

Measuring Zn Transference with Precision: Insights for Dendrite-Free Zinc Metal Anodes

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ABSTRACT

Electrolyte engineering in Zn-metal batteries frequently explores the use of alkaline metal salts to enhance conductivity and reduce overpotential for Zn plating and stripping. While these additives improve conductivity, the presence of more mobile alkali cations can negatively affect the Zn^{2+} transference number. Optimizing the Zn^{2+} transference number is crucial for high-rate performance, efficiency, and safety, as a high Zn^{2+} transference number minimizes concentration polarization and dendrite formation during high-current cycling. However, reliably measuring the transference number of Zn ions in non-binary electrolytes presents significant experimental challenges due to the dynamic nature of Zn metal interfaces, rendering traditional methods ineffective. Here, we introduce a modified Hittorf-type method to reliably measure Zn^{2+} transference numbers in complex electrolytes. Supported by MD simulations, we apply this method to accurately obtain transport numbers of Zn^{2+} , K^+ and acetate ions in Zn-K acetate electrolytes. By varying the Zn^{2+} fraction, we study the impact of co-electrolytes on transport properties and correlate these with the Zn solvation environment using X-ray absorption spectroscopy. We reveal that while overall ionic conductivity notably increases with the addition of KOAc co-salt, the Zn^{2+} transference number dramatically decreases. Electrolytes with higher Zn^{2+} transference numbers enable longer high-rate cycling, underscoring the importance of optimizing Zn^{2+} transference for improved performance and stability of Zn-metal anodes.

INTRODUCTION

Lithium-ion batteries, despite their current dominance, face significant challenges for large-scale, long-term grid energy storage, including high cost, safety concerns, and environmental impact.^{1, 2} Aqueous batteries, particularly Zn metal batteries, emerge as a compelling alternative due to the high theoretical capacities of Zn metal anodes ($\sim 820 \text{ mAh g}^{-1}$ gravimetric and $\sim 5800 \text{ mAh cm}^{-3}$ volumetric), their lower cost, enhanced safety and sustainability.^{3, 4} However, the commercialization of Zn metal batteries is challenged by the dendrite formation during Zn plating and the concurrent hydrogen evolution reaction (HER).⁵ These processes reduce cycle life and compromise safety, ultimately leading to inefficient operation and shorter battery life.^{5, 6}

Recently, electrolyte engineering emerged as an effective approach to improve the performance and longevity of Zn-metal anodes. Many studied electrolyte formulations often incorporate alkali metal supporting salts (e.g. LiTFSI,⁷ KOAc,⁸ NaClO₄,⁹ LiOTf¹⁰), which enhance ionic conductivity and therefore reduce the overpotential for Zn plating/stripping and/or can enable very high concentrations for water-in-salt regimes⁷⁻¹⁰ that help suppress HER. While these co-salts can boost electrolyte conductivity,^{11, 12} they also introduce competing mobile cations which can negatively impact the Zn^{2+} transference number.^{13, 14}

For Li metal batteries the clear correlation was demonstrated that high transference number of Li^+ and improved high-rate performance and cycling efficiency.^{15, 16} A high transference number minimizes concentration gradients during polarization, thus reducing charge/discharge overpotential and mitigating

dendrite formation during high-current cycling.^{15, 17-19} However, for Zn-metal batteries, the effect of co-salts on the Zn^{2+} transference number is less well understood, despite its crucial role in determining battery performance and stability. This can be explained by the fact that measuring the Zn^{2+} transference number in non-binary electrolyte systems presents significant experimental challenges.²⁰⁻²³ Traditional approaches, such as the Bruce-Vincent method, fail to yield accurate transference numbers in complex multicomponent electrolytes due to the single ion quantification capabilities.^{15, 24} Moreover, the dynamic nature of Zn metal interfaces, make this approach suboptimal for robust transference number quantification.^{25, 26} Other methods such as pulse field gradient NMR are not practical for Zn as its only NMR-active ^{67}Zn isotope is a low sensitivity nucleus with strong quadrupolar moment requiring high fields and complex pulse sequences.^{27, 28, 29, 30} This limitation underscores the need for robust approach that can reliably quantify the transport properties of Zn^{2+} in the presence of co-electrolytes.^{31, 32}

In this work, we address these challenges by introducing a modified Hittorf-type method for reliably measuring the Zn^{2+} transference number in complex, non-binary concentrated electrolytes. This method enables us to investigate the effects of co-electrolytes on the transport properties of Zn^{2+} , K^+ , and acetate (OAc^-) ions in multi component electrolytes. Additionally, we employ X-ray absorption spectroscopy (XAS) to correlate transport properties with the solvation environment of Zn^{2+} , providing deeper insights into how co-salts influence Zn^{2+} mobility and coordination. We then correlate our findings with the Zn plating/stripping efficiency, morphology and cycling stability for different current densities.

RESULTS AND DISCUSSION

Electrolyte physicochemical properties

In this work, we investigate the influence of co-salt fractions on the solvation environment of Zn cations, transport properties, Zn deposition efficiency, and morphology. To achieve this, we examine a $\text{Zn}_x\text{K}_{1-x}\text{OAc}_{1+x}\cdot 30\text{H}_2\text{O}$ electrolyte series ($x = 0.2, 0.4, 0.6, 0.8, 1$), systematically varying the Zn^{2+} fraction. By fixing the concentration at 30 H_2O molecules per cation, we ensure a consistent basis for comparison, avoiding contributions from concentration-induced changes in solvation environment and electrolyte properties.⁸ The 30 H_2O per cation concentration was selected as it corresponds to the maximum solubility of ZnOAc_2 , allowing us to explore a broad range of Zn:K compositional ratios.

