Supporting Information

Anode-free Na Metal Batteries Enabled by Nearly Fully Reversible Na plating on Zn Surface

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1. Complete experimental details, materials, and methods

Materials: diglyme (>99.0%, TCI), $NaPF_6$ (98.5%, Alfa Aesar), sodium sticks (99%, Alfa Aesar), Zn foil, Mo foil (Alfa Aesar), stainless steel (TBI Inc.), Al and Cu foil (Alfa Acesr), oxalic acid (Fischer Scientific), carbon nanotubes (>95 wt %, Cheap tubes Inc), NaH_2PO_4 $2H_2O$ (99%, Alfa Aesar), isopropanol (99%, Fischer Scientific), PTFE dispersion (Polysciences Inc.), molecular sieve 4A (Alfa Aesar), super-P carbon black (MTI Corp.). All chemicals were used as received without further purification.

Preparation of current collectors:_ Zn foil was mechanically polished to a mirror surface and the surface cleaned using 95% alcohol. Rolling mill was used to obtain flat and smooth edges Zn foil. Cu foil was washed by immersing it in 0.5M HCl for 10 minutes, followed by rinsing separately with deionized water, acetone and 95% ethanol three times. The foils were then quickly dried in a vacuum oven at room temperature. Al foil was used as supplied with no pretreatment.

$Na_3V_2(PO_4)_3$/carbon nanotube composite: First, 1mM V_2O_5 (1 mmol) and 3mM $H_2C_2O_4$ $2H_2O$ were dissolved in 20 ml water and stirred at 70 °C to obtain a blue solution. 3mM $NaH_2PO_4.2H_2O$ was then added to the above solution with continuous stirring for 1hr to make solution A. 22.8 mg carbon nanotubes (CNTs) was dispersed into 50 ml isopropanol

with ultrasonic (solution B). Thereafter, solution B was added to solution A and stirred at 70 °C. After drying, the precursor was grounded in a mortal and then pretreated at 400 °C for 4 hours and later annealed at 750 °C for 8 hours (5 °C /min) under Ar to obtain the final product. NVP self-supporting cathode was fabricated by mixing NVP/C, super-P carbon black and PTFE with a weight ratio of 7:2:1, respectively. The thin membrane was dried at 70°C overnight under vacuum and were punched into 1.1 cm^2 discs. Typical mass loading was ~ 40 mg cm^{-2}.

Material characterization

SEM images were collected using a field-emission Hitachi S-4700-II SEM; and EDX spectra were collected using an Bruker Analytical EDS detector. The electrodes for SEM/EDX were washed repeatedly inside a glovebox prior to analysis.

Electrochemical measurements

Electrochemical tests were performed using type 2025 coin cells. These coin cells were assembled in the glove box using Celgard separator and the electrolytes was 1.0 M $NaPF_6$ in diglyme unless otherwise stated. Battery cycling behavior was studied using Neware CT-4008 battery analyzers. Electrochemical impedance data were acquired at room temperature with a frequency range of 0.1 Hz to 100 kHz. Cyclic voltammograms were carried out using a coin cell consisting of a working electrode (Zn, Cu, Al) and Na as a counter and reference electrodes. For the current collectors, the potential was regulated from -0.15 to 1V at a scan rate of 2.0 mV s^{-1}. Anode-free full cells were cycled at a voltage range of 2.6 – 3.6 V at desired rate capacities and areal capacity of ~ 3.0 mAh cm^{-2}. Preconditioning of current collectors for accurate CE measurements Zn//Na, Cu//Na and Al//Na half cells are performed with a single Na plating high enough capacity 6mAh cm^{-2}, then stripping the Na to 0.5 V prior to depositing the excess Na reservoir (Q_T =6mAh cm^{-2}) at 3 mA cm^{-2}. After which all the cells were cycled (Q_c =1.5 mAh cm^{-2}) for 100 cycles at 3 mA cm^{-2} and final stripping performed 0.5 V at 3 mA cm^{-2}.

