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Unraveling the Significance of Zinc Ratio in Water-in-Salt Electrolytes

Fekadu Wubatu Fenta and Roza Bouchal*

Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany.

Roza.Bouchal@mpikg.mpg.de

1. Abstract

Water-in-salt electrolytes (WISEs) have been proposed as an effective approach to suppress the side reactions related to free water activity on zinc (Zn) metal anode, thereby enhancing its electrochemical performance. While most WISEs correlate total salt concentration with water content and Zn^{2+} solvation structure, the impact of Zn ratio has been largely overlooked. In this work, we prepared a range of WISEs with varying Zn molar ratios while ensuring low water content, and scrutinized the impact on Zn nucleation behavior, Zn plating/stripping overpotential, and overall Zn metal anode stability. Our results demonstrated that the increase of Zn content in the electrolyte promotes high transference number and the 3D Zn^{2+} diffusion process – thus enhancing the Zn anode stability and reversibility. Moreover, we identified an optimized Zn molar ratio of approximately 0.5, suggesting that beyond this threshold, the impact diminishes. Our findings show that reaching the WISE region is insufficient to improve Zn metal performance; instead, an optimal concentration of Zn^{2+} ions is the determining factor. Consequently, we advocate for the optimization of Zn ratio in the future design of WISEs for high-performance Zn-ion batteries.



27

28 **2. Introduction**

29 Aqueous batteries have attracted great attention for grid-scale energy storage systems due to
30 their low cost and high safety attributed to the use of non-flammable aqueous electrolytes.¹
31 Among these, aqueous Zn ion batteries (AZIBs) are promising alternatives for large-scale energy
32 storage technologies owing to their high theoretical gravimetric (820 mAh g⁻¹) and volumetric
33 (5855 mAh cm⁻³) capacities, low redox potential (-0.76 V versus the standard hydrogen
34 electrode, SHE), high abundance, and low toxicity of Zn metal anode.^{2,3} However, the undesired
35 electrochemical reactions on the Zn anode such as hydrogen (H₂) evolution, uncontrolled
36 dendrite growth, accumulation of dead Zn, and formation of byproducts severely affect the
37 lifespan of AZIBs.⁴

38 It is widely acknowledged that the parasitic H₂ evolution occurring on the Zn anode in
39 conventional diluted electrolytes promotes dendrite growth while also resulting in the formation
40 of inactive Zn deposits.⁴ In dilute electrolytes, the Zn²⁺ solvation shell typically consists of six
41 water molecules, wherein the interaction between Zn²⁺ and water prompts water molecules to
42 undergo ionization. The electric field generated by Zn²⁺ exerts a force on water molecules,
43 facilitating electron transfer from coordinated H₂O to vacant orbitals of Zn²⁺. This process notably
44 weakens the O-H bonds of water molecules and promotes H₂ evolution.⁵ In addition, the
45 formation of a hydrogen bonding network among free water molecules leads to the rapid
46 transport of protons (H⁺) and hydroxide anions (OH⁻) through the Grotthuss mechanism, thereby
47 enhancing H₂ evolution.⁶ These lead to continuous electrolyte consumption and pressure build-
48 up in a cell, thus reducing the reversibility and cycling stability of Zn anode. Several approaches
49 have been proposed to address the above-mentioned challenges by limiting water activities.^{7,8}
50 One of the common approaches to mitigate H₂ evolution is the development of highly
51 concentrated electrolytes also called WISEs. The higher salt-to-water ratio in WISEs does not
52 contain sufficient water to fully coordinate the Zn²⁺ ions, thereby disrupting the original hydrogen
53 bonding network of water, which enables the coordination of anions in the Zn²⁺ solvation
54 structure.⁹ Thus, the partial replacement of water by anions in the Zn²⁺ solvation structure are



55 assumed to mitigate the H₂ evolution upon Zn electrodeposition, improving the cycling stability
56 and Columbic efficiencies of Zn metal batteries. For example, Zhang *et al* reported dendrite free
57 Zn metal anode using 30 m ZnCl₂ electrolyte (m = mol of salt/1 Kg of solvent), which improved the
58 Zn plating/stripping reversibility.¹⁰ Yang *et al* showed that Zn reduction occurs before H₂
59 evolution as the concentration of ZnCl₂ increases due to the high overpotential against H₂
60 evolution on Zn metal.¹¹ This expands the voltage gap between Zn reduction and H₂ evolution
61 that helps to minimize parasitic reactions. On the other hand, due to the limited solubility of most
62 Zn salts in water, the reported WISEs are combined with another salt such as lithium
63 bistrifluoromethanesulfonimide (LiTFSI) or potassium acetate (KAc) and others e.g. 1 m
64 Zn(TFSI)₂ + 20 m LiTFSI,⁹ 1 m Zn(Ac)₂ + 31 m KAc,¹² and 0.5 m Zn(ClO₄)₂ + 18 m NaClO₄.¹³ This results
65 in a very low Zn salt content, accounting for only 2-8 % of the total electrolyte concentration,
66 thus causing a high overpotential above 0.1 V. The latter leads to kinetic limitations, heat
67 generation, and uneven distribution of electrode active material, resulting in dendrite formation.
68 However, a high Zn cation density near the electrode interface is necessary to counterbalance
69 the poor ionic conductivity in WISEs, which otherwise fosters dendrite formation and slows down
70 electrode kinetics. Elevated viscosity also contributes to high overpotential, known as
71 concentration polarization, occurring when the rate of mass transport of reactants to/from the
72 electrode restricts current to flow. Despite numerous reports correlating electrolyte
73 concentrations with water quantity and Zn²⁺ solvation structure, the impact of Zn content in
74 WISEs on Zn anode performance has been largely overlooked. Hence, it is crucial to comprehend
75 to what extent the elevation of salt concentration to achieve the WISE region is significant in
76 relation to the Zn molar ratio.

77 Herein, we prepared WISEs based on Brønsted-Lowry concept by mixing Zn chloride (ZnCl₂) and
78 lithium acetate (LiAc).¹⁴ This concept allows us to obtain various Zn molar ratios while
79 maintaining the WISE region with a very low water content. Thus, we prepared four WISEs by
80 varying the ZnCl₂ molar ratio in ZnCl₂/LiAc mixtures (0.2, 0.5, 0.8, and 1) and compared with the
81 widely studied WISE (1m Zn(Ac)₂ + 31 m KAc) by Chen *et al*.¹² Furthermore, we examined how
82 the total salt and Zn²⁺ concentrations in WISEs affect the Zn nucleation behavior, Zn²⁺
83 transference number, and Zn plating/stripping efficiency. Moreover, to establish a correlation



84 between the Zn ratio and water concentration, we examined a diluted version of 0.5 ratio
85 electrolyte and compared it with the recently reported WISE-like solution by Vazquez *et al*
86 composed of Zn(Ac)₂ and KAc salts.¹⁵ Our primary objective in this study is to comprehend the
87 influence of the Zn²⁺ molar ratio in WISEs on Zn anode cycling stability, supplemented by an
88 analysis of the impact of water concentration. This study will help to target the future design of
89 Zn aqueous electrolytes by considering both the Zn molar ratio and the amount of water, which
90 is an efficient strategy to find a balance between high energy and high power densities.