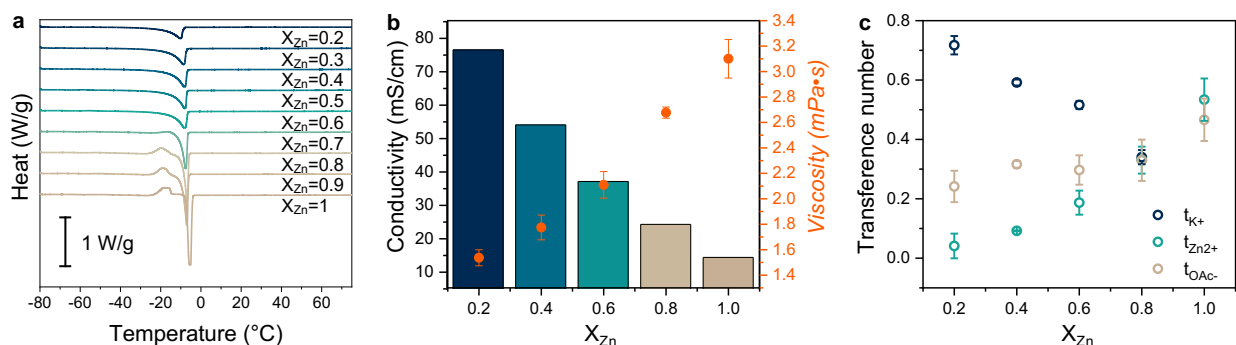


Figure 1. Physicochemical properties of the electrolytes $\text{Zn}_x\text{K}_{1-x}\text{OAc}_{1+x}\cdot 30\text{H}_2\text{O}$, for $0 < x < 1$. **a.** DSC data collected from -80°C to 80°C (phase transitions T_g is a positive peak, and T_m is a negative peak). **b.** Viscosity and conductivity changes as function of Zn fraction (X_{Zn}). **c.** Transference number values as obtained from Hittorf-ICP-OES technique for electrolytes with different Zn fraction.

First, we studied thermal properties of the electrolytes: Differential Scanning Calorimetry (DSC) profiles can be seen in **Figure 1a**. For Zn-rich systems, an exothermic peak at $\sim -16^{\circ}\text{C}$ is observed before the melting point. This peak is often correlated to the crystal nucleation and growth. The decrease of this peak with increase in K^+ reflects a phase transition to a more disordered single-phase frozen brine at lower Zn fractions.^{33, 34} The melting temperature (T_m) increases from -5.5°C ($X_{\text{Zn}} = 1$) to -9.9°C ($X_{\text{Zn}} = 0.2$, **Figure S1**) as Zn fraction decreases which can be attributed to changes in the ionic interactions,^{35, 36} solvation structure,³⁴ and overall system disorder³⁷ as the composition shifts from Zn-rich to K-rich system.

As shown in **Figure 1b** and **Table S1**, the electrolyte's viscosity decreases by a factor of 2 with a reducing X_{Zn} fraction, dropping from ~ 3 mPas ($X_{\text{Zn}}=1$) to ~ 1.5 mPas ($X_{\text{Zn}}=0.2$). This trend aligns with DSC data, suggesting weaker inter-ionic interactions and increased disorder in the electrolyte structure at lower Zn content. Concurrently, the conductivity increases sharply, from 14.4 mS/cm ($X_{\text{Zn}} = 1$) to 76.5 mS/cm ($X_{\text{Zn}} = 0.2$) which still notably below the value of 138 mS/cm for the pure KOAc $30\text{H}_2\text{O}$ solution (measured at 25°C). At first glance, this suggests that potassium-rich electrolytes have superior transport properties for battery applications.

Zn²⁺ transport properties and solvation environment

Next, we evaluated Zn-specific transport by measuring its transference number (t_{Zn}) in our electrolyte series at varying Zn:K ratios. As discussed, to address the challenges associated with measuring transference numbers in multicomponent electrolytes with dynamic interfaces, we developed a robust approach based on a modified Hittorf method. This method, detailed in *Materials and Methods Section*, utilizes the Hittorf cell (**Figure S2**)^{14, 38, 39} and employs ICP-OES to quantify changes in the Zn and K concentrations in each compartment due to electromigration. By analyzing these concentration changes, we can accurately determine transference numbers not only for Zn^{2+} but also for the supporting cations (K^+) and anions in the electrolyte.

Figure 1c and **Table S2** shows a rapid decrease in the Zn^{2+} transference number (t_{Zn}) as the KOAc fraction increases. In pure $\text{Zn}(\text{OAc})_2$ ($X_{\text{Zn}} = 1$), the $t_{\text{Zn}} = 0.53 \pm 0.071$, which is in good agreement with value for $\text{Zn}(\text{OAc})_2$ under infinite dilution.⁴⁰ Introducing K^+ at a 0.2 fraction ($X_{\text{Zn}} = 0.8$) causes t_{Zn} to drop significantly to 0.330 ± 0.046 , while the K^+ transference number (t_{K}) is 0.340 ± 0.024 . At $X_{\text{Zn}} = 0.2$, the t_{Zn} decreases down to 0.04 ± 0.04 , while t_{K} rises to 0.71 ± 0.031 and $t_{\text{OAc}} = 0.242 \pm 0.053$, indicating that Zn-ionic species are transported primarily by diffusion in this electrolyte. These results highlight a key trend: while electrolytes with high K fractions have higher total conductivity (**Figure 1 b**), Zn^{2+} contributions to total ion transport are substantially reduced in those. Thus, Zn-specific ionic conductivity remains relatively high only at Zn fractions of $X_{\text{Zn}} \geq 0.8$ (**Figure S3**).