2. Supplemental Tables

Table S1: Estimated unit energy densities of SMB and Af-SMB (pouch cell)

Average voltage: 3.4 V; capacity: 0.9Ah; Cell dimension: 54 mm x 36 mm, 7 layers			
	Cell parameters	**SMB**	**Af-SMB (This work)**
Cathode (NVP)	specific capacity (mAh g^{-1})	100	101
	mass loading (mg cm^{-2})	32	32
	areal capacity (mAh cm^{-2})	3	3
	cathode weight (g)	8.1	8.2
Al foil current collector	weight (g)	0.42	0.42
Na anode mass		6	0
Cu current collector		0.2	0.2
Electrolyte		5	1.6
Separator		0.4	0.4
Specific energy density	per unit	153 Wh kg^{-1}	306 Wh kg^{-1}

Average voltage: 3.4 V; capacity : 0.005Ah; Coin cell diameter: 12mm			
	Cell parameters	**SMB**	**Af-SMB (This work)**
Cathode (NVP)	specific capacity (mAh g^{-1})	101	101
	mass loading (mg cm^{-2})	32	32
	areal capacity (mAh cm^{-2})	3.2	3.2
	cathode weight (mg)	43.2	43.2
Al foil current collector	weight (mg)	5.6	5.6
Na anode mass		33	0
Cu current collector		4.8	11.5
Electrolyte		35	14
Separator		2	2
Specific energy density	per unit	137 Wh kg^{-1}	222 Wh kg^{-1}

Table S2: Estimated unit energy densities of SMB and Af-SMB (coin cell)

Table S3: Performance comparison of Zn//Na (Half cell) and Zn//NVP (Anode-free) batteries developed in this work with typical half cells and anode-free batteries reported in the literature

Anode	**Electrolyte (volume)**	**Current density (mA cm^{-2})**	**Capacity (mAh cm^{-2})**	**CE (%) (cycles)**	**Full cell capacity retention (cycles)**	**References**
Na@Zn	1.0 M $NaPF_6$/DGM (5µL)	2.0	3.0	99.90 (150)		**This work**
Na@Zn	1.0 M $NaPF_6$/DGM (20µL)	2.0	3.0	99.91 (500)	90 (100)	**This work**
Na@Cu	1.0 M $NaPF_6$/DGM (25µL)	0.5	1.0	99.90 (300)		1
Na@Cu	1.0 M $NaBF_4$/TGM (30µL)	0.5	0.5	99.90 (100)	76 (100)	2
Na@Cu	1.0 M $NaPF_6$/DME (80µL)	1.0	2.0	85.00 (350)		3
Na@Al	1.0 M $NaPF_6$/TGM (30µL)	0.5	1.0	99.28 (150)		4
Na@Bi	1.0 M $NaPF_6$/TGM (40µL)	0.5	2.0	99.85 (50)	70.4 (100)	5
Na@C	1.0 M $NaPF_6$/TGM (40µL)	0.5	2.0	99.90 (50)	82.5 (100)	5
Na@Cu -C	1.0 M $NaPF_6$/DGM (40µL)	1.0	1.0	99.80 (600)		6
Na@Cu	1.0 M $NaPF_6$/DGM (40µL)	0.5	.25	99.80 (340)		7
Na@Cu	0.9 M $Na(HCB_{11}H_{11})$ /DGM (not stated)	0.5	1.0	99.50 (300)		8

