}.

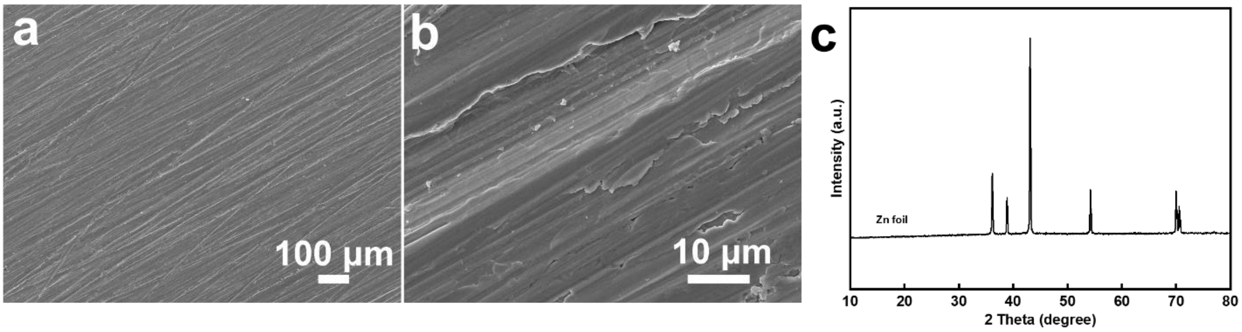

Figure S9. (a-b) The SEM image of Zn foil at different magnifications; (c) XRD pattern of Zn foil.

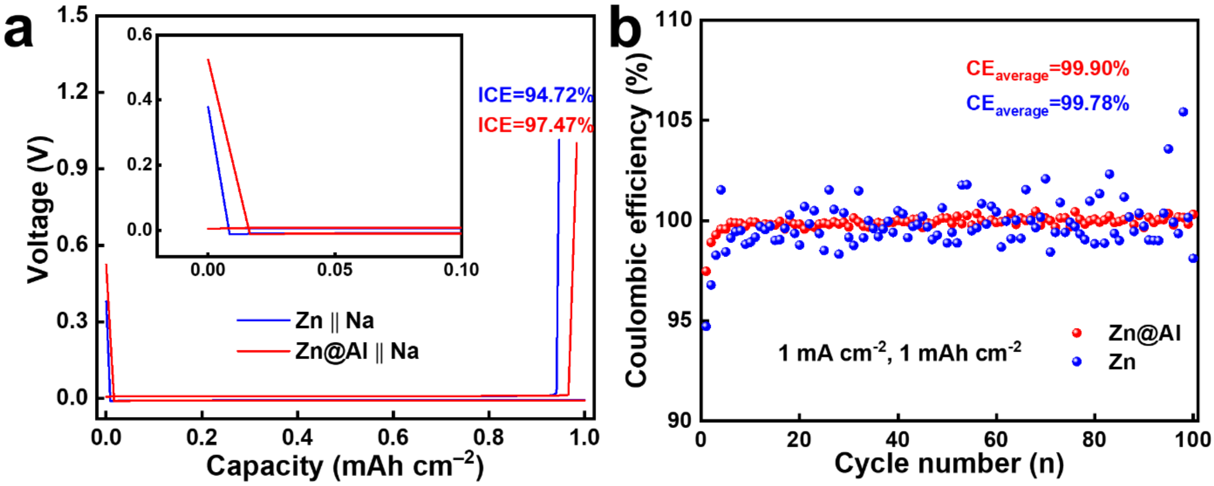

Figure S10. Electrochemical performance of Zn foil and Zn@Al electrodes. (a) Voltage profiles of Na‖Zn foil half-cell and Na‖Zn@Al half-cell plated/stripped at 1 mA cm^{-2} and 1 mAh cm^{-2} in the first cycle; (b) Cycling properties of the Na‖Zn foil and Na‖Zn@Al half-cell cells at 1 mA cm^{-2} and 1 mAh cm^{-2} for 100 cycles.

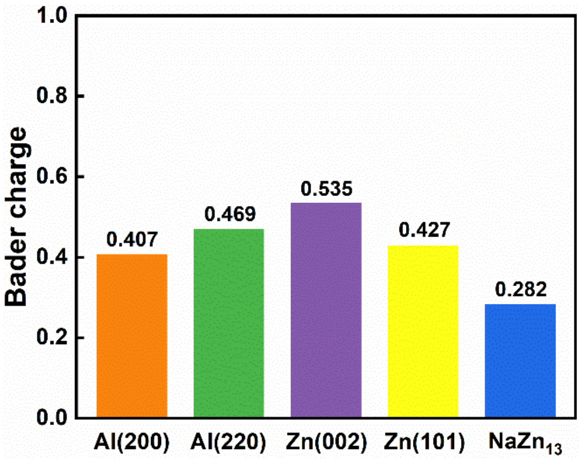

Figure S11. Summary of the calculated bader charge.

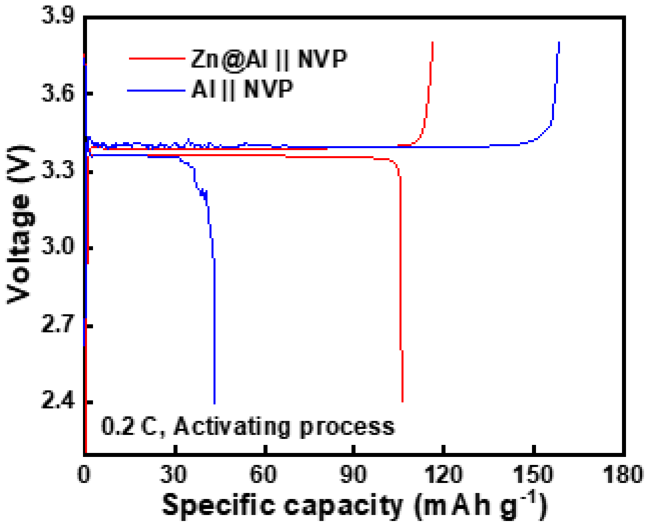

Figure S12. Capacity voltage curves of Al‖NVP and Zn@Al‖NVP full cells at 0.2 C during the initial activating process.