To better understand the observed Zn transference number trends and their connection to electrolyte structure, we examined how the Zn solvation environment changes with electrolyte composition using X-ray absorption spectroscopy (XAS). **Figure 2a** and **Figure S4a** show that as KOAc fraction increases, Zn K-edge shift by ~ 0.4 eV to lower energy (see **Figure 2a** inset), indicating a more electronegative Zn^{2+} coordination environment due to the partial displacement of the H_2O molecules by the acetate anions (on average).⁸

Extended X-ray absorption fine structure (EXAFS) analysis (**Figure 2b**) confirms this observation, showing a decrease in the Zn-O peak intensity at ~ 1.5 Å with increasing KOAc content. To quantify these changes, we fit the coordination environments at $X_{\text{Zn}}=0.2$ and $X_{\text{Zn}}=1$ with a pre-optimized model⁸ comprising $(1-y)\text{Zn}(\text{OAc})_4^{2-} + y\text{Zn}(\text{H}_2\text{O})_6^{2+}$ (**Figure S5**, **Table S3**), where “y” is the fraction of Zn^{2+} coordinated by water ($\text{Zn}(\text{H}_2\text{O})_6^{2+}$). The presence of isosbestic points in the EXAFS data (**Figure S4**) allowed for linear combination fitting for intermediate compositions (**Figure S6**, **Table S4**).⁸ As shown in **Figure 2b**, the decreasing Zn-O

intensity corresponds to a reduction in the coordination number (CN): the transition from water-rich to acetate-rich Zn^{2+} solvation is reflected in the CN change from 5.2 at $X_{\text{Zn}} = 1$ ($y=0.6$) to 4.8 at $X_{\text{Zn}} = 0.2$ ($y=0.4$), see **Figure 2 c**, providing strong evidence of increased ion-pair formation at higher KOAc fractions. Notably, as KOAc concentration increases, the evolving solvation environment of Zn^{2+} mirrors the changes in t_{Zn} (**Figure 1 c**). The decrease in $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ species and the corresponding increase in ion-paired $\text{Zn}(\text{OAc})_4^{2-}$ complexes result in less mobile Zn^{2+} , thus contributing to the Zn transference number reduction.