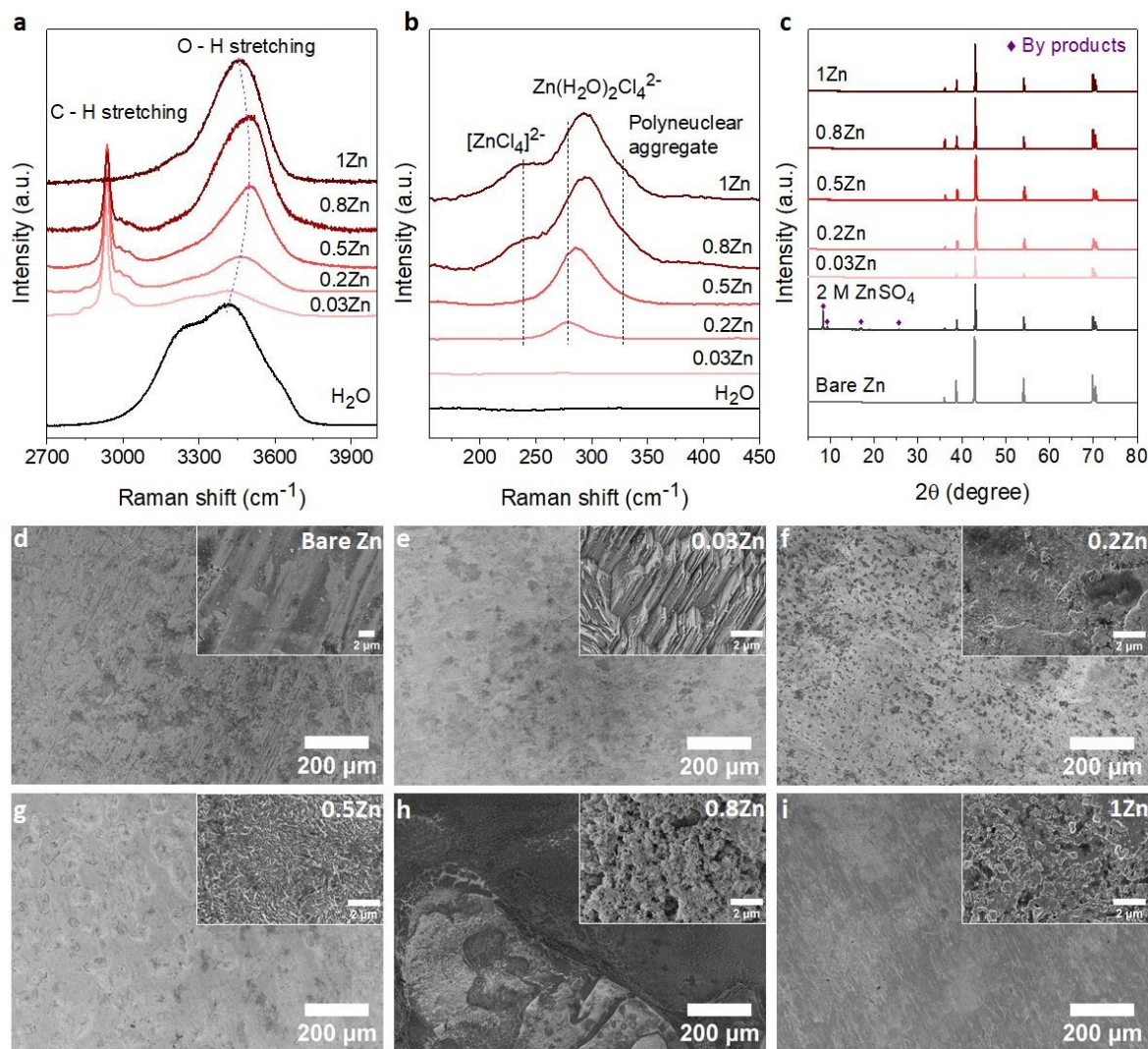
91 3. Results and discussion

92 3.1. Electrolyte formulation and solvation structure

93 To demonstrate the correlation between Zn molar ratio and Zn anode stability, a series of WISEs
94 was prepared by mixing ZnCl₂ and LiAc salts at room temperature. ZnCl₂ is used because of its
95 high solubility and dissociation constant. LiAc is used as a supporting salt to achieve the WISE
96 region while varying the ZnCl₂ salt ratio. In addition, the lithium cation (Li⁺) is a weak acid which
97 could not increase the Brønsted-Lewis acidity of the electrolyte. In such WISEs, the molar ratio
98 of ZnCl₂ and LiAc in (ZnCl₂)_x(LiAc)_{1-x}/(H₂O)_n mixtures are varied, where “x” is the molar ratio of
99 ZnCl₂ (x= 0, 0.2, 0.5, 0.8, 1), whereas “n” is the water content per total salt. After here, **xZn** is used
100 for simplicity to represent the WISEs. The measured Liquidus line in **Fig. S1** shows that the
101 solubility of (ZnCl₂)_x(LiAc)_{1-x}/(H₂O)_n slightly increases as the ZnCl₂ increases, where the water
102 content varies from n = 2.38 to n = 1.77. Note that, the solubility limit changes with the salts ratio
103 and obtaining the exact same salt concentrations for all electrolytes is not possible. The
104 corresponding total salt concentrations are 23, 27, 28, and 31 m while that of Zn²⁺ concentrations
105 are 5, 14, 25, and 31 m for **0.2**, **0.5**, **0.8**, and **1Zn** electrolytes, respectively. The pH value
106 continuously decreases from basic to highly acidic as the Zn molar ratio increases from **0.03** to **1**,
107 see **Table S1**. This increase in acidity is attributed to the complex Zn solvation structures, primarily
108 consisting of (Zn(H₂O)Cl₄)²⁻ and Zn(H₂O)₆²⁺ species.^{16, 17} Hydrogen ions are released from the
109 coordination shell of the octahedral hydrated Zn complex, leading to the increased acidity of the
110 solution. This indicates the number of hydration molecules directly affects the pH of the solution.
111 The lower hydration levels significantly strengthen the proton activity in the electrolyte thus
112 resulting in lower acidity. According to the Pourbaix diagram, when pH < 4.0, Zn has a high



113 solubility and can be easily dissolved as Zn^{2+} .¹⁸ The $(\text{ZnCl}_2)_x(\text{LiAc})_{1-x}/(\text{H}_2\text{O})_n$ WISEs were compared
 114 with previously reported Zn-deficient WISE composed of 1 m $\text{Zn}(\text{Ac})_2$ + 31 m KAc .¹² This
 115 electrolyte was selected because it is a benchmark for WISE having high total salt concentration
 116 (32 m) and a very low mole of Zn^{2+} (**0.03**), abbreviated as **0.03Zn** hereafter. Thus, in total, we
 117 prepared five WISEs with Zn molar ratios ranging from **0.03** to **1**, as demonstrated in **Fig. S1**.



118
 119 **Figure 1: Electrolyte structure and Zn foil stability:** (a) and (b) Raman spectra of WISEs corresponding to water
 120 region and Zn coordination, respectively. (c) XRD patterns of the Zn foils before and after immersing in different
 121 WISEs for 10 days at room temperature, compared with diluted 2M ZnSO_4 . SEM images of (d) bare Zn foils and
 122 soaked Zn foil in (e) 0.03Zn, (f) 0.2Zn, (g) 0.5Zn, (h) 0.8Zn, and (i) 1Zn WISEs.

123 Raman spectroscopy was conducted to study the evolution of H-bonds, Zn^{2+} coordination, and
 124 cation-anion interactions in the prepared WISEs. **Figure 1a** shows the O-H stretching Raman



125 spectra for water in the high-frequency region (2700 – 3900 cm^{-1}). The broad peak of the water
126 region narrows and initially shifts to higher frequencies and then to the lower frequencies as the
127 ZnCl_2 molar ratio increases. It is important to note that the water environment is not directly
128 influenced by the amount of Zn molar ratio, but rather by the electrolyte composition and
129 concentration. Notably, an important blue shift of the O-H stretching mode is observed in the
130 **0.5Zn** electrolyte. This observation suggests that Ac anions influence the strengthening of O-H
131 bonds in water molecules by interacting with the oxygen atoms of Ac and the hydrogen atoms of
132 water. However, compared to the **0.5Zn** electrolyte, water region shifts to the lower frequencies
133 for **0.8** and **1Zn** electrolytes, indicating the weakening of O-H bonds probably due to the
134 interaction of water with Zn^{2+} and/or Li^+ ions. Furthermore, the peaks related to the water region
135 were deconvoluted into three sub-bands corresponding to non H-bond (coordinated water),
136 weak H-bond, and strong H-bond, as shown in **Fig. S2**.¹⁹ The results show difference in H-bonding
137 environments depending on the ratio of LiAc and ZnCl_2 salts in each electrolyte, making difficult to
138 obtain a correlation between salt ratios and the H-bonding environments of water. The above
139 results indicate that the changing of molar ratios of ZnCl_2 and LiAc influence the interaction
140 between water molecules and Zn^{2+} , Ac, and Li^+ ions. This in turn, affects the position and intensity
141 of O-H stretching mode of water molecules in the each electrolyte.

142 **Figure 1b** illustrates the Zn^{2+} coordination in the low-frequency region ($\sim 140 - 500 \text{ cm}^{-1}$), resulting
143 from the interaction of Zn^{2+} with H_2O molecules and Cl^- ions. As expected, no peaks
144 corresponding to **0.03Zn** electrolyte are observed in this region due to the absence of Cl^- ions.
145 The peak at 278 cm^{-1} in **0.2Zn** electrolyte is assigned to $\text{Zn}(\text{H}_2\text{O})\text{Cl}_4^{2-}$ complex. The latter shows
146 an increase in intensity and shifting to higher frequencies with the rising Zn molar ratio (**Fig. 1b**).
147 The additional peaks observed at 240 and 328 cm^{-1} , in **0.8** and **1Zn** electrolytes, are attributed to
148 the $[\text{ZnCl}_4]^{2-}$ complex and Zn-Cl polynuclear aggregate, respectively, according to previously
149 reported works.¹⁴

150 Furthermore, the coordination of Zn^{2+} with Ac anions can be examined in the $400 - 1450 \text{ cm}^{-1}$. For
151 a better correlation, the reported WISEs were compared with saturated LiAc (sat. LiAc) solution.
152 The in-plane O-C-O rocking vibration at 476 cm^{-1} in sat. LiAc completely shifts to the higher
153 frequencies upon increasing ZnCl_2 ratio (**Fig. S3a**), indicating the interaction of Zn^{2+} with Ac



