

Leveraging cation effect for low temperature aqueous Zn-based batteries

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this work, the authors proposed the cation effect of Al^{3+} can simultaneously exert a deshielding effect on both H and O in water, which significantly weakens the water hydrogen bond and lowers Tt to $-117\text{ }^{\circ}\text{C}$ at a low salt concentration of 2.8 m. Additionally, dual-cation effects further facilitate the formation of an Al–Zn alloy layer for anode safeguarding. However, I think the novelty of this work is insufficient for the Nature series, some similar works on the effect of different cation–water interactions on Tt in aqueous solution has been reported previously (Nature Energy, 2024, 9, 839-848; Angew. Chem. Int. Ed. 2024, 63, e202407659; Sci. Adv. 2016, 2, e1600345). Enhancing the interaction of cation and water by introducing cations with high ionic potential to disrupt the hydrogen bond network is a rather common and intuitive strategy. Moreover, the mechanisms related to deshielding effect of both H and O on Tt of water is not clear and in-depth enough. The analysis and results presented in this work do not provide new insight into the intrinsic correlation among cation-effect and Tt. Overall, I don't think this manuscript is suitable for published in Nature Communications. Several detailed issues are listed below:

1. The expression of Tt can easily bring confusion for readers since it is either common nor clear enough to correctly denote the specific solid–liquid transition point. Commonly Tf or Tm is utilized to express freezing point or melting point, respectively.
2. The sequence order of cation deshielding effect on both H and O in water is different in this work. Which effect plays a dominant role and has a greater impact on the freezing point? What's the relationship between the deshielding effect of H atom and the freezing point? The authors stress the core point of this manuscript to the cation effect on low temperature performance of aqueous solutions. However, no solid experiments support the idea of Al^{3+} system possessing the lowest freezing point compared to other cation systems. The authors should supply these measurements (DSC or Raman) on freezing points of different cation systems and discuss the correlation with their corresponding deshielding effect of H atom.
3. Due to the different valence state of different cations, how can the authors exclude the effect of the concentration of Cl^{-} on the freezing point?
4. Why the increased electron density on H implies a high proton activity of H atom to form HBs with O? H atom with lower electron density exhibits a more positive electrostatic potential and theoretically should more easily form HB with the O atom of adjacent water molecules.
5. Higher deposition capacity ($>0.2\text{ mAh cm}^{-2}$) test at room temperature and low temperature of symmetric Zn–Zn symmetric cells should be supplied.
6. The author mentions the viscosity of the electrolyte several times in the manuscript (page 8, lines 155 and 165, etc), and the relevant data should be provided.
7. In the Figure. 1g, please provide more comprehensive reasons to explain why the 4Al electrolyte system has the best anti-freezing performance.
8. Why are Zn^{2+} salts chosen to construct dual-cation electrolytes instead of other cation salts? If not for application to Zn-based batteries, are there other better options of cation to enhance the migration kinetics of electrolytes?

Reviewer #2

(Remarks to the Author)

This paper designs an aqueous Zn battery electrolyte (DCE41) based on the dual-cation effect of Al^{3+} and Zn^{2+} , achieving high ionic conductivity and stability even under ultra-low temperatures. The proposed strategy effectively reconfigures hydrogen bond networks and forms a corrosion-resistant Al–Zn alloy layer on the Zn anode, significantly enhancing battery performance at low temperatures. The systematic analysis of the deshielding effect and the mechanism for improved low-

temperature performance based on cation effects is impressive. However, the study lacks sufficient data to elucidate the electrolyte structure and validate the mechanisms underlying performance improvement, as well as data proving its superiority compared to existing literature.