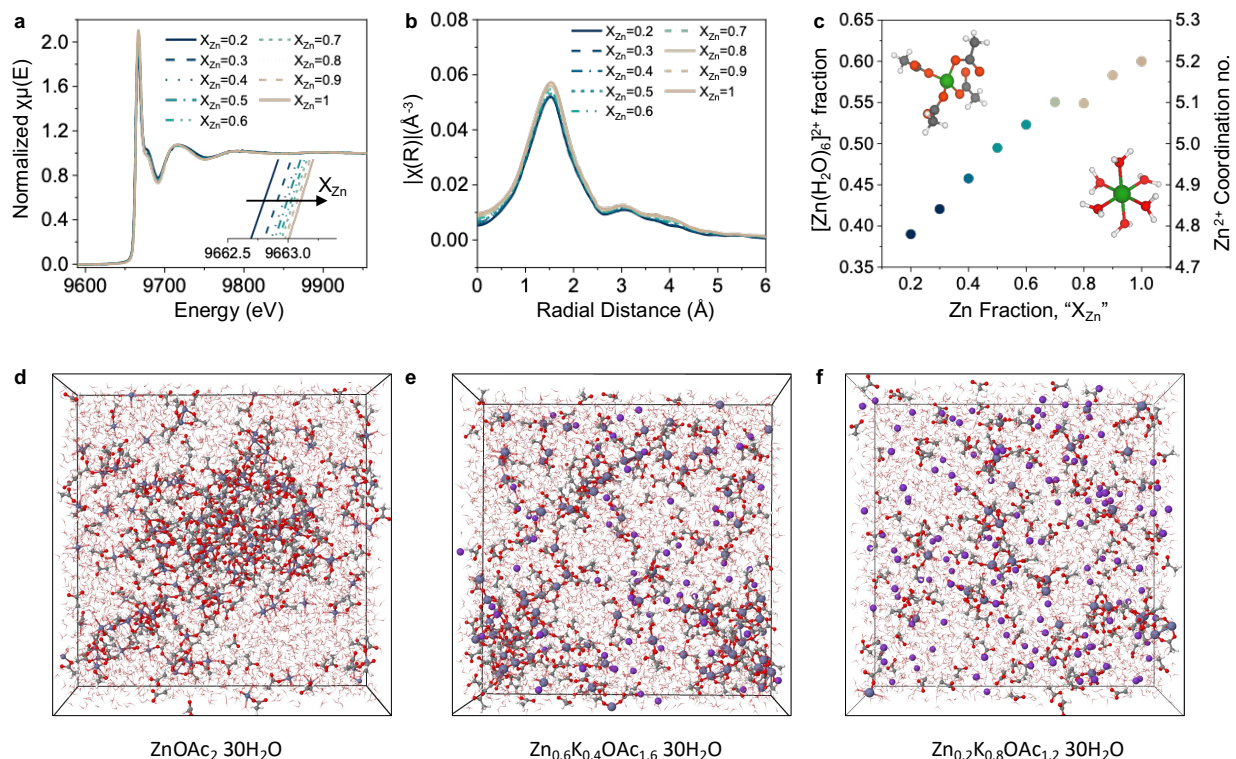


Figure 2. Zn coordination environment studied by X-ray adsorption spectroscopy (XAS) as function of electrolyte composition $\text{Zn}_x\text{K}_{1-x}\text{OAc}_{1+x}30\text{H}_2\text{O}$, where $0 < x < 1$. **a.** Normalized XAS plot and an inset including a zoom-in of the XANES region. **b.** EXAFS changes in radial space. **c.** Zn coordination environment and Zn^{2+} coordination numbers obtained from EXAFS fitting following.⁸ **d-f.** MD simulation boxes for the electrolytes with $X_{\text{Zn}} = 1, 0.6$ and 0.2 .

Molecular dynamics (MD) simulations provided additional insight into the structure and transport of electrolytes for $X_{\text{Zn}} = 0.2, 0.6$ and 1.0 at 333 K that was chosen to speedup equilibration. Snapshots of MD simulation boxes shown in **Figure 2 d-f**, while the most representative clusters are shown in **Figure S7**. A wide distribution of Zn^{2+} solvates is observed, with $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Zn}(\text{OAc})(\text{H}_2\text{O})_5^+$, $\text{Zn}(\text{OAc})_2(\text{H}_2\text{O})_4$ solvates having near octahedral coordination ($\text{Zn-O CN} = 6$) while solvates with 3 or 4 OAc^- bound to zinc showing a near tetrahedral geometry ($\text{Zn-O CN} = 4$). A fraction of the octahedrally coordinated Zn^{2+} is close to 45-50% in MD simulations with the other half of solvates being tetrahedrally coordinated. It is in good agreement with the analysis of EXAFS data that yielded fractions of the octahedrally and tetrahedrally coordinated Zn^{2+} solvates being in the range of 40 – 60%, albeit using a simpler $(1-y)\text{Zn}(\text{OAc})_4^{2-} + y\text{Zn}(\text{H}_2\text{O})_6^{2+}$ model. MD simulations yielded conductivities 18-36% higher than experiments as shown in **Table S5**. We consider this to be sufficiently good predictions. Transference number approximated from self-diffusion coefficients (see **Table S5**) closely follow the trends observed experimentally.

Zn deposition morphology

To correlate the transference number with the Zn deposition morphology, we compared Zn deposits obtained after single plating in electrolytes with different Zn fraction ($X_{\text{Zn}} = 0.2, 0.6, 1$) under current densities of 1, 5 and 10 mA/cm² with plating capacity of 5 mAh/cm² (**Figure S8**). At 1 mA/cm², the density and homogeneity of the Zn deposits differ markedly, as seen from transverse (**Figure 3a-c**) and top-view (**Figure S9**) SEM images. In Zn(OAc)₂ 30H₂O ($X_{\text{Zn}} = 1$) conformal deposition with ~60% density is achieved (**Figure 3c, Figure S10c**). In contrast, in Zn_{0.2}K_{0.8}(OAc)_{1.2} 30H₂O electrolyte, highly porous (“mossy”) Zn deposition with density around ~20% is observed (**Figure S10a**). At intermediate composition Zn_{0.6}K_{0.4}(OAc)_{1.6} 30H₂O, the Zn deposition exhibited significant heterogeneity (**Figure 3b, Figure S10b**), displaying both “mossy” and flatter regions, resulting in lower deposit density of ~30% (**Figure S10b**).