154 anions.²⁰ Similar to the peaks related to COO bending at 656 cm⁻¹, the C-C stretching at 932 cm⁻¹, and C=O stretching at 1419 cm⁻¹, which all undergo a blue shift with ZnCl₂ concentration in the
155 prepared WISEs. The C=O stretching peak at 1419 cm⁻¹ split into two for **0.5** and **0.8Zn**
156 electrolytes (**Fig. S3b**), suggesting simultaneous coordination of Ac to Li⁺ and Zn²⁺.²⁰ These results
157 indicate the preference of Ac anion to interact with Zn²⁺ rather than to Li⁺. Finally, regarding
158 **0.03Zn** electrolyte, all the peaks show a red shift in comparison to all electrolytes including sat.
159 LiAc. These results indicates the dominant interaction of K⁺ to Ac anions due to low amount of
160 Zn²⁺ cations in **0.03Zn** electrolytes.
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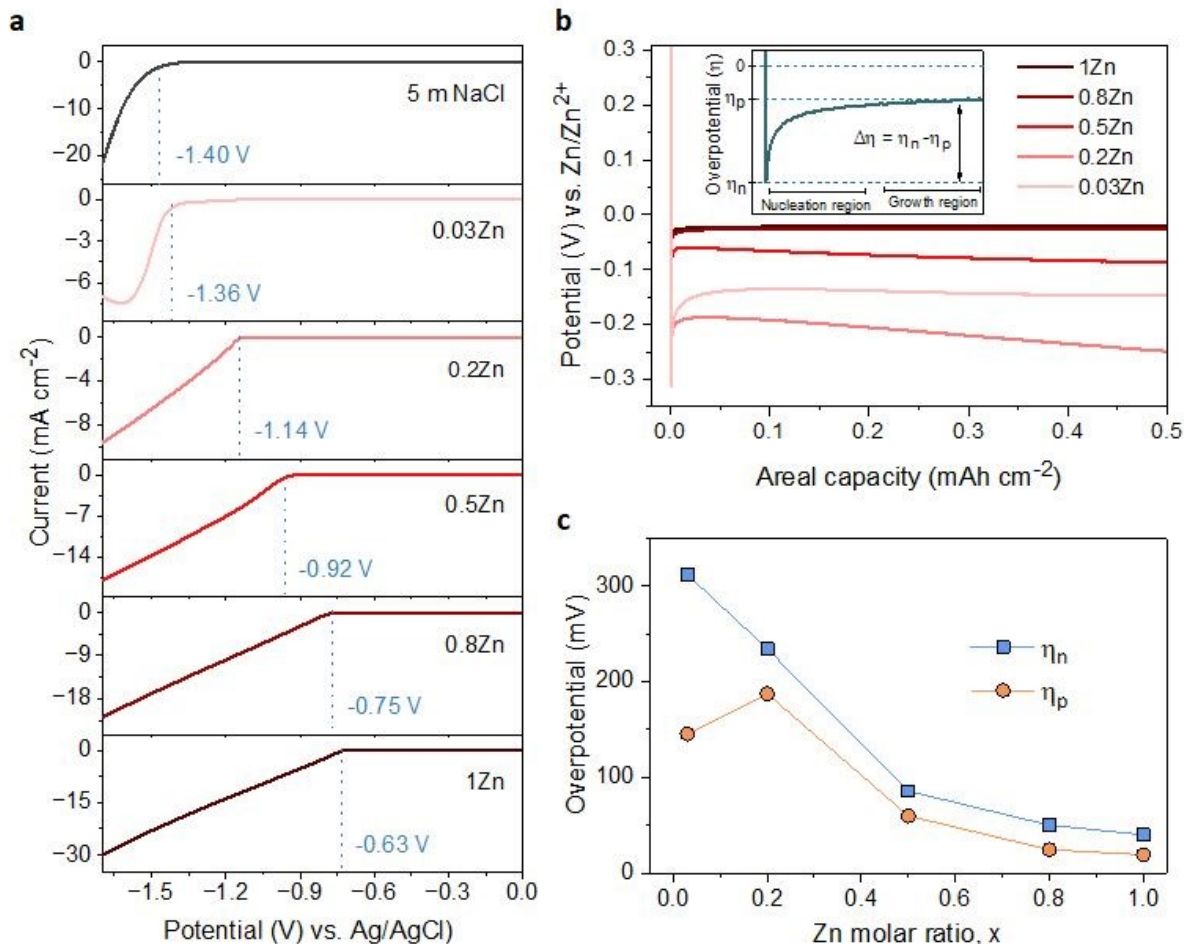
162 3.2. Stability of Zn foil in different WISEs

163 According to Raman results, water molecules interact with anions and cations present in each
164 WISEs in distinct ways. Prior to electrochemical tests, immersion experiments were conducted to
165 assess the impact of these WISEs on the thermodynamic stability of Zn metal anodes. For this, a
166 Zn foil was immersed in the prepared WISEs for a period of 10 days, subsequently rinsed with
167 deionized water, and dried under vacuum. The surface change of Zn foil before and after soaking
168 were then analyzed using X-ray powder diffraction (XRD) and scanning electron microscopy
169 (SEM). For comparison, the XRD pattern of the Zn foils immersed in WISEs were compared with
170 those immersed in 2M ZnSO₄ and 1 m ZnCl₂ diluted electrolytes. As expected the 2M ZnSO₄ shows
171 a distinct byproduct formation, which is identified as Zn₄SO₄(OH)₆·5H₂O byproduct ((see **Fig. 1c**),²¹
172 while only one characteristic byproduct peak is observed in 1 m ZnCl₂ (**Fig. S4**).²² In contrast, no
173 XRD patterns of byproducts are observed on the Zn foil soaked in different WISEs. This suggests
174 that byproduct formation is influenced by both the type of Zn salt and concentration. In addition,
175 SEM images are performed to analyze the surface of Zn metal in relation to the Zn molar ratio
176 (**Fig. 1d-i**). The bare Zn foil has a rough and uneven surface as indicated in **Fig. 1d**, which could
177 have been caused by the manufacturing process. In **Fig. 1e**, the electrode displays surface etching
178 in structured form parallel to each other in **0.03Zn** electrolyte. Dark spots and white small mossy
179 particles cover the Zn surface in **0.2** and **0.5Zn** electrolytes (**Fig. 1f-g**), while the Zn surface in **0.8**
180 and **1Zn** (**Fig. 1h-i**) displays pitting spots and particles formation, especially in **0.8Zn** electrolyte.
181 The latter is related to corrosion byproduct due to increased acidity. Overall, in all WISEs clear
182 corrosion is observed only at higher magnification except for **0.8Zn**. The immersion test reveals



183 that the side reactions generated from the direct interaction between the Zn anode and WISEs
184 are lower in comparison to diluted electrolytes.

185 3.3. Zn electrodeposition behavior



186
187 **Figure 2:** H₂ evolution and Zn deposition potentials in different WISEs. (a) LSV profiles of different
188 electrolytes at 10 mV s⁻¹ using a three-electrode system on Ti substrate. (b) Galvanostatic Zn
189 electrodeposition on Ti in Zn||Ti half cells at 1 mA cm⁻² and 0.5 mAh cm⁻² using different WISEs. Inset:
190 Schematic illustration showing nucleation overpotential (η_n), plateau overpotential (η_p), and the change
191 in overpotential (Δη). (c) The corresponding change in η_n, η_p, and Δη with Zn molar ratio.

192 To examine the effect of Zn molar ratio on H₂ evolution and Zn reduction potential in different
193 WISEs during electrodeposition processes, linear sweep voltammetry (LSV) measurements were
194 conducted. Indeed, it is common that in Zn²⁺ containing aqueous electrolytes, the H₂ evolution
195 occurs during Zn electrodeposition at similar reduction potential.²³ As a result, to discriminate
196 the Zn reduction from H₂ evolution, the WISEs were compared to a Zn-free electrolyte, here 5 m
197 NaCl solution. The experiments were performed using titanium foil (Ti) as working, Ag/AgCl as



198 reference, and platinum as counter electrodes at a scan rate of 10 mV·s⁻¹. The 5 m NaCl solution
199 reveals a reduction potential occurring at -1.4 V (**Fig 2a**), indicative of H₂ evolution, given the
200 absence of Zn²⁺ in the NaCl solution. In contrast, the onset reduction potential of **0.03Zn**
201 electrolyte is -1.36 V, which corresponds to Zn²⁺ reduction voltage – given that the water content
202 is very low. As the Zn ratio increases from **0.2** to **1**, reduction potentials of -1.14, -0.92, -0.75,
203 and -0.63 V are observed. Moreover, we conducted additional LSV experiments on a glassy
204 carbon (GC) substrate using a three-electrode system at scan rates of both 10 and 1 mV s⁻¹ (**Fig.**
205 **S5a** and **b**, respectively). The resulting reduction potentials in each electrolyte were similar to
206 those obtained with a Ti substrate, indicating similar kinetics limitations using different
207 substrates and scan rates. This result is consistent with previous findings in the literature by using
208 different ZnCl₂ concentration ranging from 1 to 30 m.^{11, 24} Therefore, the positive Zn reduction
209 potential observed with increasing Zn molar ratios is primarily attributed to the increased Zn²⁺
210 activity due to the lower acidity of the electrolyte, according to the Nernst equation below:

$$211 \quad E = E^\circ + \frac{RT}{2F} \ln \alpha_{[Zn^{2+}]} \quad (1)$$

212 Where E is the reduction potential, E° is the the standard reduction potential, R is the universal
213 gas constant, T is the temperature in kelvin, F is the Faraday's constant, and α is the activity of
214 Zn²⁺ ions. In addition, the LSV of the **0.03Zn** electrolyte with a pH of 10.9 was compared to a **31**
215 **m KAc** solution without Zn salt displaying a similar pH of 11.4, as shown in **Fig. S6**. The reduction
216 potential increased from -1.60 V and -1.62 V in **31 m KAc** to -1.37 and -1.33 V in **0.03Zn** on Ti
217 and GC at 10 and 1 mV s⁻¹, respectively. This increase in onset potential suggests that Zn
218 deposition occurs before H₂ evolution in the **0.03Zn** electrolyte. Similar findings were reported
219 by Daniel *et al* in an electrolyte containing 10 m KAc + 0.5 m ZnAc.²⁵ As a conclusion, the Zn
220 deposition potential increases with Zn molar ratio, while the H₂ evolution potential remains
221 constant, expanding the voltage gap between H₂ evolution and Zn deposition. The large voltage
222 gap minimizes H₂ evolution and other side reactions, thereby improving Zn anode performance.²⁶
223
224 The suppression of H₂ evolution may not consistently indicate dendrite free Zn deposition.
225 Additional insights into the effect of Zn²⁺ concentration in the electrolyte on Zn deposition are
226 necessary. It is widely acknowledged that the final morphology of deposited metal relies on the



