Supporting Information

Natural seawater-based electrolytes for zinc-ion batteries

Chuancong Zhou ^{a,#}, Zhenming Xu ^{b,#}, Min Chen ^{c,#}, Qing Nan ^a, Jie Zhang ^a, Yating Gao ^a, Zejun Zhao ^a,

Zhenyue Xing a, Jing Li a, Peng Rao a, Zhenye Kang a, Xiaodong Shi a,*, and Xinlong Tian a,*

^a School of Chemistry and Chemical Engineering, School of Marine Science and Engineering, State Key

Laboratory of Marine Resource Utilization in South China Sea, Hainan University, Haikou 570228, China

^b College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics,

Nanjing 210016, China

^c School of Materials Science and Engineering, Dongguan University of Technology, Dongguan 523808,

China

* Corresponding authors emails: shixiaodong@hainanu.edu.cn; tianxl@hainanu.edu.cn

[#]Co-first authors: These authors contributed equally.

1. Experimental content

1.1 Preparation of NH₄V₄O₁₀ cathode

In details, 2.106 g NH₄VO₃ was dissolved in 90 mL ultrapure water and formed a light-yellow solution under the heating temperature of 80 °C. Subsequently, 3.404 g $H_2C_2O_4$ ·2H₂O powder was added to the above solution under continuous magnetic agitation until the mixture color became dark-blue. The solution was transferred to three autoclaves (50 mL) and heated in an oven at 140 °C for 48 h. The hydrothermal reaction product was collected and washed repeatedly with ultrapure water after the autoclaves were naturally cooled to room temperature. The NH₄V₄O₁₀ material was obtained after drying the product at 80 °C for 12 h.

1.2 Preparation of α-MnO₂ cathode

A total of 2.25 mmol of MnSO₄·H₂O was dissolved in 15 mL of deionized water under magnetic stirring until the solution became clear. Subsequently, 1.5 mmol of KMnO₄ powder was gradually introduced into the aforementioned solution, and the mixture was stirred for one hour. Following this, the resulting solution was transferred to a Teflon-lined autoclave and heated at 160 °C for a duration of 12 hours. After cooling to room temperature, the resultant product was collected via centrifugation, washed three times with deionized water, and dried in an oven at 80 °C for another 12 hours.

1.3 Material characterizations

The microstructure morphology of $NH_4V_4O_{10}$ cathode and zinc metal anode was characterized by scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, JEOL JEM-2100F). The crystalline structure and zinc storage mechanism of $NH_4V_4O_{10}$ were characterized by X-ray diffraction (XRD, Cu K α radiation, Rigaku D/max 2500) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). The composition of seawater and the intercalation content of cations in $NH_4V_4O_{10}$ were detected by Inductive coupled plasma-optical emission spectrometer (ICP-OES, SPECTRO BLUE SOP). The contact angle measurements were carried out by a contact angle goniometer (Ram'e Hart 260), and the amount of electrolyte is 10 μ L. The *in-situ* pH test was performed by the JENCO 6173R instrument with Mirco5 pH meter (Ohaus, USA) in a cuvette electrolyzer with 1.5 mL electrolyte at the current density of 200 mA g⁻¹ for Zn//NH₄V₄O₁₀ cells and 5 mA cm⁻² for Zn//Zn cells. The *in-situ* dendrite observation of Zn//Zn cells was conducted by an optical microscope (JINXIANLW750LJT).

1.4 Electrolyte configurations

Seawater used in this work was collected from Sanya Yazhou Bay in the South China Sea, and it was only physically filtered to remove the impurity without other chemical treatments. For the configuration of seawater electrolytes, the filtered seawater was used as solvent and ZnSO₄·7H₂O with different concentrations (0.47M/0.94M/1.41M/1.88M) were adopted as solute. For the configuration of conventional electrolytes, seawater was replaced by ultrapure water. As the contrast electrolytes, 1.88 M ZnSO₄-0.47 M NaCl, 1.88 M ZnSO₄-0.016 M KCl, 1.88 M ZnSO₄-0.018 M CaCl₂, 1.88 M ZnSO₄-0.056 M MgCl₂, 0.018 M CaCl₂, 0.016 M KCl, 0.47 M NaCl and 0.056 M MgCl₂ electrolytes were configurated in ultrapure water based on the ICP result (**Table S1**). Especially, the electrolyte usage for each cell in this work is 200 µL.