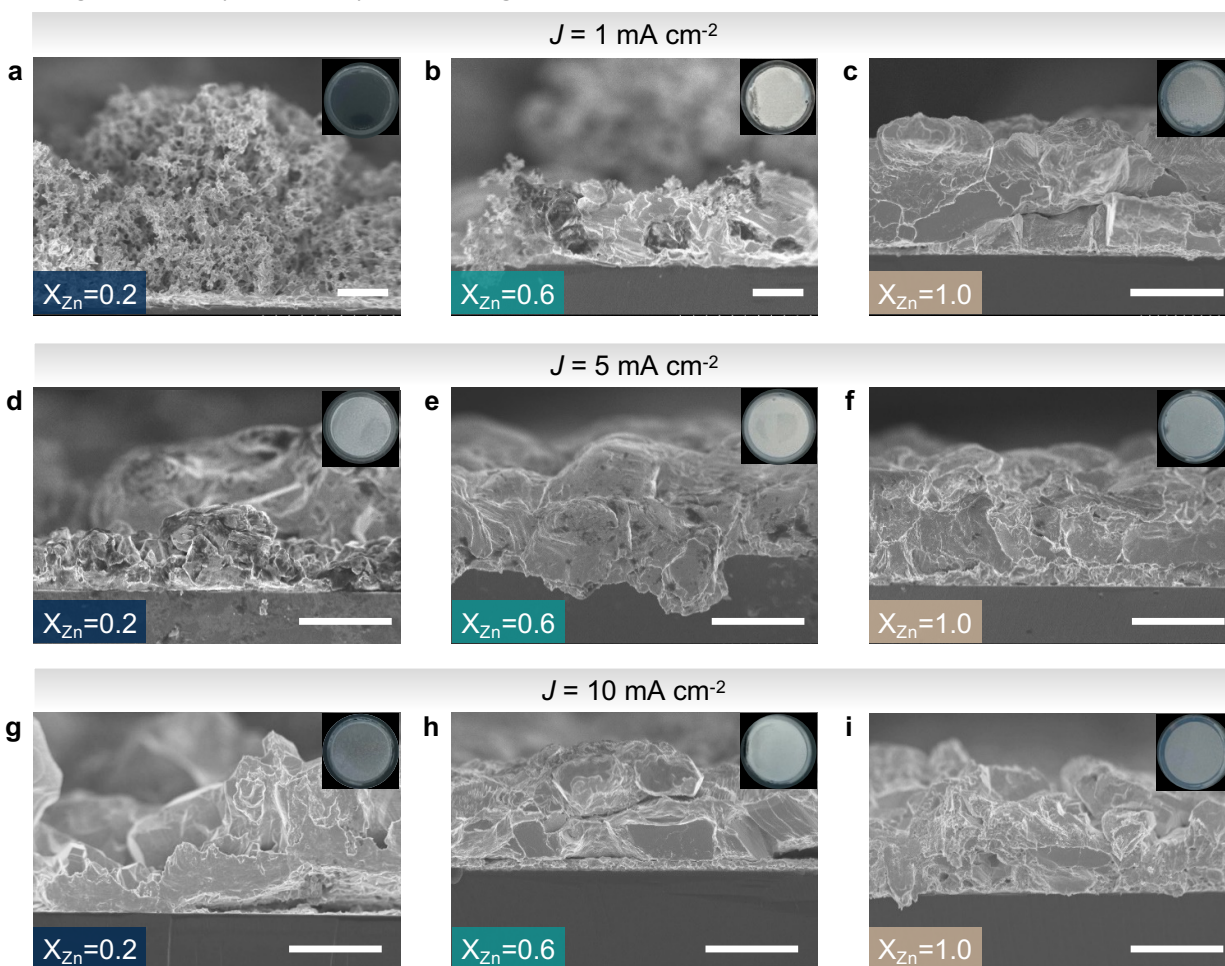


Figure 3. Transversal SEM visualization for the plating of 5 mAh/cm² on Si/Zn substrates (200 nm Zn) at different current densities for the electrolytes Zn _{x} K_{1- x} (OAc)_{1+ x} 30H₂O, for 0.2 < x < 1. Scale bar corresponds to 10 μm. a-c. Deposition current of 1 mA/cm². d-f. Deposition current of 5 mA/cm². g-i. Deposition current density of 10 mA/cm². Insets show digital photographs of the deposits from the top.

At a higher deposition rates of 5 mA/cm² and 10 mA/cm², homogenous and compact Zn deposition with ~65 and 85% density was maintained in Zn(OAc)₂ 30H₂O ($X_{\text{Zn}} = 1$, **Figure S10 f and i**). In contrast, in electrolytes with low Zn fraction ($X_{\text{Zn}} = 0.2$) we observed heterogenous deposition: while overall the Zn deposits appear more conformal and dense (**Figure 3 d and g, Figure S9 d and g, Figure S10 d and g**) during deposition

we observed significant detachment and visible suspension of the metallic Zn deposits within the electrolyte, indicative of localized formation of Zn dendrites. In $\text{Zn}_{0.6}\text{K}_{0.4}(\text{OAc})_{1.6} \cdot 30\text{H}_2\text{O}$ electrolyte, the improved deposition density ($\sim 70\%$ at 5 mA/cm^2 and 80% at 10 mA/cm^2 , **Figure S9**), and notably flatter morphology is observed. The observed flatter morphology at higher Zn deposition currents can be explained by reduced nucleation sites formation at higher current densities (higher overpotentials), resulting in larger crystallites and denser deposits.^{41, 42} Overall, we observe that higher t_{Zn} in electrolytes leads to formation of the more uniform and denser Zn deposits.

Zn plating/stripping performance

To assess the impact of Zn content on electrochemical performance, we evaluated Zn plating and stripping efficiencies using the Aurbach protocol in electrolytes with $X_{\text{Zn}} = 0.2, 0.6$, and 1 . Coulombic Efficiency (CE) increases with increased Zn fraction and electrolyte t_{Zn} (Error! Reference source not found.**a,b**): 94.3% ($X_{\text{Zn}}=0.2$), 97.8% ($X_{\text{Zn}}=0.6$), and 98.1% ($X_{\text{Zn}}=1$). This suggests that higher Zn concentrations promote more efficient plating.