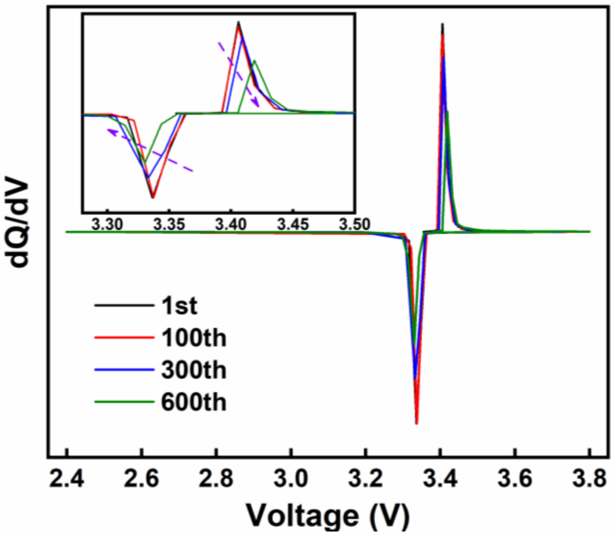

Figure S13. The dQ/dV curves of Zn@Al at different specific cycle numbers (rate:1.0 C).

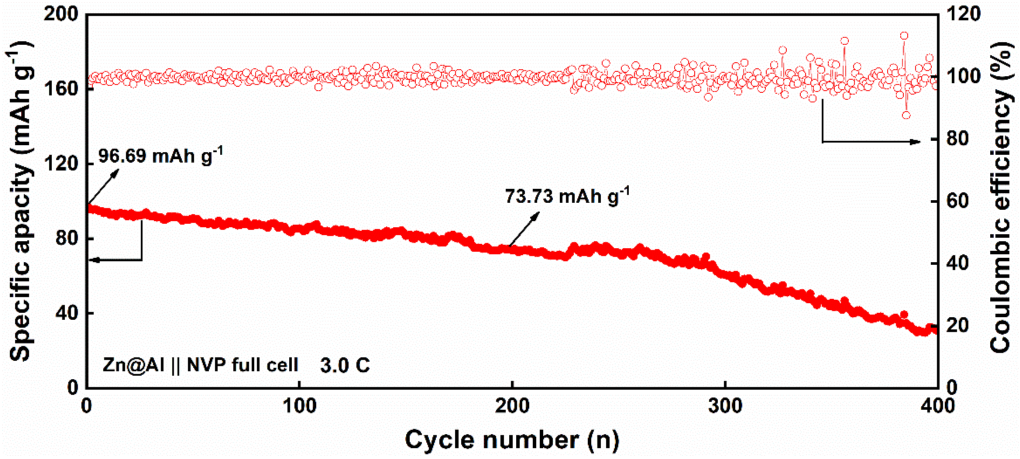

Figure S14. Cycling performance of anode-free Zn@Al||NVP full cell at 3.0 C.

Table S1. Comparison of the cycling performances of the AFSMBs.

Anode	Cathode	Rate	Cycle number	Retention	Journal	Ref
Zn@Al	$Na_3V_2(PO_4)_3$	1.0 C	100 300 600	94.0% 82.5% 61.0%	This work	
Graphitic C@Al	$Na(Cu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3})O_2$	0.5 C	260	80.0%	Nature Energy	3
Porous Al	$Na\text{-}TiS_2$	<1.0 C	200	70.0%	Nano Letters	4
Li-C45	$Na_3V_2(PO_4)_3$	0.33 C	100	97.4%	Energy Storage Materials	5
MgF@NCHNFs	$Na_3V_2(PO_4)_3$	2.0 C	50	91.2%	Energy Storage Materials	6
Cu_3P@Cu	$Na_3V_2(PO_4)_3$	0.5 C	75	87.0%	Advanced Materials	7
Cu@Bi	$Na_3V_2(PO_4)_3$	1.0 C	80	97.9%	Batteries	8
FCTF	$Na_3V_2(PO_4)_3$	2.0 C	400	56.0%	Science Advances	9
NOCS	$Na_3V_2(PO_4)_3$	0.5 C	350	79.0%	Small Methods	10
F-A-Al	$Na_3V_2(PO_4)_3$	0.3 C	50	46.1%	Advanced Energy Materials	11
Al-Cu@C	$Na_3V_2(PO_4)_3$	1.0 C	50	75.0%	Advanced Energy Materials	12
SnNCNF	$Na_3V_2(PO_4)_3$	2.0 C	80	89.0%	Advanced Materials	13
KJB@Cu	$Na_3V_2(PO_4)_3$	0.5 C	150	94.16%	ACS Energy Letters	14
NST	$Na_3V_2(PO_4)_3$	1.0 C	100	77.0%	Advanced Materials	15
PC-CFe	$Na_3V_2(PO_4)_3$	0.55 C	100	97.0%	Advanced Materials	16
3D Zn@Al	$Na_3V_2(PO_4)_3$	0.5 C	100	98.8%	Nano Energy	17

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