3. Supplemental Figures

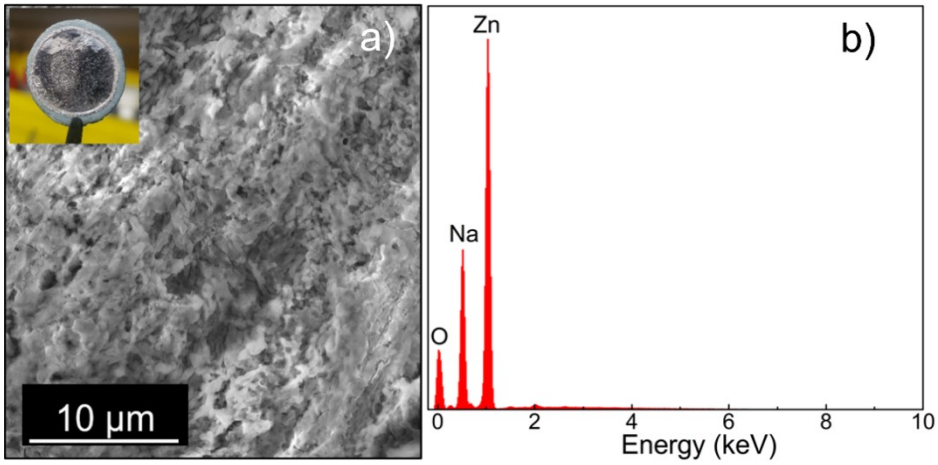

Figure S1: a) SEM image and photograph (inset) of Na anode electroplated on Zn foil at 30 mAh cm^{-2} capacity b) EDS analysis that verifies elemental composition of electroplated Zn foil after 30 mAh cm^{-2} Na plating

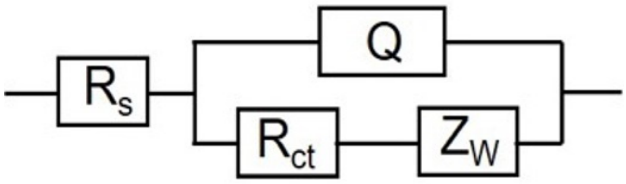

Figure S2: Equivalent circuit model suggesting analysis of R_{ct} in half cells assembled using Zn and Cu foils

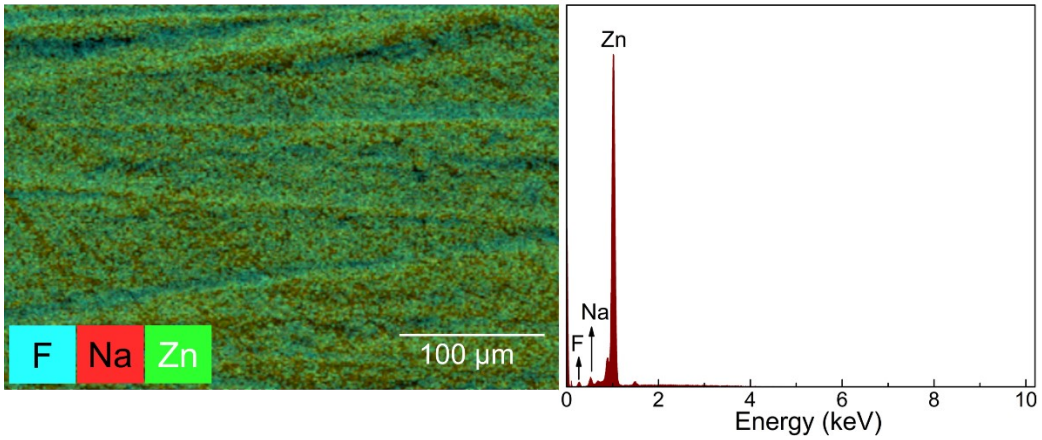

Figure S3: EDS elemental analysis of cycled Zn foil and mapping that verify uniform composition of Zn foil after cycling

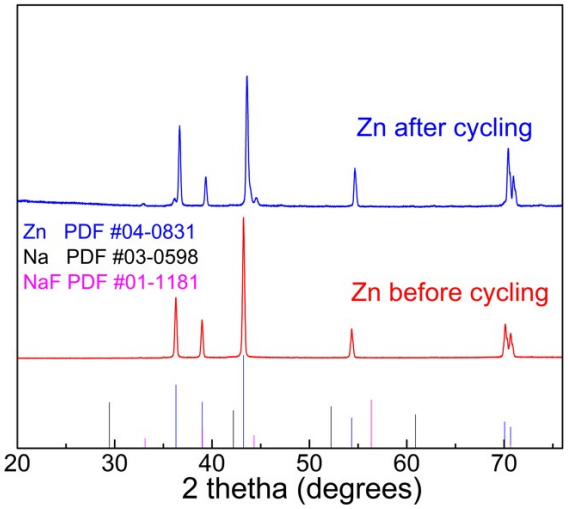

Figure S4: XRD analysis of cycled Zn foil after reversible Na plating and stripping