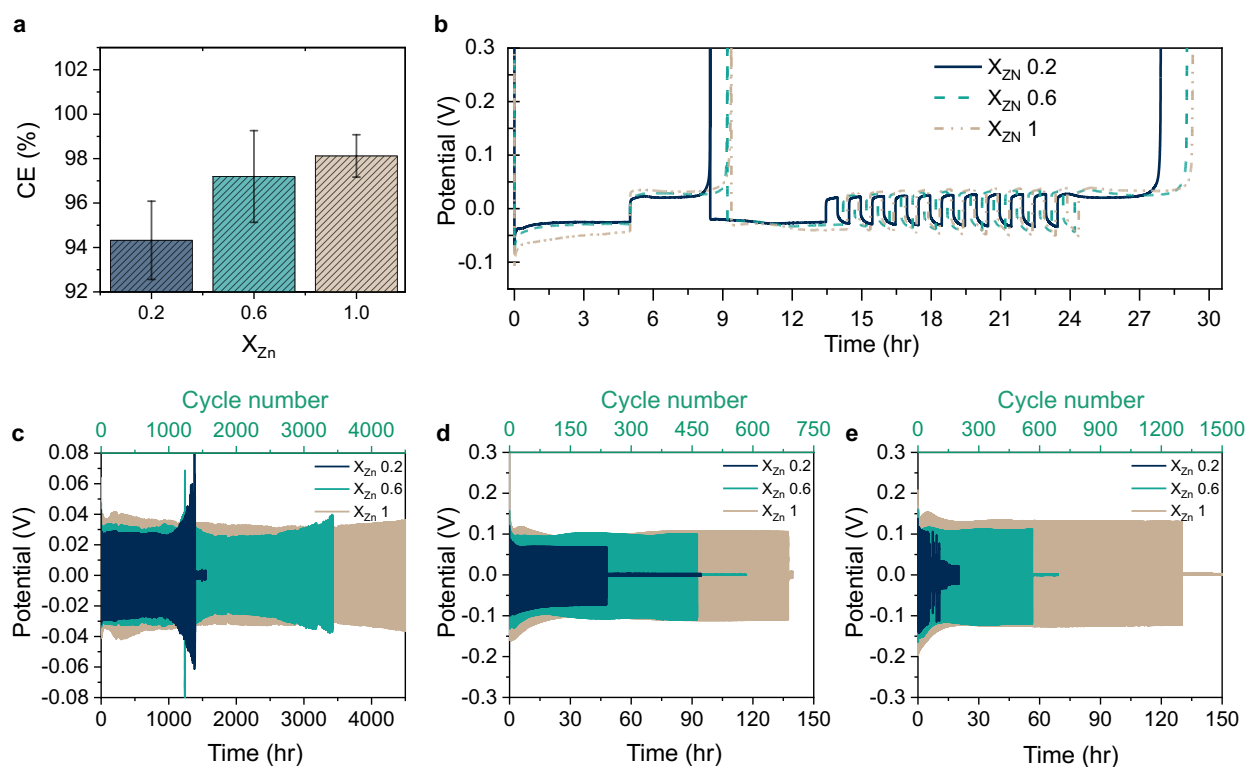


Figure 4. Electrochemical performance of $\text{Zn}_x\text{K}_{1-x}\text{OAc}_{1+x} \cdot 30\text{H}_2\text{O}$ electrolytes across different compositions ($0.2 < x < 1$). **a.** Coulombic efficiency (CE) evaluated using the Aurbach protocol. Pre-cycling at 1 mA/cm^2 for 5 mAh/cm^2 , followed by cycling at 1 mA/cm^2 for 0.5 mAh/cm^2 . **b.** Representative Aurbach profiles collected at 1 mA/cm^2 for 0.5 mAh/cm^2 . **c-e.** Symmetric Zn|Zn cell cycling at current densities of 1, 5, and 10 mA/cm^2 , highlighting the impact of composition on long-term stability and plating/stripping behavior.

Finally, to investigate the impact of electrolyte Zn transference number (t_{Zn}) on dendrite formation and cycling stability, we conducted long-term symmetric Zn-Zn cycling tests at varying current densities ($1, 5$, and 10 mA/cm^2). These current densities represent practical charging rates, including fast charging conditions,⁴³ which significantly reduce the Sand's time (**Figure S11**) and expected to amplify the influence of t_{Zn} on concentration gradients and therefore dendrite formation.¹⁹ As shown in Error! Reference source not f

ound. **c-e**, electrolytes with higher t_{Zn} values exhibited significantly enhanced cycling stability across all current densities. At 1 mA/cm² and 0.5mAh/cm², the cell with Zn_{0.2}K_{0.8}(OAc)_{1.2} 30H₂O electrolyte cycled for ~1390 h (1400 cycles) before failure, while the cell with Zn_{0.6}K_{0.4}(OAc)_{1.6} 30H₂O cycled for ~3150 h (3300 cycles), although a potential micro-short circuit may have occurred ~1240 h (see Zoom in **Figure S12**). The Zn(OAc)₂ 30H₂O electrolyte with $X_{\text{Zn}} = 1$ enabled the best cycling stability, operating for over 4500 h (4500cycles) with no short-circuit (still functioning at the time of writing). At higher current densities 5 mA/cm² and 10 mA/cm², the trends remain the same: the higher the t_{Zn} of electrolyte the longer the cell can cycle before short-circuiting due to dendrite formation (see **Figure S13**). However, the total number of cycles decreases drastically.

CONCLUSIONS

Our study demonstrates that while adding KOAc markedly boosts overall ionic conductivity, it dramatically lowers the Zn²⁺ transference number — a trade-off that negatively affects Zn metal anodes during cycling. Using a modified Hittorf method, we accurately quantify transference numbers in complex Zn-K acetate electrolytes and, with the aid of X-ray absorption spectroscopy and MD simulations, established how evolving Zn²⁺ solvation environments correlates with the reduced Zn²⁺ mobility. By systematically varying the Zn²⁺ fraction, we show that higher Zn²⁺ transference numbers and Zn-specific ionic conductivity yield more uniform and dense Zn deposits, improved cycling stability, and minimized dendrite formation even at high current densities. These insights underscore the necessity of quantitatively measuring and optimizing Zn²⁺ transference, alongside with total conductivity, when designing aqueous Zn-metal battery electrolytes. Moving forward, this framework provides a robust approach for guiding electrolyte formulations that balance conductivity gains with targeted Zn²⁺ transport properties, ultimately paving the way for safer, longer-lived Zn-based batteries.