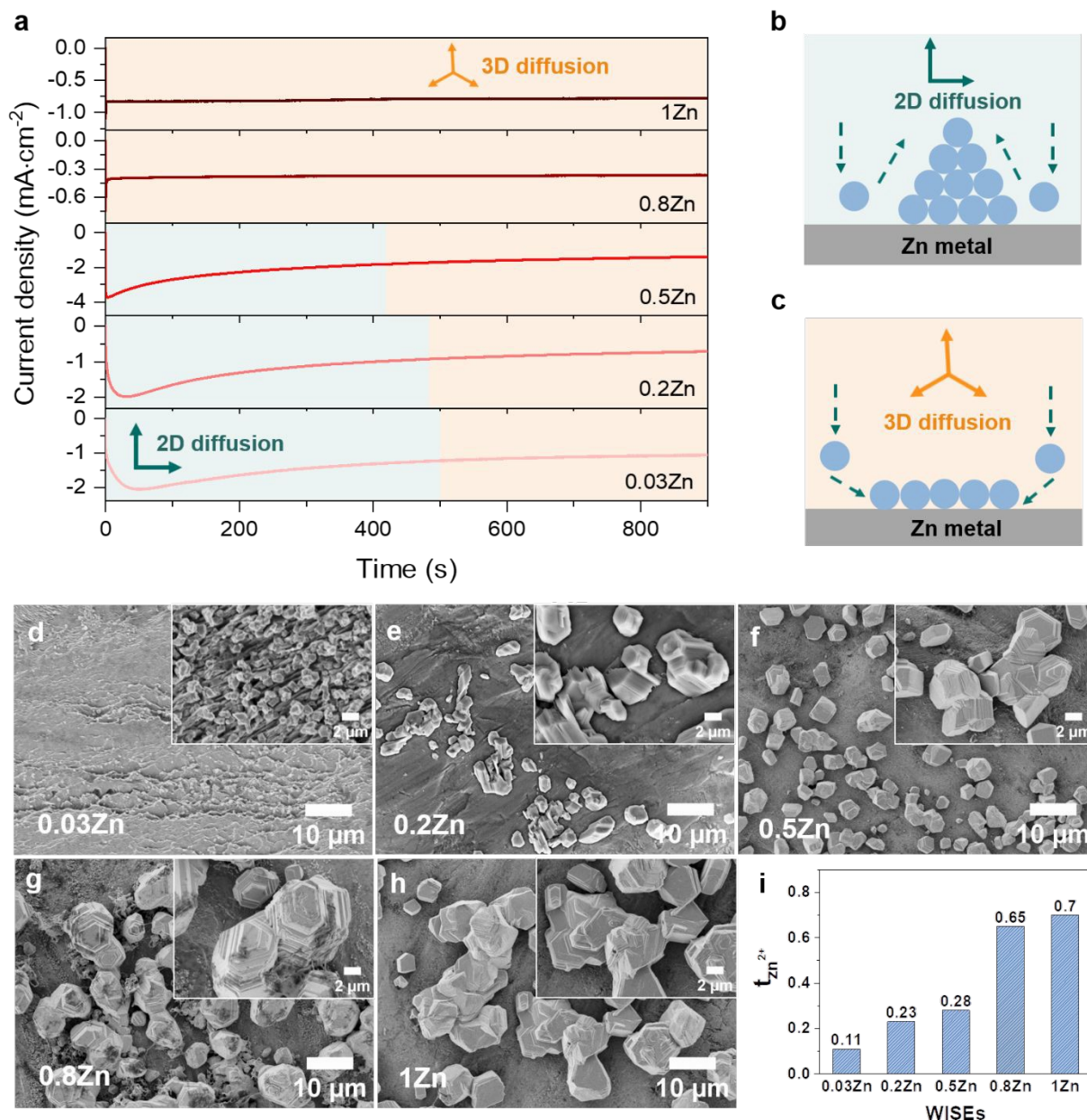
227 initial nucleation behavior.²⁷ Understanding the mechanism of nucleation behavior is crucial for
228 addressing the formation of Zn dendrites which can be assessed through nucleation
229 overpotential (η_n), driving the nucleation of Zn embryos.²⁸ A smaller nucleation overpotential
230 implies a lower energy barrier for initiating the Zn nucleation process, thereby facilitating uniform
231 Zn nucleation site formation.^{29, 30} Hence, cyclic voltammetry (CV) experiments were conducted
232 in a three-electrode system on Ti foil and GC substrates as the working electrode, platinum wire
233 as the counter electrode, and Ag/AgCl as the reference electrode, with a scan rate of 10 mV S⁻¹
234 within a potential range of -1.7 to 1.0 V. The CV curves (**Fig. S7**) for both electrodes exhibit similar
235 Zn deposition/dissolution behavior across various WISEs, indicating reversibility and the absence
236 of new redox reactions. However, the redox potential shifts to the right with increasing Zn ratio
237 due to higher Zn²⁺ activity at greater Zn²⁺ concentrations. Additionally, η_n can be calculated from
238 the potential difference between point (A), where Zn²⁺ ions begin to reduce, and the crossover
239 at point (A') formed during the right potential sweep as depicted in **Fig. S8**. The η_n measured
240 using Ti electrode decreases as the Zn²⁺ concentration increases: 103, 65, 43, and 37 mV
241 corresponding to **0.03**, **0.2**, **0.5**, **0.8**, and **1Zn** electrolytes, respectively. However, with the
242 exception of the **0.5Zn** electrolyte, no clear potential difference between A and A' was observed,
243 which cannot be explained.

244 Furthermore, the galvanostatic Zn deposition process is commonly employed not only to
245 determine η_n but also to assess another crucial parameter linked to growth, known as plateau
246 overpotential (η_p). η_n represents the magnitude of the potential spike at the onset of Zn
247 deposition, while η_p denotes the potential at the plateau following nucleation (see **Fig. 2b**).³¹
248 Additionally, the overpotential difference ($\Delta\eta$) is defined as the gap between η_n and η_p . The η_n
249 values are notably larger than the η_p values in all electrolytes due to the higher energy barrier
250 involved in forming a stable Zn atomic cluster (embryo) compared to adding a Zn atom onto
251 existing Zn nuclei (**Fig. 2c**), indicating that the electrodeposition of Zn follows the instantaneous
252 nucleation process.³² For instance, the η_n decreases as the Zn molar ratio increases: 311, 234, 86,
253 50, and 40 mV for **0.03**, **0.2**, **0.5**, **0.8** and **1Zn** electrolytes, respectively (**Fig. S9**). Simultaneously,
254 the η_p values are 145, 187, 60, 25, and 19 corresponding to **0.03**, **0.2**, **0.5**, **0.8** and **1Zn**
255 electrolytes, respectively. Similarly, $\Delta\eta$ decreases with Zn molar ratio; 166, 47, 26, 25, and 19 mV



256 for **0.03, 0.2, 0.5, 0.8, and 1Zn** electrolytes, respectively. The results show that the high Zn^{2+}
 257 concentration reduces the energy barrier for Zn nucleation and growth, likely due to reduced
 258 kinetics/diffusion resistance - promoting homogeneous Zn deposition.^{33,30}

259



260

261 **Figure 3: Zn diffusion process and the corresponding ions mobility in different WISEs.** (a)
 262 Chronoamperograms (CAs) of Zn deposition at an applied potential of -150 mV for 900 s. Insets: 2D (left)
 263 and 3D (right) diffusion for 0.03, 0.2, and 0.5Zn electrolytes; 3D diffusion for 0.8 and 1Zn electrolytes.
 264 Schematics showing (b) 2D and (c) 3D diffusion processes. The corresponding SEM images of deposited



265 Zn in (d) 0.03, (e) 0.2, (f) 0.5, (g) 0.8, and (h) 1Zn electrolytes. (i) The transference number in different
266 electrolytes.