1.5 Electrochemical test

 $NH_4V_4O_{10}$ powder was mixed with conductive carbon (Ketjen black) and polyvinylidene fluoride (PVDF) binder under the weight ratio of 7:2:1. With the addition of N-Methyl pyrrolidone (NMP), the obtained black slurry was coated on stainless steel mesh and dried at 80 °C in a vacuum oven for 12 h. After weighing, the average mass loading of $NH_4V_4O_{10}$ in the cathode (d=12 mm) is about 1.2 mg cm⁻². The Zn// $NH_4V_4O_{10}$ full cells were assembled with zinc foil (d=12 mm, thickness~0.1 mm), $NH_4V_4O_{10}$, and glass fiber (Whatman, GF-D) as anode, cathode and separator, respectively. The Zn//Zn cells were assembled with zinc foil as both working electrode and counter electrode, and the Zn//Cu cells were packaged with Cu foil and zinc foil as working electrode and counter electrode. The button battery type is CR2025 (d=20 mm, thickness~2.5 mm), and the button battery package pressure is 50 MPa. Galvanostatic charge/discharge curves of Zn//NH₄V₄O₁₀ cells were investigated by LAND CT2001A battery-testing instrument within 0.4-

1.4 V (vs. Zn^{2+}/Zn). Cyclic voltammetry (CV), electrochemical impedance spectra (EIS), Tafel, chronoamperometry (CA), linear sweep voltammetry (LSV) of the corresponding cells were tested on an electrochemical workstation (CHI660E) at the temperature of 25 °C.

1.6 Computational details

Density Functional Theory (DFT) calculations were performed on CP2K package¹ by using the CP2K package mixed Gaussian and plane-wave scheme² and the Quickstep module,³ with the help of Multiwfn software.⁴ The Perdew-Burke-Ernzerhof (PBE) exchange correlation functional,⁵ Goedecker-Teter-Hutter (GTH) pseudopotential⁶ were used to describe the system.³ A plane-wave energy cut-off and relative cut-off of 400 Ry and 55 Ry have been employed, respectively. The energy convergence criterion was set to 1.5×10^{-5} Hartree. The DFT-D3 level correction for dispersion interactions was applied.⁷ Structural optimization was performed using the Broyden-Fletcher-Goldfarb-Shannon (BFGS) optimizer, until the maximum force is below 0.00045 Ry/Bohr (0.011 eV/Å). The calculation of ion migration energy barrier is based on nudged elastic band (NEB) method.⁸

2. Relevant equations for electrochemical calculations

2.1 Calculating the activation energy of interface reaction

To calculate the activation energy of interface reaction between zinc foil and electrolyte, the Nyquist plots of Zn//Zn cells and Zn//NH₄V₄O₁₀ cells in 1.88 M ZnSO₄-seawater electrolyte and 1.88 M ZnSO₄ electrolyte at different temperatures (30-70 °C) have been measured. The values of solution resistance (R_s) and the interfacial charge transfer resistance (R_{ct}) can be obtained by fitting the Nyquist plots based on the corresponding equivalent circuit diagram. According to the Arrhenius equation:

$k = Ae^{-Ea/RT}$ Equation S1

Where k is the rate constant of the reaction; A is called the Arrhenius constant; E_a is the activation energy of the interface reaction, and is regarded as a constant when the temperature range is not large; R is the gas constant (8.314 J mol⁻¹ K⁻¹); T is the corresponding Kelvin temperature of testing condition (K). After the logarithm process of Equation S1, the Arrhenius equation can be converted to Equation S2:

$$\ln k = -E_a/RT + \ln A$$
 Equation S2

Where $1/R_s$ or $1/R_{ct}$ can be employed as the reaction rate constant (*k*). Thus, the activation energy of E_a corresponding to each interface reaction can be determined by linearly fitting the curves of $\ln 1/R$ and 1/T.