MATERIALS AND METHODS

Materials

High purity Zn foil (>99.95%) was acquired from Goodfellow. The TOPAS (cyclic polyolefin) microfluidic channels for XAS were purchased from ChipShop Germany. Potassium acetate (>99%), Zn acetate dihydrate (>99%), and other chemicals were acquired from Sigma Aldrich.

Electrolyte conductivity

The conductivity was measured using an Oakton 2700 benchtop conductivity meter.

Viscosity

The measurements were carried out on an ARES-G2 oscillatory rheometer from TA Instruments, using a cone-plate geometry for samples with higher viscosity. Shear rates varied between 10 and 1000 Hz, with viscosity values determined from measurements at frequencies above 100 Hz.

Differential scanning calorimetry (DSC)

The thermal properties of the electrolytes were evaluated using a DSC 2500 (TA Instruments). Samples were initially cycled once from -80°C to 80°C, followed by a second cycle back to -80°C at a rate of 10°C per minute. Data was subsequently collected from -80°C to 80°C at a slower rate of 1°C per minute.

X-ray absorption spectroscopy (XAS)

Following the same procedure as in our previous work,⁸ X-ray absorption spectroscopy (XAS) measurements were conducted at the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI) on the X10DA-SuperXAS beamline. Data sets were collected in Quick Scanning XAS mode around the Zn K-edge, with Zn metal used for calibration during a 5-minute scan.⁴⁶ The electrolyte was continuously pumped through a microfluidic channel at a flow rate of 100 µL/min to minimize beam-induced damage. Data analysis was performed using the Demeter software package. XANES normalization was achieved by setting the edge energy (E^0) at the zero of the second derivative and manually adjusting the pre- and post-edge regions. EXAFS data were processed over a wave number range of 3-12 Å⁻¹ to maintain a low signal-to-noise ratio, with results presented using a k^3 -weighting. For fitting, the amplitude reduction factor (S_0^2) was set to 1, as established in prior studies.⁴⁷

Transference number measurements: Modified Hittorf method

Experiments were performed using a glass Hittorf cell (**Figure S2**). Each chamber had a total volume of 5 mL and was filled with 4 mL of electrolyte. Coiled Zn foil strips were used to maximize surface area. These electrodes were dried at 80°C and weighed before and after experiments to verify coulombic efficiency during Zn plating and stripping in respective chambers. For each electrolyte composition measurement was performed at least 3 times to obtain statistically significant data.

After assembly, the cell was connected to a potentiostat and subjected to galvanostatic polarization. The total charge transferred corresponded to 10% of the chemical equivalents in solution (based on anion concentration), ensuring sufficient change in Zn concentration takes place to accurately calculate the transference number.

To reduce measurement variability, the cell compartments and electrodes were flushed with 4 mL of water (resulting in a 1:1 dilution). Immediately after, a further dilution (1:20 with 10% nitric acid) was prepared to prevent Zn oxyhydroxide precipitation. Additional dilutions were performed as needed to achieve analyte

concentrations between 20 and 40 ppm (mg/L), thereby minimizing measurement errors across different ions. Finally, resulting Zn and K concentrations were measured using ICP-OES.

Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES)

The samples were diluted to a target concentration of 20-40 ppm by 10% nitric acid. Calibration standards for Zn^{2+} and K^+ were prepared at 10, 50, and 100 ppm, and the instrument was calibrated before each set of measurements. Dilutions were prepared from the control solution, anodic chamber, middle chamber, and cathodic chamber. Each electrolyte was measured four times with alternating sequences to minimize instrument drift. After every four Hittorf measurement sets (each set consisting of four samples), the instrument was recalibrated using Zn^{2+} and K^+ standards.

The dilution factors were then back-calculated to determine the concentrations and masses in each chamber. The control solution served as the baseline for all chambers. Data was used for further analysis only if the middle chamber concentration and electrode weights deviated by less than 3% from the ideal case (no diffusion in the middle chamber and 100% coulombic efficiency for Zn/Zn^{2+} redox).

The transference numbers were calculated based on the mass balance in the ionic chambers:

$$m_{ion} = m_{ion}^0 \pm m_{redox} \pm m_{migration}$$

Here, m_{ion}^0 represents the initial mass of the Zn^{2+} ion in solution, while m_{redox} accounts for the mass change due to redox reactions, and $m_{migration}$ corresponds to the mass transported via migration.

The mass balance for Zn^{2+} in the anodic chamber is expressed as:

$$m_{\text{Zn}-\text{Anode}} = m_{ion}^0 + W_{\text{Zn}}nFQ - W_{\text{Zn}}nFQt_{\text{Zn}}$$

where:

- $m_{\text{Zn}-\text{Anode}}$ is the mass of Zn^{2+} in the anodic chamber after the experiment,
- W_{Zn} is the molecular weight of Zn,
- n is the number of electrons in the reaction.
- F is the Faraday constant, and
- Q is the total charge passed during the experiment.