267
268 The Zn nucleation and growth behavior were further analyzed on Zn metal by
269 chronoamperometry (CA) experiment at a fixed potential of -150 mV for 30 min using Zn||Zn
270 symmetric cells. The fluctuation of current transients can indicate a change in nucleation
271 processes and surface morphology.²⁷ As depicted in **Fig. 3a**, the current density exhibits a steady
272 rise over 50, 30, and 5 seconds in **0.03**, **0.2**, and **0.5Zn** electrolytes, respectively, followed by a
273 plateau, suggesting an initial phase of uncontrolled 2D diffusion transitioning into 3D diffusion.
274 During 2D diffusion process, Zn atom diffuse laterally to get the energetically favorable sites for
275 deposition,³⁴ which brings inhomogeneous nucleation on the Zn metal surface and accelerates
276 dendrite growth (**Fig. 3b**). In contrast, in **0.8** and **1Zn** electrolytes, a constant current density was
277 observed from the beginning referring to as 3D diffusion process (**Fig 3b**). This implies that the
278 Zn²⁺ ions are homogeneously deposited on the Zn electrode surface as the concentration of Zn²⁺
279 ions increases. These results are supported by the SEM images of the corresponding deposited
280 Zn in **Fig. 3d-g**. The electrolyte with the lowest Zn ratio (**0.03Zn**) shows a very small and
281 distributed Zn deposition particles (**Fig. 3d**). As the Zn molar ratio increases, the size of Zn nuclei
282 grows and interconnect each other to form a dense and compact Zn deposition (**Fig. 3e-h**),
283 indicating 3D deposition process. The results from CA and the corresponding SEM images
284 consistent with the η_n results in **Fig. 3c**, demonstrating that a higher Zn molar ratio contributes
285 to uniform and 3D Zn²⁺ deposition processes. This suppresses dendrite formation by enhancing
286 nucleation sites.²⁹

287 Furthermore, the cationic mobility in the bulk electrolyte is examined through transference
288 number which represents the ionic current carried by cations only. The Zn²⁺ transference number
289 ($t_{Zn^{2+}}$) was measured using the steady-current method, employing constant applied potential to
290 generate current-time(I-t) transient using Zn||Zn symmetric cells (**Fig. S10**).^{35, 36} The $t_{Zn^{2+}}$ for **0.03**,
291 **0.2**, **0.5**, **0.8**, **1Zn** WISEs are calculated to be 0.11, 0.23, 0.28, 0.65, and 0.70, respectively. This
292 indicates that electrolytes containing high Zn²⁺ concentrations exhibit higher $t_{Zn^{2+}}$ compared to
293 those with lower concentrations, suggesting that Zn²⁺ ions serve as the primary mobile ions to
294 reduce polarization.³⁷ This explains why the η decreases when the Zn²⁺ ions concentration

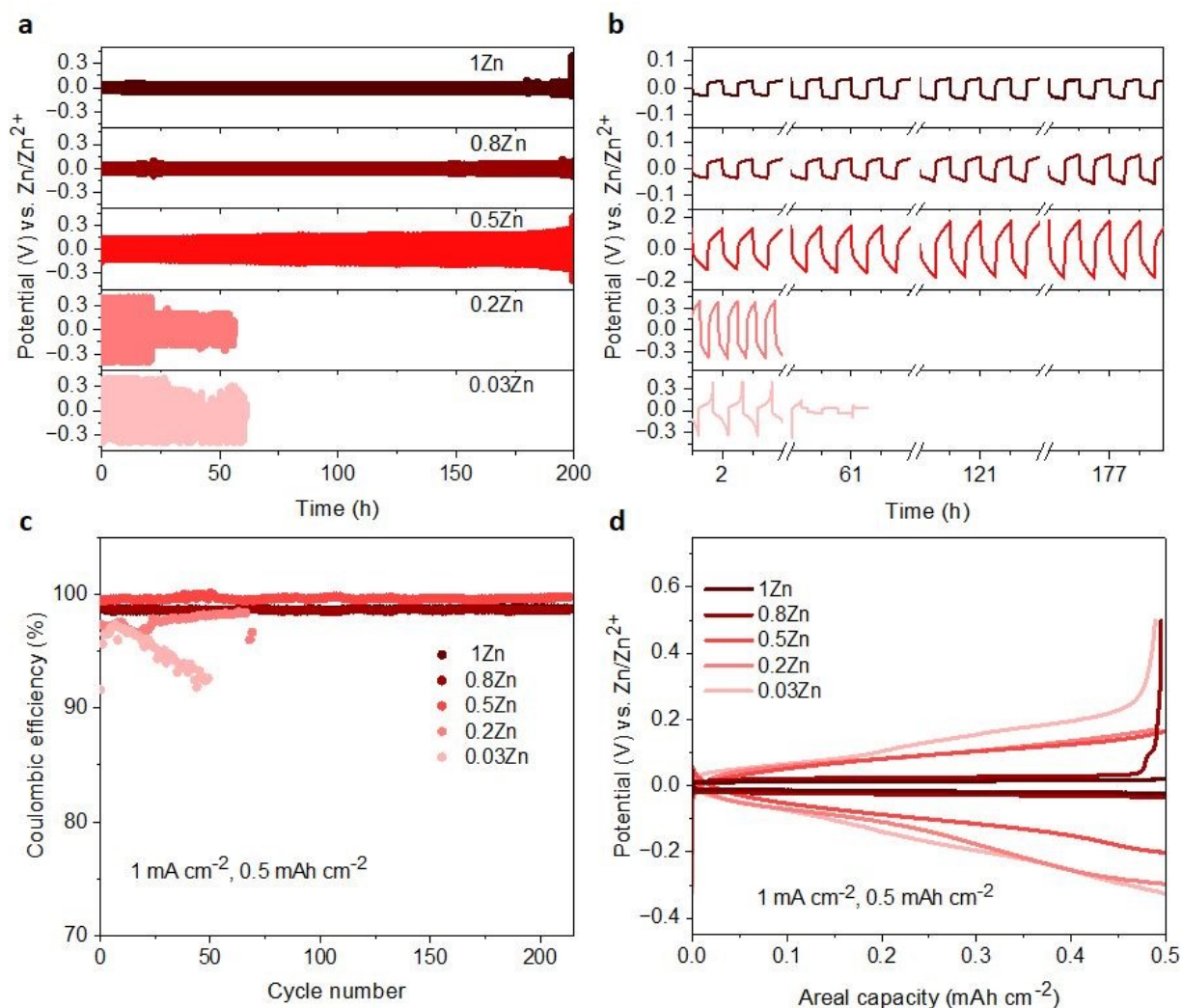


295 increases, as demonstrated in **Fig. 2b-c**. Moreover, the high $t_{\text{Zn}^{2+}}$ effectively enhances the anode's
296 electrochemical performance, and significant $t_{\text{Zn}^{2+}}$ can mitigate dendrite growth.¹⁹ Additionally,
297 the transport properties of WISEs including ionic conductivity, viscosity and ionicity were further
298 characterized and compared to $t_{\text{Zn}^{2+}}$. The viscosity values for **0.03**, **0.2**, **0.5**, **0.8**, and **1Zn**
299 electrolytes are 48, 537, 265, 317, and 465 mPa·s, respectively, while the corresponding ionic
300 conductivity values are 29, 4, 8, 5, and 6 mS cm⁻¹, respectively (**Table S1**). All WISEs display low
301 ionic conductivity and high viscosity except **0.03Zn** electrolyte which displays an opposite trend
302 (**Fig. S11a**). The later may be attributed to the high solubility of KAc and the lower acidity of K⁺
303 which results in lower ion pairing and allows for greater ion mobility, further enhancing ionic
304 conductivity. These findings confirm that the increase in the $t_{\text{Zn}^{2+}}$ is directly related to the Zn
305 molar ratio. Furthermore, a Walden plot was used to investigate the relationship between the
306 ionic conductivity and viscosity which reflects the ionicity of the electrolytes. **Fig. S11b** indicates
307 no direct correlation between the Zn molar ratio and ionicity, which is expected. Electrolytes with
308 Zn molar ratios of **0.03**, **0.2**, and **0.5Zn** exhibit a higher degree of dissociation, with **0.03** and **0.2Zn**
309 displaying super ionicity as they are located above the KCl ideal line. In contrast, the other
310 electrolytes, including **0.8**, **1Zn**, and diluted **0.5Zn**, show a slightly lower degree of ionicity, around
311 90%.