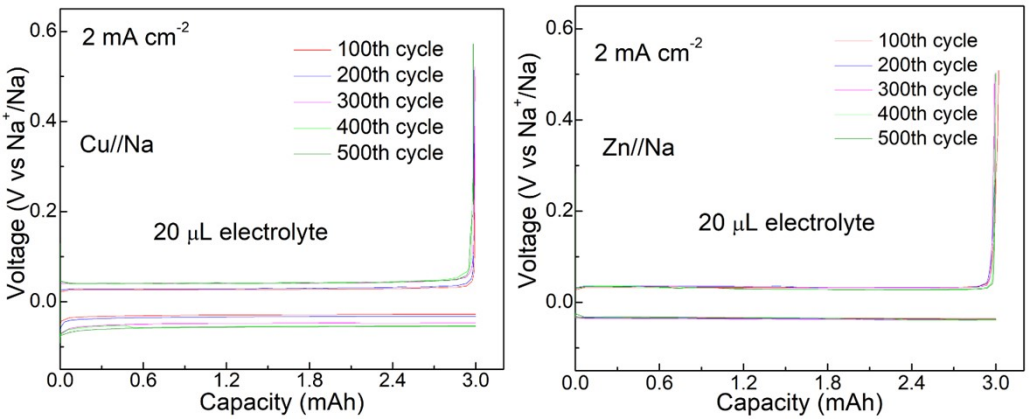

Figure S5: Analysis of voltage profiles that compare FE during cycling using 20 μL electrolyte volume on Cu and Zn foils.

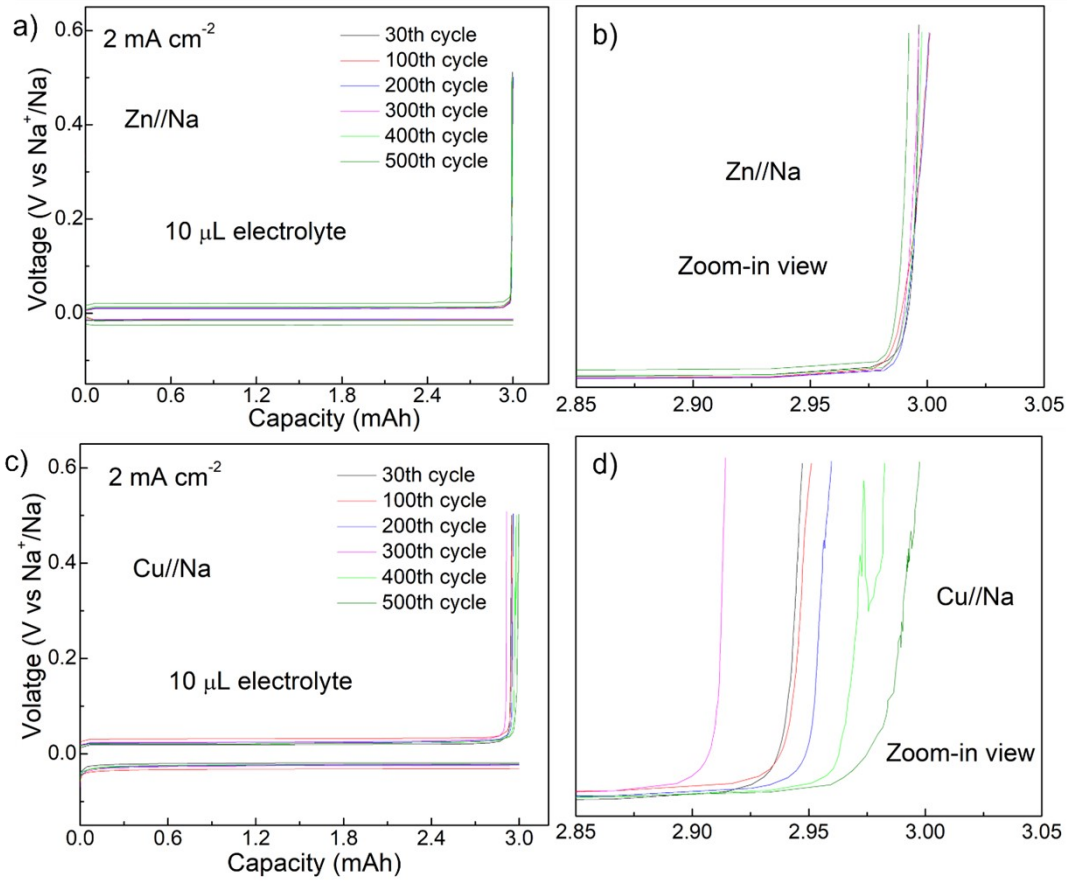

Figure S6: Analysis of voltage profiles that compare FE during cycling using 10 μL electrolyte volume on Cu and Zn foils.