2.2 Calculating the Zn²⁺ transference number

The Zn^{2+} transference number 1.88 M ZnSO₄-seawater electrolyte and 1.88 M ZnSO₄ electrolyte was conducted by testing the EIS of the Zn//Zn cells before and after the activation process.

$$t_{+} = \frac{I_{s}(\Delta V - I_{i}R_{i})}{I_{i}(\Delta V - I_{s}R_{s})}$$
Equation S3

Where ∇V is the applied voltage (0.01 V), I_I and R_I are the initial current and charge transfer resistance, I_S and R_S refer to the steady-state current and charge transfer resistance.

2.3 Calculating the b value and capacitive contribution ratio

The parameter of **b** could be calculated as the slope value of the fitting linear of log(i) vs. log(v).

$$i = a v^b$$
 Equation S4
 $log(i) = log a + b log(v)$ Equation S5

The response current (i) could be divided into two components by introducing new parameters of k_1 and k_2 .

$$i = k_1 v + k_2 v^{1/2}$$
 Equation S6

 $k_1 v$ originates from the capacitive contribution, $k_2 v^{1/2}$ originates from the diffusion-limited Faradaic processes. k_1 value could be acquired through the linear relationship between $i/v^{1/2}$ and $v^{1/2}$.

$$i/v^{1/2} = k_1 v^{1/2} + k_2$$
 Equation S7



Figure S1 Cycling performance of (a) Zn//Zn cells and (b) Zn//NH₄V₄O₁₀ cells in the seawater electrolytes with different molar concentration of ZnSO₄; (c) Cycling performances of $Na_{0.33}V_2O_5$, NaV_3O_8 and $NH_4V_4O_{10}$ cathodes in 1.88 M ZnSO₄-seawater electrolyte at 500 mA g⁻¹.



Figure S2 Electrochemical impedance spectroscopy of Zn//Zn cells in (a) 1.88 M ZnSO₄ electrolyte and (b)

1.88 M ZnSO₄-seawater electrolyte at different temperatures (30-70 °C).



Figure S3 Current variation of Zn//Zn cells in (a) 1.88 M ZnSO₄ electrolyte and (b) 1.88 M ZnSO₄-seawater electrolyte during polarization process; Nyquist plots of Zn//Zn cells in (c) 1.88 M ZnSO₄ electrolyte and (d) 1.88 M ZnSO₄-seawater electrolyte before and after polarization.



Figure S4 (a) Dynamic contact angles of $ZnSO_4$ and $ZnSO_4$ –seawater electrolytes on the surface of zinc foil; (b) Nyquist plots of Zn//Zn cells in different electrolytes; Electrochemical impedances of glass fiber separator wetted by (c) 1.88 M ZnSO₄-seawater and 1.88 M ZnSO₄ electrolyte, and (d) seawater and ultrapure water.

To test the ionic conductivity of 1.88 M ZnSO₄-seawater and 1.88 M ZnSO₄ electrolyte, the glass fiber separator is fully wetted by the corresponding electrolyte, then placed in the middle of two stainless steel gaskets, and assembled into a CR2025 coin cell. The ionic conductivity can be calculated based on the following equation, where L is the impacted thickness of glass fiber separator, S is the surface area of glass fiber separator, and R is the tested resistance.

$$\sigma = L/(R \times S)$$

As summarized in **Table S2**, the ionic conductivity of 1.88 M ZnSO_4 -seawater is 12.3 mS cm^{-1} , higher than that of 1.88 M ZnSO_4 electrolyte (11.6 mS cm^{-1}) owing to the inherently higher ionic conductivity of seawater than ultrapure water.