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324 3.4. Zn anode cycling stability



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326 **Figure 4: Zn plating/stripping stability.** Potential profiles for Zn||Zn cells conducted in 0.3, 0.2, 0.5, 0.8, and 1Zn electrolytes at current densities of (a) 2 mA cm⁻² with 0.5 mAh cm⁻² and (b) the corresponding
 327 overpotentials at different cycles. (c) CE of Zn plating/stripping on Cu substrate in different electrolytes at
 328 1 mA cm⁻² and 0.5 mAh cm⁻² current and capacity densities, respectively. (d) The corresponding potential
 329 profiles at 40th cycle.
 330

331 The Zn plating/stripping stability was evaluated in Zn||Zn symmetrical cells under current
 332 densities of 1 and 2 mA cm⁻², maintaining an areal capacity of 0.5 mAh cm⁻². The cycle lifespans
 333 of cells in **0.03Zn**, **0.2Zn**, **0.5Zn**, **0.8Zn**, and **1Zn** WISEs at 1 mA cm⁻² are 85, 55, 300, 350, and 500
 334 hours, respectively (**Fig. S12a**). The results indicate an improved cycling stability upon increasing
 335 Zn ratio except for **0.2Zn** electrolyte which exhibits slightly shorter cycle lifespan compared to
 336 **0.03Zn** electrolyte. In addition, lower plating-stripping overpotentials are observed for



337 electrolytes with higher Zn molar ratios from ~ 0.35 V in **0.03** to ~ 0.1 V in **1Zn** (Fig. S12b).
338 Increasing the current density to 2 mA cm^{-2} with the same areal capacity of 0.5 mAh cm^{-2} results
339 in cells failing after 25 hours of cycling in **0.03** and **0.2Zn** electrolytes, while cells in **0.5Zn**, **0.8Zn**,
340 and **1Zn** electrolytes sustains 200 hours of cycling (Fig. 4a). The corresponding overpotentials in
341 **0.03Zn** and **0.2Zn** electrolytes are around 0.7 V, while in **0.5Zn**, **0.8Zn**, and **1Zn** electrolytes,
342 overpotentials slightly decrease with increasing Zn ratios to 0.3 V for **0.5Zn** and 0.18 V for **0.8Zn**
343 and **1Zn** electrolytes (Fig. 4b). The overpotential in **0.5Zn** electrolyte slightly increased with
344 cycling time, while for **0.8Zn** and **1Zn**, remains constant. The decrease in overpotential as the Zn
345 molar ratio increases underscores the role of Zn^{2+} mobility in reducing overpotential. Deviation
346 of overpotential from the ideal value of 0 V vs Zn/Zn^{2+} during Zn plating/stripping process
347 suggests contributions from several factors, including H_2 evolution, corrosion byproducts such as
348 $\text{Zn}(\text{OH})_2$ and ZnO , or low transference number.^{23, 27} As all electrolytes exhibit reduced water
349 content, suggesting suppression of H_2 evolution during Zn plating/stripping. Consequently, Zn^{2+}
350 concentration becomes a determining factor in compensating for Zn loss attributed to the
351 formation of $\text{Zn}(\text{OH})_2$ and ZnO . Therefore, achieving an optimal Zn^{2+} concentration in WISEs
352 becomes crucial for enhancing the stability of Zn anodes. Hence, electrolytes with **0.5Zn**, **0.8Zn**,
353 and **1Zn** compositions demonstrate favorable reversibility and plating kinetics of Zn.
354 Moreover, the Coulombic efficiency (CE) serves as a pivotal metric for assessing the reversibility
355 of the Zn anode. To mitigate the influence of Zn^{2+} ions originating from the Zn electrode, CE
356 assessments should be conducted using a different substrate. Consequently, the CE of Zn
357 plating/stripping across various WISEs was evaluated employing $\text{Zn}||\text{Cu}$ at a current density of 1
358 mA cm^{-2} and a capacity of 0.5 mAh cm^{-2} , as shown in Fig. 4c. An initial CEs of 91.6, 97.3, 99.4,
359 99.1, and 98.7% are obtained in **0.03**, **0.2**, **0.5**, **0.8** and **1Zn** electrolytes, respectively. The cells
360 using **0.03** and **0.2Zn** electrolytes fail after 50 and 70 cycles with an average CE of 94.9 and 96.9%,
361 respectively. Low CE values are observed in Zn-deficient electrolytes during Zn plating/stripping
362 in contrast to the cells employing **0.5**, **0.8**, and **1Zn** electrolytes demonstrating a stable
363 reversibility with an average CEs of 99.6, 98.6, and 98.6 % after 214 cycles, respectively.
364 Remarkably, the CE value generally increases with rising Zn^{2+} concentration, except for the 0.5Zn
365 electrolyte, where the highest CE is observed. However, no significant differences are observed

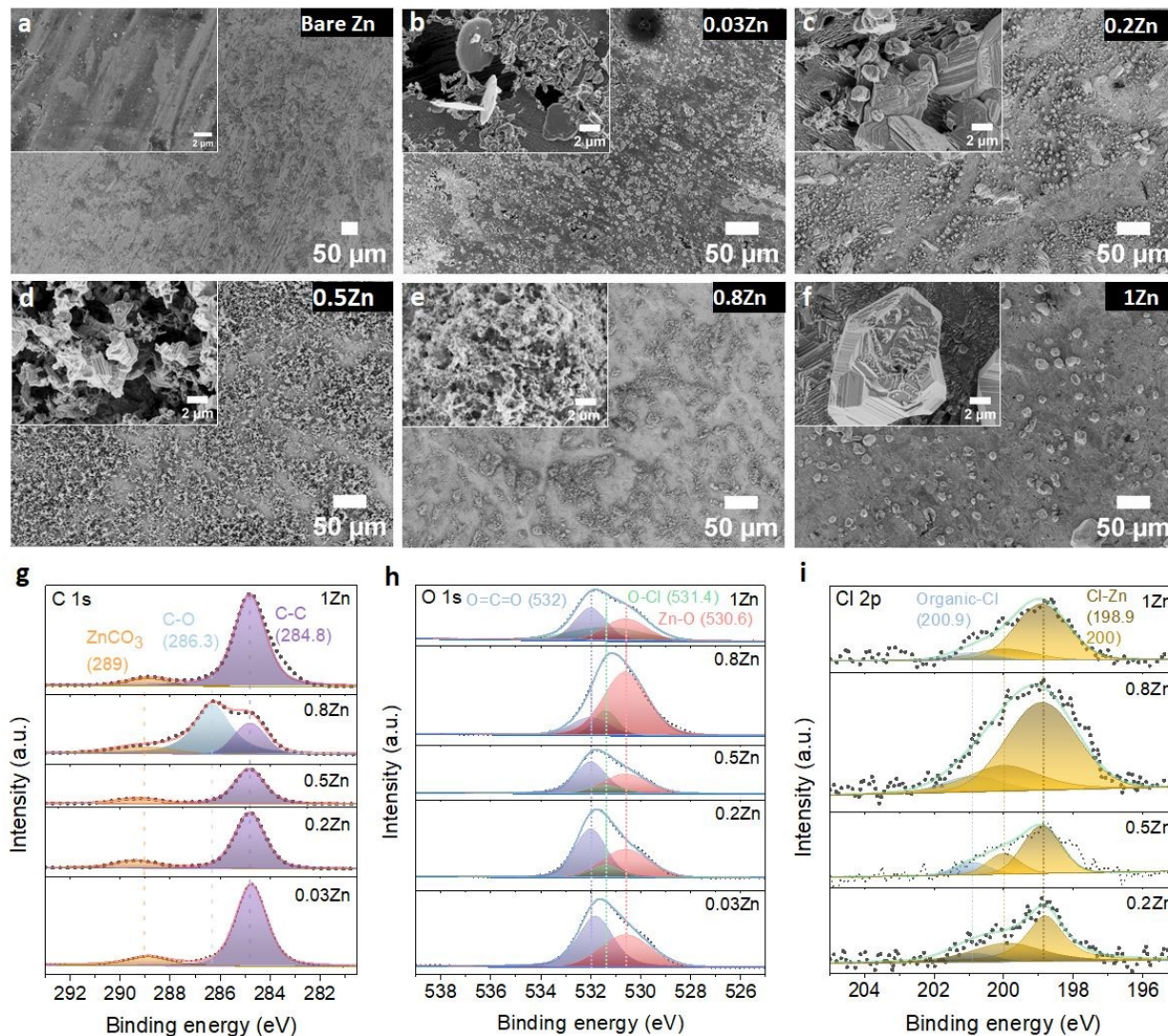


366 among CE values starting from a **0.5Zn** ratio. Furthermore, a similar trend in CE is shown using Ti
367 as substrate in Zn||Ti half-cells (**Fig. S13**) at 1 mA cm^{-2} and 0.5 mAh cm^{-2} . Short cycling life is
368 obtained in **0.03Zn** and **0.2Zn** electrolytes, however, as the concentration of Zn^{2+} increases the
369 cell runs for 100, 180, and 260 cycles with (>96%) CE in **0.5Zn**, **0.8Zn**, and **1Zn** electrolytes,
370 respectively.

371 Furthermore, **Fig. 4d** and **Fig. S14** display the potential profiles in Zn||Cu half-cells which
372 demonstrate a lower and stable plateau overpotentials as the Zn ratio increases. A higher
373 overpotential of 183 mV is obtained in **0.03Zn** electrolyte, whereas an overpotentials of 164, 135,
374 47 and 30 mV are obtained in **0.2**, **0.5**, **0.8**, and **1Zn** electrolytes after 40th cycles, respectively.
375 The above results show that the Zn molar ratio of **0.5** and above provide better Zn anode
376 performance compared with **0.03** and **0.2**. Thus, suggesting an optimum amount of Zn^{2+}
377 concentration should be present in the electrolyte rather than simply increasing the supporting
378 salt to achieve WISE region. This in turn reduces the interfacial resistance related with the
379 supporting salt, which is manifested by the lower overpotentials and polarization for Zn
380 plating/stripping. According to these results, Zn molar ratios less than **0.5** have a significant
381 influence, whereas those greater than **0.5** have less influence, indicating the need for an optimal
382 Zn^{2+} concentration to achieve enhanced Zn plating/stripping in WISEs.

383 **3.5. Zn surface composition after cycling**

384 To further examine the influence of Zn molar ratio on facilitating uniform Zn^{2+} deposition, the
385 surface morphology of Zn and the resulting interphase following cycling were analysed employing
386 SEM and X-ray photoelectron spectroscopy (XPS) techniques.