Based on this mass balance, the Zn^{2+} transference number (t_{Zn}) can then be calculated as follows:

$$t_{\text{Zn}} = \frac{m_{ion}^0 - m_{\text{Zn}-\text{Anode}}}{W_{\text{Zn}}nFQ} + 1$$

In the same way, mass balance for potassium lead to the following transference number equation:

$$t_{\text{K}} = \frac{m_{ion}^0 - m_{\text{K}-\text{Anode}}}{W_{\text{K}}nFQ}$$

Since acetate is not detectable via ICP-OES, its transference number is inferred based on the assumption that the total sum of transference numbers equals 1.

$$t_{\text{OAc}} = 1 - t_{\text{K}} - t_{\text{Zn}}$$

Sand's time

The Sand's time was estimated using the Sand's formula:^{19, 48}

$$t_{\text{Sand}} = \frac{\pi D_{\text{app}}(z_{\text{Zn}}C_0F)^2}{4(J(1 - t_{\text{Zn}}))^2}$$

Where D_{app} is the apparent diffusion coefficient, z_{Zn} is the charge number of Zn^{2+} , C_0 is the initial salt concentration at the bulk, F is Faraday's constant, J is current density and t_{Zn} is the cation transference number. To perform the calculations, MD extracted diffusion coefficients were employed.

Aurbach protocol

Cells were assembled in a two-electrode PFA Swagelok-like configuration using copper (Cu) rods as current collectors and 0.25-inch electrodes with separators. A compressed Whatman glass fiber separator (0.5 mm thick) separated the working and counter electrodes. The working electrode was a 5 μm -thick high-purity Cu foil, and the counter electrode was a 250 μm -thick Zn foil. Each cell contained 75 μL of electrolyte.

Cells were cycled according to the Aurbach protocol. First, 5 mAh/cm^2 of Zn was plated and stripped at a current density of 1 mA/cm^2 . Next, a Zn reservoir of 5 mAh/cm^2 was plated, followed by 10 plating/stripping cycles at 1 mA/cm^2 with a charge of 0.5 mAh/cm^2 per cycle. Finally, a stripping step was performed at 1 mA/cm^2 with a cut-off charge of 5 mAh/cm^2 .

Symmetric Zn-Zn cycling

Symmetric cells were assembled in 0.25-inch Swagelok cells using copper (Cu) current collectors and Whatman glass fiber separators. Each cell contained 30 μL of electrolyte, and the Zn disk electrodes with 0.25-inch diameter and thickness of 250 μm . The cells were cycled at current densities of 1, 5, and 10 mA/cm^2 , with 0.5 mAh/cm^2 charge for each cycle.

Scanning electron microscopy (SEM) studies: cross-section visualization

To visualize the cross-sectional Zn deposition morphology, Zn deposits were prepared on Si wafers with 200 nm of Zn metal evaporated. These Si wafers with 200 nm Zn served as working electrodes in a custom PEEK cell with a cylindrical opening (1.5 cm diameter $\times$ 1 cm height) and a 250 μm thick Zn foil served as the counter electrode. Next, Zn was electrodeposited at current densities of 1, 5, and 10 mA/cm^2 and a total charge of 5 mAh/cm^2 . After Zn electrodeposition, the samples were fractioned from the back side of the Si wafer using a diamond cutter, ensuring that the electrodeposited Zn remains unaltered. SEM images were collected using a Hitachi S-4800 SEM microscope to assess the morphology.

The deposition density was estimated from the average deposition height in the cross-sectional SEM images (**Figure S10**). Since the deposited charge is 5 mAh/cm^2 and the density of Zn metal is 7.14 g/cm^3 , yielding the resulting deposit height of ~ 8.4 μm for fully dense Zn. However, due to measurement uncertainties stemming from the localized nature of this method, it primarily serves as a comparative tool for evaluating difference in Zn deposits obtained in different electrolytes.

Molecular dynamics simulations (MD)

Molecular dynamics simulations were performed with Tinker9 (git commit 70bd052) using the AMOEBA09 polarizable force field.⁴⁹ The default mixed-precision executable was compiled with CUDA/11.6 on Nvidia A100 GPUs. Force field parameters were refined further from a previous publication⁸ to reduce the mean unsigned error in interaction energies computed across 18 clusters, sampling potassium-water, zinc-water, acetate-water, potassium-acetate, zinc-acetate, potassium-water-acetate, and zinc-water-acetate clusters. Clusters with cation-acetate interactions feature a mix of mono- and bidentate complexes. After further testing, the $R_{\text{min_ij}}$ for zinc – carboxylate oxygen interactions was tuned to predict a 1.5 kcal mol^{-1} stronger interaction energy for the $[\text{Zn}(\text{OAc})_4]^{2-}$ complex as the force field parameters derived purely from a fit to ab initio data were too dissociating and predicted large errors in the conductivity. Compositions simulated comprised

$\text{Zn}_x\text{K}_y\text{OAc}_z\cdot 30\text{H}_2\text{O}$, where $x=\{0.2, 0.6, 1.0\}$, $y=1-x$, and z is adjusted for charge neutrality, exact compositions are listed in the Supporting Information. Box sizes were equilibrated in the NPT ensemble using the Nose-Hoover barostat and thermostat with default coupling constants and a 1 femtosecond timestep until 4 independent replicate runs for each concentration showed no drift in average box size vs time. For $x=0.2$, this took 80 ns and for $x=0.6, 1.0$ this took 160 ns. After equilibrating, all 4 replicates were scaled to the same box size in a 'corrector' step in the NVT ensemble using the RESPA integrator and 2 femtosecond timestep. Finally, statistics were collected over runs lasting ~60 nanoseconds with the same settings as in the previous step. The Ewald and vdW cutoffs were set to 10 Å with a PME-grid mesh of 64^3 . Center of mass motion is removed at each timestep. Force field parameters are given in the Supporting Information.

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