Figure S5 Cycling performance of Zn//Zn cells in 1.88 M ZnSO₄ electrolyte, 1.88 M ZnSO₄-seawater electrolyte, 1.88 M ZnSO₄-0.47 M NaCl electrolyte, 1.88 M ZnSO₄-0.016 M KCl electrolyte, 1.88 M ZnSO₄-0.018 M CaCl₂ electrolyte, and 1.88 M ZnSO₄-0.056 M MgCl₂ electrolyte at 5 mA cm⁻²-1 mAh cm⁻².



Figure S6 Nucleation overpotentials of Zn//Zn cells at (a) 2 mA cm⁻²-1 mAh cm⁻², (b) 5 mA cm⁻²-1 mAh cm⁻², (c) 5 mA cm⁻²-5 mAh cm⁻² and 10 mA cm⁻²-1 mAh cm⁻² in different electrolytes.



Figure S7 Galvanostatic cycling performance of Zn//Zn cells in ZnSO₄ and ZnSO₄–seawater electrolytes at the conditions of (a) 2 mA cm⁻²–1 mAh cm⁻², (b) 5 mA cm⁻²–5 mAh cm⁻², and (c) 10 mA cm⁻²–1 mAh cm⁻²; (d) Shelving-recovery performance of Zn//Zn cells in ZnSO₄ and ZnSO₄–seawater electrolytes at the condition of 1 mA cm⁻²-1 mAh cm⁻².



Figure S8 Rate capability of Zn//Zn symmetric cells in ZnSO₄-seawater and ZnSO₄ electrolytes



Figure S9 In-situ dendrite observation of Zn//Zn cells in (a) 1.88 M ZnSO₄ electrolyte and (b) 1.88 M

ZnSO₄-seawater electrolyte during cycling for 30 mins.



Figure S10 SEM images of zinc foil in Zn//Zn cells after (a) 10 and (b) 20 cycles in the ZnSO₄ electrolyte

and after (c) 10 and (d) 20 cycles in the $ZnSO_4$ -seawater electrolyte.



Figure S11 (a) CV and (b–c) galvanostatic charge/discharge curves of Zn//Cu cells in different electrolytes; (d) Nucleation overpotential of Zn//Cu cells in different electrolytes at 2 mA cm⁻²–1 mAh cm⁻²; (e) Nucleation overpotentials of Zn//Cu cells at 2 mA cm⁻²–1mAh cm⁻², 2 mA cm⁻²–2 mAh cm⁻², and 5 mA cm⁻²–1 mAh cm⁻² in different electrolytes; (f) Plating/stripping CE of Zn//Cu cells at 2 mA cm⁻²–1 mAh cm⁻² in different electrolytes; (g) Comparison of the nucleation overpotentials of Zn//Cu cells in ZnSO₄, ZnSO₄– seawater, 1.88 M ZnSO₄–0.016 M KCl, 1.88 M ZnSO₄–0.018 M CaCl₂, and 1.88 M ZnSO₄–0.056 M MgCl₂ electrolytes at 2 mA cm⁻²–1 mAh cm⁻²; SEM images of Cu foil in Zn//Cu cells after 10 cycles in (h) ZnSO₄ and (i) ZnSO₄–seawater electrolytes.



Figure S12 Nucleation overpotential of Zn//Cu cells in different electrolytes at the condition of (a) 5 mA

 $\rm cm^{-2}\text{-}1~mAh~cm^{-2}$ and (b) 2 mA cm^{-2}\text{-}2 mAh~cm^{-2}\text{.}



Figure S13 Nucleation overpotential of Zn//Cu cells in 1.88 M ZnSO₄ electrolyte, 1.88 M ZnSO₄-seawater electrolyte, 1.88 M ZnSO₄-0.47 M NaCl electrolyte, 1.88 M ZnSO₄-0.016 M KCl electrolyte, 1.88 M ZnSO₄-0.018 M CaCl₂ electrolyte, and 1.88 M ZnSO₄-0.056 M MgCl₂ electrolyte at 2 mA cm⁻²-1 mAh cm⁻².



Figure S14 CV curves of Zn//NH₄V₄O₁₀ cells assembled with natural seawater as the electrolyte.