- This study focused on the cation effect. Why was Cl^- selected as the constant anion among various anions?
- The inclusion of hetero-cation of Al^{3+} may cause unwanted competition for ion conduction with Zn^{2+} . The authors need to differentiate the diffusion behavior of Al^{3+} and Zn^{2+} . For example, the diffusion coefficient of Zn^{2+} should be measured both in the absence and presence of Al^{3+} .
- The study claims that progressive hydrogen bond (HB) disruption leads to an increase in entropy and contributes to Low T_f . However, no analysis of the electrolyte's entropy is provided.
- The expressions used to indicate electrolyte concentrations are inconsistent and may cause confusion. Additionally, for an objective comparison, please provide the concentrations of DCE41~DCE43 in m units as well.
- Fig. 2b: In the ^1H -NMR spectra, it is mentioned that H atoms in the electrolyte become increasingly deshielded with higher salt concentrations. However, the trend reverses as the peak shows shielding from 3 Al to 5.3 Al. Please provide an explanation for this phenomenon.
- Fig. 4a, Supplementary Fig. 32: Despite DCE41 exhibiting higher ionic conductivity and lower desolvation energy than 4 Al, it shows a higher symmetric cell overpotential. Provide a detailed discussion to explain this phenomenon.
- Fig. 5a-5c: Since the full cell data only represents the DCE41 electrolyte, it is difficult to assess its superiority. Please add the electrochemical performance of the comparative 4 Al electrolyte.
- Fig. S31-S33: Comparing the performance of the 4Al electrolyte, which lacks Zn ions, with other systems appears to be an unfair comparison. It would be more appropriate to compare 1 m ZnCl_2 with DCE41 instead of 4Al.
- Table S1, Fig. 4a-3c: The areal capacity evaluated (0.2 mAh/cm^2) is too low compared to the $22 \mu\text{m}$ Zn metal, making it less meaningful to emphasize the cycle number or time. Therefore, please calculate the DOD and cumulative capacity for the evaluation and include them in Table S1.
- Table S2: It seems that recently published papers on low-temperature ZMBs have not been included. Please add the following papers and provide a comparison.

Reviewer #3

(Remarks to the Author)

The authors presented an interesting Zn-based aqueous battery system with promising low-temperature performance. The authors focused on the cations' roles in the solvation shell and water cluster reconstructions, evaluated and characterized the electrochemistry with different instrumental techniques and atomistic simulations. In general, the experimental portion suggests that the authors conducted comprehensive studies on how the dual cation effects from Al-Zn-water interactions contribute to cell performance. However, the following problems, especially regarding the simulation studies, should be addressed prior to publication:

1. In the introduction section, "The dissociated metal cations interact with the O atoms of water molecules via electrostatic interactions, leading to a reduction in the electron density around O": The interactions between metal ions and H_2O molecules are not just electrostatic interactions. The nature of M-O bonding is more complex than simple ionic bonding.
2. For Fig. 2h, I couldn't understand why the MSD vs time is such a perfect linear relationship. Explanation is needed.
3. For the claim "Nevertheless, in 4Al, Al^{3+} coordinates with four water molecules and two Cl^- ions in the first solvation shell (Fig. 3d). After the introduction of ZnCl_2 , the snapshot reveals that Al^{3+} is coordinated by four water molecules and two Cl^- ions, whereas Zn^{2+} is coordinated by five water molecules and one Cl^- ion.": Although it is presumably backed by the energetics calculated at the PBE level of theory, the snapshots of a few solvation structures are not representative enough to reflect global behavior. The evolutions or means of water-ion and ion-ion counts would be more solid evidence.
4. The DFT calculation in this study was conducted with the Material Studio package, which I do not believe is the best option. There are many other open-source DFT packages including ORCA, that offer more reliable molecular modeling than Materials Studio.
5. This study used the PBE functional to perform molecular orbital calculations, which usually have unacceptable error ranges, especially the obtained energetics. Without systematic benchmarks against higher level of theory, the results cannot be published. This point is related to the validity of Fig. 3d, 3e, Supplementary Fig. 7, and Supplementary Fig. 9.
6. The water model implemented in this study is TIP3P. ff19SB with OPC model was reported to have much better performance than TIP3P model. At least a benchmark between these two models or against DFT should be provided to support the simulation results.
7. In the MD simulations of "different cation systems", Abm99sb-ildn may be reasonably good for simulating Zn-water interactions, according to the literature. However, for other metal ion cases including Al and Ca, additional evaluation of this FF is needed to support these results.
8. Related to question 2, no evidence suggests that the system reached equilibration in any MD simulations. In the model initiation step, instead of using nPT to allow simulation cell, the authors relaxed the system with the conjugate gradient minimization method, without considering any intermolecular collisions at the corresponding temperature. Without a comparison of the obtained density with experimental values, this simulation approach cannot prove its efficacy, especially since temperature effects are of major research interest. Additionally, for those of single salt systems, only 0.5 ns of nVT simulation was performed, which is far from reaching any statistically meaningful conclusions.
9. In the investigation of electrolyte systems, the authors switched the force field and timestep without explanation or benchmark.
10. The authors performed many batches of MD simulations of the electrolyte systems with decently long lengths. Ionic transport properties such as ion diffusivity/conductivity could be provided based on these simulations to provide more intriguing conclusions.