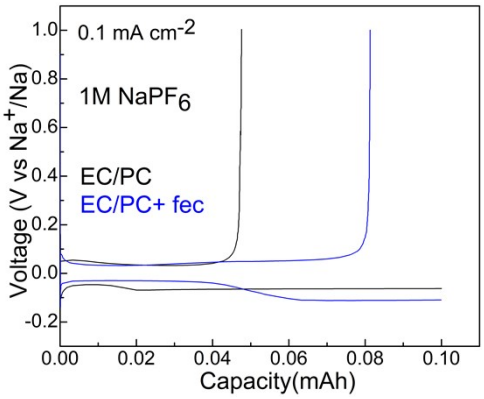

Figure S7: Voltage profiles showing Na plating-stripping behaviors on Zn foil using 1.0 $NaPF_6$ in carbonate electrolyte (EC/PC) with and without the fluorinated ethylene carbonate additive.

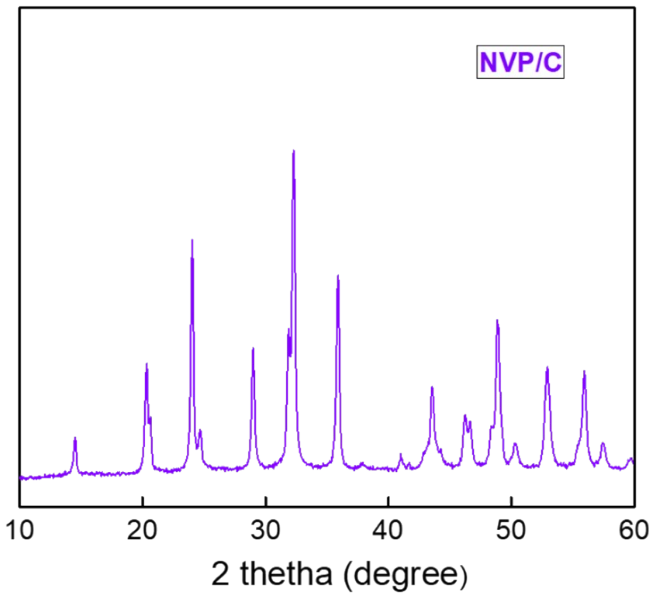

Figure S8: XRD pattern of as-synthesized $Na_3V_2(PO_4)_3$ /C powder.

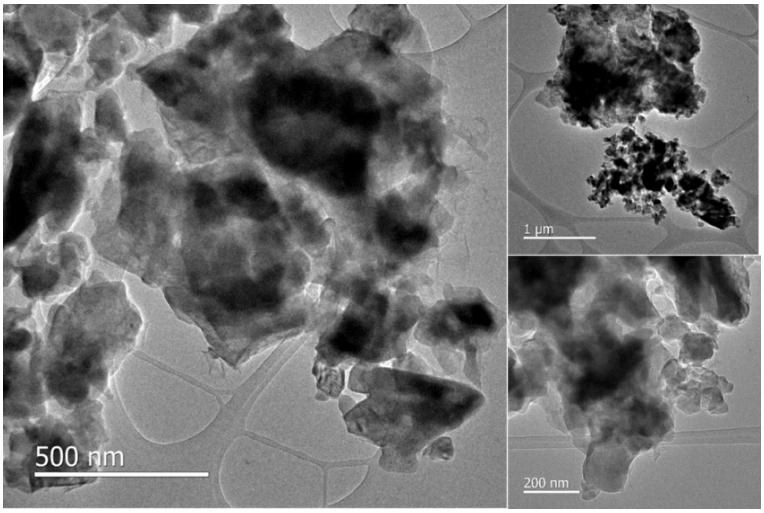

Figure S9: TEM images of as-synthesized $Na_3V_2(PO_4)_3$ /C powders.

Reference

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