Figure S15 Cycling performance of $NH_4V_4O_{10}$ cathode at 500 mA g⁻¹ in the electrolyte of seawater, ultrapure water, 0.47 M NaCl solution, 0.016 M KCl solution, 0.018 M CaCl₂ solution and 0.056 M MgCl₂ solution.



Figure S16 Self-discharge performances of Zn//NH₄V₄O₁₀ batteries in (a) ZnSO₄–seawater and (b) ZnSO₄ electrolytes after long shelving time of 48 h for two cycles.



Figure 17 (a) XRD patterns of zinc foil in $Zn/NH_4V_4O_{10}$ cells after 10 cycles in $ZnSO_4$ electrolyte and $ZnSO_4$ -seawater electrolyte; SEM images of zinc foil in $Zn/NH_4V_4O_{10}$ cells after 10 cycles in (b) $ZnSO_4$ electrolyte and (c) $ZnSO_4$ -seawater electrolyte.



Figure S18 (a) Digital photograph of the in-situ pH monitoring system and (b) a close-up view of the





Figure S19 (a) Cyclic voltammetry curves of $NH_4V_4O_{10}$ cathode tested at different scan rates (0.2-1.0 mV s⁻¹) in ZnSO₄-seawater electrolyte; (b) the *log (i) vs. log (v)* plots and the corresponding *b* values for redox peaks at specific peak currents in ZnSO₄-seawater electrolyte; (c) Pseudocapacitive contribution area of $NH_4V_4O_{10}$ cathode in the CV curve tested at 1.0 mV s⁻¹ in ZnSO₄-seawater electrolyte; (d) Pseudocapacitive contribution ratio of $NH_4V_4O_{10}$ cathode at different scan rates (0.2-1.0 mV s⁻¹) in ZnSO₄-seawater electrolyte.



Figure S20 (a) Cyclic voltammetry curves of $NH_4V_4O_{10}$ cathode tested at different scan rates (0.2-1.0 mV s⁻¹) in ZnSO₄ electrolyte; (b) the *log (i) vs. log (v)* plots and the corresponding *b* values for redox peaks at specific peak currents in ZnSO₄ electrolyte; (c) Pseudocapacitive contribution area of $NH_4V_4O_{10}$ cathode in the CV curve tested at 1.0 mV s⁻¹ in ZnSO₄ electrolyte; (d) Pseudocapacitive contribution ratio of $NH_4V_4O_{10}$ cathode at different scan rates (0.2-1.0 mV s⁻¹) in ZnSO₄ electrolyte.



Figure S21 Electrochemical impedance spectroscopy of $Zn/NH_4V_4O_{10}$ cells in (a) 1.88 M ZnSO₄ electrolyte and (b) 1.88 M ZnSO₄-seawater electrolyte at different temperatures (30-70 °C).



Figure S22 (a) XRD pattern and crystalline structure, (b) the initial V 2p spectra of $NH_4V_4O_{10}$ material.



Figure S23 (a) O 1s and (b) Zn 2p spectra of NH₄V₄O₁₀ cathode in 1.88 M ZnSO₄-seawater electrolyte at

different charge and discharge state.



Figure S24 Na 1s spectra of NH₄V₄O₁₀ cathode in 1.88 M ZnSO₄-seawater electrolyte at different charge

and discharge state.



Figure S25 V 2p spectra of $NH_4V_4O_{10}$ cathode at the state of (a) discharged to 0.7 V, (b) discharged to 0.4

V, (c) charged to 0.8 V and (d) charged to 1.4 V.



Figure S26 The corresponding TEM, HAADF and elemental mapping images of NH₄V₄O₁₀ cathode in 1.88

M ZnSO₄-seawater electrolyte at (a) fully discharged state and (b) fully charged state.



Figure S27 XRD pattern of NH₄V₄O₁₀ cathode after 30 cycles in ZnSO₄-seatear electrolyte.