387

388 **Figure 5: Morphology evolution and surface composition of Zn electrodes after 20 cycles of Zn**
 389 **plating/stripping in different WISEs at 1 mA cm⁻² and 0.5 mAh cm⁻².** SEM images of (a) bare Zn and cycled
 390 Zn anode in (b) 0.03, (c) 0.2, (d) 0.5, (e) 0.8, and (f) 1Zn electrolytes. The corresponding XPS spectra of (g)
 391 C 1s, (h) O 1s, and (i) Cl 2p.

392

393 First, the morphology of the Zn anode after 20 cycles at 1mA cm⁻² current and 0.5 mAh cm⁻²
 394 capacity densities was investigated by SEM. The SEM images on Zn anode shows uneven
 395 morphology with black spots and pits in **0.03Zn** electrolyte (**Fig. 5b**), which may be due to
 396 corrosion byproduct formation. The **0.2Zn** electrolyte (**Fig. 5c**), on the other hand, displays
 397 deposition of small particles distributed on the Zn surface while these particules are multiplied
 398 in **0.5Zn** indicating a more porous surface (**Fig. 5d**). The Zn surface becomes denser and compact
 399 as the Zn ratio increases in **0.8** and **1Zn** electrolytes (**Fig. 5e** and **f**). The SEM results show that



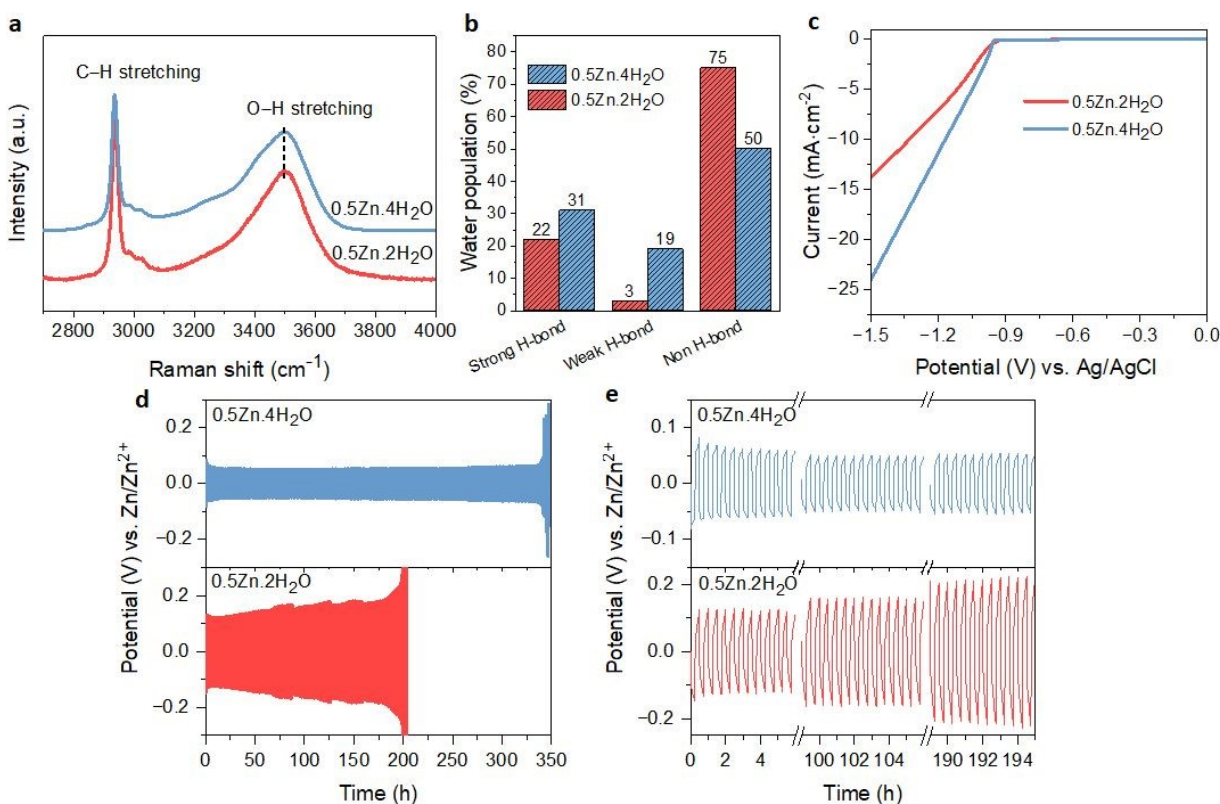
400 there is no direct correlation between all Zn molar ratios, particularly those below **0.5Zn**.
401 However, the surface of Zn foil is less rough with lower surface porosity upon increasing the Zn
402 molar ratio from **0.5Zn**. In addition, the magnified image of the electrode, in particular in the **1Zn**
403 electrolyte, reveals a more compact and denser morphology. XPS analysis were conducted to
404 further examine the chemical composition of cycled Zn surface. The C 1s peaks (**Fig. 5g**) are
405 deconvoluted into three components. The binding energy at 284.8 and 286.3 eV are attributed
406 to C-C and C-O peaks, respectively, while the peak at 289 eV is assigned to CO₃. However, the
407 peak at 286.3 eV is observed only in **0.8Zn** electrolyte, indicating the formation of more
408 carbonate containing species. The C 1s peaks in **1Zn** electrolyte may be originated from adsorbed
409 organic residues contamination. The O 1s spectra (**Fig. 5h**) demonstrates the presence of three
410 components corresponding to O=C=O (532 eV), O-Cl (531.4 eV), and Zn-O (530.6 eV) in **0.2**, **0.5**,
411 **0.8**, and **1Zn** electrolytes, indicating the existence of inorganic residues from electrolyte
412 decomposition. For **0.03Zn** electrolyte, since there is no chlorine, only C-O and Zn-O bonds of the
413 Zn carbonate and Zn oxides are observed. The Cl 2p spectra shows two chlorine species
414 corresponding to inorganic and organic chlorine at 198.9 and 200.9 eV (**Fig. 5i**). Moreover, the 2p
415 orbital of Zn is separated into two peaks (**Fig. S15**), corresponding to 2p_{3/2} (1021.9 eV) and 2p_{1/2}
416 (1045 eV). The above result indicates the cycled Zn surface contains organic/inorganic layer, the
417 organic species generated from acetate (Ac) decomposition while the chlorine and Zn containing
418 inorganic species are derived from the ZnCl₂. Overall, the composition of each species generated
419 from electrolyte decomposition on Zn anode surface after cycling are similar in the different
420 electrolytes.

422 3.6. WIS-like dilute electrolyte

423 The results aboved showed that the suppression of free water in WISEs is not enough for the
424 stability of Zn anode, instead, it is the of Zn molar ratio that plays an important role. On the other
425 hand, the water-deficient and anion-rich solvation structure of Zn²⁺ can be also achieved in dilute
426 electrolytes if the solvation ability of anion is higher than that of water.^{15, 38} Recently, this idea
427 was demonstrated in Zn(Ac)₂·2H₂O and KAc hybrid electrolyte since the Ac anions have a stronger
428 coordination ability to Zn²⁺ than water. Specifically, optimal CE and rate performance were



429 attained with a water-to-cation ratio of 10 in the $\text{Zn}_{0.2}\text{K}_{0.8}\text{OAc}_{1.2} \cdot 10\text{H}_2\text{O}$ electrolyte (abbreviated
430 here as $0.2\text{Zn} \cdot 10\text{H}_2\text{O}$).¹⁵ To validate this concept within our prepared WISEs $[(\text{ZnCl}_2)_x(\text{LiAc})_{1-x}/(\text{H}_2\text{O})_n]$,
431 we chose the **0.5Zn** electrolyte because it contains a high amount of Ac anion and
432 considered the optimal ratio for improving CE and rate performance.



433
434 **Figure 6: Solvation structure and electrochemical stability of Zn anode in 0.5Zn.4H₂O electrolyte**
435 **compared to concentrated 0.5Zn.2H₂O.** (a) Raman spectra in the water region. (b) The corresponding
436 water population percentages. (c) LSV curves on Ti substrate (d) Zn plating/stripping at 2 mA cm⁻² and 0.5
437 mAh cm⁻² in Zn||Zn symmetric cells. and (e) The corresponding potential profiles.

438
439 The **0.5Zn** (labeld as 0.5Zn.2H₂O herein after) WISE was diluted to 15 m by increasing the water-
440 to-cation ratio (n) to 4 (labeled as 0.5Zn.4H₂O). Raman spectroscopy was employed to investigate
441 the H-bonding enviroments of water in the 0.5Zn.4H₂O electrolyte and compared with that of
442 0.5Zn.2H₂O. As shown in **Fig. 6a**, the Raman spectra of the 0.5Zn.4H₂O electrolyte displays
443 broader peaks compared to the 0.5Zn.2H₂O, indicating a higher concentration of water molecules
444 relative to Ac anions. Furthermore, the deconvoluted spectra of the 0.5Zn.4H₂O compared to
445 0.5Zn.2H₂O electrolytes reveales distinct hydrogen-bonding environments in the water region.