Figure S28 Solvation structure of (a) Ca²⁺, (b) K⁺, (c) Mg²⁺, (d) Na⁺ and (e) Zn²⁺ ions in aqueous electrolyte.



Figure S29 Adsorption energy model of (a) Ca^{2+} , (b) K^+ , (c) Mg^{2+} , (d) Na^+ and (e) Zn^{2+} ions in the crystal

structure of $NH_4V_4O_{10}$.



Figure S30 Insertion energy of (a) Ca²⁺, (b) K⁺, (c) Mg²⁺, (d) Na⁺ and (e) Zn²⁺ ions in the crystal structure

of NH₄V₄O₁₀.



Figure S31 Binding energy model of (a) Ca^{2+} , (b) K^+ , (c) Mg^{2+} , (d) Na^+ and (e) Zn^{2+} ions in the crystal

structure of NH₄V₄O₁₀.



Figure S32 Diffusion paths of (a) Ca^{2+} , (b) K^+ , (c) Mg^{2+} , (d) Na^+ and (e) Zn^{2+} ions in the crystal structure of

NH₄V₄O₁₀.



Figure S33 XRD pattern of α -MnO₂ powder.



Figure S34 Cycling performances of α -MnO₂ cathode in 1.88 M ZnSO₄ electrolyte, 1.88 M ZnSO₄-seawater electrolyte, 1.88 M ZnSO₄-0.47 M NaCl electrolyte, 1.88 M ZnSO₄-0.016 M KCl electrolyte, 1.88 M ZnSO₄-0.018 M CaCl₂ electrolyte, and 1.88 M ZnSO₄-0.056 M MgCl₂ electrolyte at 0.2 A g⁻¹; (b) The galvanostatic charge/discharge curves of Zn// α -MnO₂ batteries at 0.2 A g⁻¹ in ZnSO₄ and ZnSO₄-seawater electrolytes.

Table S1 The molar concentration of metal cations in seawater determined by ICP spectrometer.

Seawater composition	Na ⁺	\mathbf{K}^{+}	Ca ²⁺	Mg ²⁺
Molar concentration/M	0.47	0.016	0.018	0.056

Table S2 The corresponding impedances and currents before and after polarization process

Electrolyte	Δ^{V} (mV)	$R_i(\Omega)$	$R_{s}\left(\Omega ight)$	<i>I_i</i> (μA)	<i>I</i> _s (µA)	t+
1.88 M ZnSO ₄ -SW	10	239.36	571.98	15.79	6.82	0.44
1.88 M ZnSO ₄	10	547.96	683.97	15.72	10.77	0.36

Table S3 Comparison of the ionic conductivity of 1.88 M ZnSO₄-seawater, 1.88 M ZnSO₄ electrolyte,

Electrolyte	$R\left(\Omega ight)$	<i>S</i> (cm ²)	<i>L</i> (cm)	σ (mS cm ⁻¹)
1.88 M ZnSO ₄ -SW	1.09	2.01	0.0303	13.8
1.88 M ZnSO ₄	1.16	2.01	0.0303	13.0
Seawater	1.61	2.01	0.0303	9.3
Ultrapure water	3.78	2.01	0.0303	4.0

seawater and ultrapure water.

References

(1) Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. J. W. I. R. C. M. S. cp2k: atomistic simulations of condensed matter systems. *WIREs Computational Molecular Science* **2014**, *4* (1), 15-25.

(2) Lippert, B. G.; PARRINELLO, J. H.; Physics, M. J. M. A hybrid Gaussian and plane wave density functional scheme. *Mol. Phys.* **1997**, *92* (3), 477-488.

(3) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. J. C. P. C.

Quickstep: fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* 2005, *167* (2), 103-128.

(4) Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33 (5), 580-592.

(5) Goedecker, S.; Teter, M.; Hutter, J. J. P. R. B. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* 1996, *54* (3), 1703.

(6) Perdew, J. P.; Burke, K.; Ernzerhof, M. J. P. r. l. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865.

(7) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. T. J. o. c. p. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

(8) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **2000**, *113* (22), 9901-9904.