446 As shown in **Fig. 6b** and **Fig. S16a**, the area under the sub-band associated with strongly
447 hydrogen-bonded water molecules in the 0.5Zn.4H₂O electrolyte (31%) is slightly higher
448 compared to that of the 0.5Zn.2H₂O electrolyte (22%). Notably, the corresponding peak position
449 exhibits a slight shift towards lower frequencies in the 0.5Zn.4H₂O electrolyte (3255 cm⁻¹)
450 compared to the 0.5Zn.2H₂O (3285 cm⁻¹) (**Fig. S16b**). In addition, the weak hydrogen-bond peak
451 area increased from 3% to 19% in the diluted 0.5Zn.4H₂O electrolyte. The peak area attributed
452 to non-hydrogen-bonded water is 54% in 0.5Zn.4H₂O, which decreased in comparison to
453 0.5Zn.2H₂O electrolyte. Thus, the higher proportion of strongly hydrogen-bonded water
454 molecules and lower proportion of non-hydrogen-bonded water in 0.5Zn.4H₂O compared to
455 0.5Zn.2H₂O suggests the presence of free water molecules.

456 The influence of free water molecules on Zn surface morphology and corrosion byproducts was
457 investigated following immersion test in the 0.5Zn.4H₂O electrolyte for 10 days. Subsequent
458 analysis using XRD techniques reveals no XRD patterns indicative of corrosion byproducts (**Fig.**
459 **S17a**). However, The SEM images show many black spots and mossy particles (**Fig. S17b**),
460 suggesting the formation of byproducts formation due to the presence of free water molecules.
461 The CV analysis of Zn plating/stripping on Ti foil in 0.5Zn.4H₂O electrolyte exhibits comparable
462 profiles to those observed in the 0.5Zn.2H₂O electrolyte (**Fig. S18a**), suggesting the absence of
463 new electrochemical reactions. However, the cell utilizing 0.5Zn.4H₂O shows higher nucleation
464 overpotential (14 mV) compared to that of 0.5Zn.2H₂O. The corresponding LSV curve (**Fig. 6c**)
465 demonstrates a notably higher cathodic current in 0.5Zn.4H₂O electrolyte compared to the
466 0.5Zn.2H₂O electrolyte, confirming the contribution of H₂ evolution in 0.5Zn.4H₂O electrolyte.

467
468 Furthermore, the effect of free water molecules in 0.5Zn.4H₂O electrolyte on the nucleation and
469 growth process of Zn were investigated through CA using Zn||Zn symmetric cells similar to the
470 previous protocol (**Fig. S18b**). The Zn anode in 0.5Zn.4H₂O electrolyte shows a 2D diffusion
471 process for 19 s longer than in 0.5Zn.2H₂O, followed by a constant 3D diffusion process
472 thereafter. However, the corresponding SEM images in **Fig. S18d** displays similar size and
473 morphology as the particles in concentrated 0.5Zn.2H₂O – indicating similar growth mechanism.
474 Furthermore, the $t_{Zn^{2+}}$ in 0.5Zn.4H₂O electrolyte is 0.54 (**Fig. S18c**), which is higher than in



475 0.5Zn.2H₂O electrolyte due to lower viscosity combined with increased ionic conductivity (**Table**
476 **S1**).

477 The Zn anode plating/stripping reversibility in 0.5Zn.4H₂O electrolyte was demonstrated using
478 Zn||Zn half-cell at different current density with a fixed capacity of 0.5 mA cm⁻², as demonstrated
479 in **Fig. 6d-e** and **Fig. S19**. The cell utilizing the 0.5Zn.4H₂O electrolyte failed after 130 cycles at
480 lower current density of 1 mA cm⁻², whereas the cell with the 0.5Zn.2H₂O electrolyte sustain for
481 300 cycles (**Fig. S19a** and **b**). In contrast, the cell with the 0.5Zn.4H₂O electrolyte at 2 mA cm⁻²
482 current density sustains over 350 cycles without experiencing potential fluctuations, whereas the
483 cell using 0.5Zn.2H₂O electrolytes experienced short circuits around 200 cycles (**Fig. 6d** and **e**).
484 These results demonstrate that the 0.5Zn.4H₂O electrolyte offers superior Zn stability at higher
485 current densities, while the reverse is observed at lower current densities, consistent with the
486 LSV data in **Fig. 6c**.

487 The diluted electrolyte was also compared to the recently reported WIS-like Zn_{0.2}K_{0.8}OAc_{1.2} 10H₂O
488 electrolyte (abbreviated as 0.2Zn.10H₂O).¹⁵ As depicted in **Fig. S19c** and **d**, the Zn||Zn cell with the
489 0.2Zn.10H₂O electrolyte cycled for over 150 cycles with significant potential fluctuations at 1 mA
490 cm⁻² and 0.5 mAh cm⁻², while the 0.5Zn.4H₂O electrolyte provides 130 cycles but without any
491 potential fluctuation. Doubling the current density with the same capacity yields approximately
492 160 cycles in the 0.2Zn.10H₂O electrolyte with higher overpotential. However, the 0.5Zn.4H₂O
493 electrolyte deliver over 350 cycles without any potential fluctuation compared to the
494 0.2Zn.10H₂O electrolyte. Again these results indicates the importance for Zn molar ratio for Zn
495 cycling stability in particular at high current density. Note, the obtained stability of 0.2Zn.10H₂O
496 is different in this work from the reported paper. This can be explained by the difference in the
497 Zn anode size, where here we used 13 mm in contrast to 6 mm diameter. As the Zn electrode size
498 decreases, better contact between electrodes results from increased pressure. This heightened
499 pressure, in turn, influences the ion flux and distribution of current. Hence, the homogeneisation
500 of the Zn anode size is important for future research.

501 Finally, the cycled Zn electrodes after 20 cycles at 1 mA cm⁻² and 0.5 mAh cm⁻² were analysed
502 using SEM and XPS. The SEM image illustrates a similar morphology to the Zn electrode in
503 0.5Zn.2H₂O electrolyte (**Fig. 5d**). However, the Zn electrode in the 0.5Zn.4H₂O electrolyte displays



504 a more porous and non-uniform structure (**Fig. S20**), indicative of dendrite growth and byproduct
505 formation likely caused by the presence of free water molecules. The composition of the cycled
506 Zn electrode was further analyzed by XPS. As shown in **Fig. S21a**, the survey spectra indicate the
507 presence of C, O, Zn, and Cl elements. The presence of characteristic C 1s peaks at 284 eV (C-C)
508 and 289 eV (CO₃) in **Fig. S21b** suggests the adsorption or decomposition of Ac anions on the surface
509 of the Zn electrode. The O 1s spectra reveal the presence of C-O and C-Cl species (**Fig. S21c**),
510 while the Cl 2p (**Fig. S21d**) exhibit organic and inorganic chlorine species. The type and position
511 of each peak in this electrolyte are consistent with those observed in the 0.5Zn.2H₂O electrolyte
512 discussed previously. The organic species may originate from Ac, while the inorganic species may
513 be derived from ZnCl₂. Therefore, these findings indicate that optimizing the mixing salt ratio in
514 dilute solutions also enhance Zn anode stability, particularly at higher current densities, if WISE-
515 like coordination of Zn²⁺ ions is achieved.

516 517 **4. Conclusion**

518 In summary, we conducted a systematic investigation into how varying Zn molar ratios affect the
519 nucleation behavior, deposition process, and cycling stability of Zn metal anodes across different
520 WISEs. Our findings reveal a direct correlation between Zn overpotentials, deposition process,
521 and cycling stability with the concentration of Zn²⁺ in the electrolyte. With increasing Zn molar
522 ratio, there is an expansion in the potential difference between Zn reduction and H₂ evolution
523 due to the positive shift in Zn reduction potential. Moreover, we observed the formation of
524 interconnected, larger and dense Zn nuclei on Zn foil at Zn molar ratio. This phenomenon can be
525 attributed to lower nucleation and growth overpotentials resulting from increased nucleation
526 sites with rising Zn²⁺ concentration. Consequently, Zn metal anodes perform better in 0.5, 0.8,
527 and 1Zn WISEs compared to 0.03 and 0.2Zn WISEs, owing to enhanced $t_{Zn^{2+}}$ and lower
528 overpotentials. Cycling stability analysis indicates an optimal Zn molar ratio around 0.5. Beyond
529 the later ratio, the impact of Zn molar ratio primarily affects only Zn plating/stripping
530 overpotentials while maintaining similar cycling times. Furthermore, taking the 0.5Zn electrolyte,
531 the impact of water content was studied by diluting the solution by half. For the examined diluted
532 electrolyte (0.5Zn.4H₂O), a WISE-like coordination environment is achieved around Zn²⁺, enabling



533 to achieve high rate performance compared to most other concentrated electrolytes. However,
534 to the expense of lower stability at low current density due to promoted H₂ evolution as a result
535 of increased free water population. Hence, this study shows the importance of increasing the Zn
536 salt concentration during the preparation of WISEs. An optimum Zn molar ratio of 0.5 was found
537 which is already considered high in comparison to most reported WISEs in the literature. Hence,
538 this study brings a new insight for the future design of WISEs to achieve high performant AZIBs.

539

540 Declaration of interests

541 The authors declare no competing interests.

542

543 Data availability

544 The data supporting this article have been included as part of the Supplementary Information.

545

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Data availability

The data supporting this article have been included as part of the Supplementary Information.