11. For Supplementary Fig. 7, it seems that no effort was put into eliminating the bias from different numbers of HBs among water molecules in the solvation shell. In addition, since the study of binding energy is mainly of kinetics interests, thermal corrections should be applied to obtain free energy instead of total electronic energy (presumably).

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

We can see the authors have paid great effort to illustrate the main novelty of this work. Regrettably, I still retain my original opinion that the manuscript fails to meet the criteria for publication in Nature Communications. The reasons for this are as follows:

1. Novelty is still the main reason. Actually the deshielding effect of cations is essentially the same as the cation ionic potentials since their effect on water molecules shows no difference. Besides, in addition to the previously mentioned studies on cation-water interactions, a number of cation-regulated hydrogen bonding mechanisms have been reported. Specifically, the deshielding effect of several cations (especially "super-hydration structure" effect of Ca^{2+}) on both H and O of water have also been proposed and confirmed in previous research (Angew. Chem. Int. Ed. 2024, 63, e202407659). Therefore, this work can only supply some support on this effect, thus not reaching the high standard of Nature Communications.
2. The authors mention that the deshielding effect of Al^{3+} on H atoms and O atoms also plays a role in lowering the freezing point in Respond manuscripts. Is it possible to establish a metric to quantify this?
3. Is there a direct relationship between the deshielding effect of cations and the ionic conductivity of their electrolyte systems?

Reviewer #2

(Remarks to the Author)

The authors have appropriately addressed the raised concerns by providing clear explanations and referencing relevant literature. Overall, the revised manuscript demonstrates improved clarity, added experimental depth, and presented strong evidence for its superior low-temperature performance. The following comments need to be addressed.

- This study introduced a dual-cation electrolyte system (DCE) based on Al^{3+} and Zn^{2+} , where Al^{3+} induces strong deshielding effects on water molecules by disrupting hydrogen bonding networks. In addition to bulk ionic conductivity, which is enhanced by the disruption of hydrogen bonding networks, charge transfer at the anode-electrolyte interface (which is affected by deshielding) is important for low temperature performance. A detailed discussion, together with the relevant results, should be added.

- PANI was used as a cathode material. The versatility of this approach should be discussed. Is this approach applicable to other cathode systems?

Reviewer #3

(Remarks to the Author)

Although an additional author is included, it is impressive that the simulation work can be revised from a novice level to a reasonably systematic degree within such a short time period. Personally, I tend to believe Yanchun Xie deserves to be treated as a co-first author, but that's up to the corresponding authors' discretion.

An additional requirement for the simulation part: a detailed energy table of all computed species should be included in SI. The atomic coordinates could be optional but should be available upon reasonable request. All the open-source packages and repositories involved in data analysis should also be cited and acknowledged.

Despite the significantly enhanced simulation work quality, I have to point out that the writing quality is still below the average of Nat Comm. A more concise and concentrated paper can benefit more researchers in the scientific community. Redundant phrasing and detailed technical descriptions can be reserved for SI.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I acknowledge the author's effort in revising the manuscript and clarify its novelty. However, after careful evaluation, I still find that the core contribution of this work largely consists of integrating and extending previously reported observations rather than establishing a genuinely novel mechanism or principle. Therefore, I do not consider the work suitable for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)

The revised manuscript has sufficiently addressed the reviewer's comments. It can be recommended for acceptance.

Reviewer #3

(Remarks to the Author)

The authors revealed that the unique cation-water structure, in the aqueous battery system with Zn-Al alloy anode, contributes to the low-temperature performance and cycling longevity.

This work is of interests to the fundamental understanding of solvation structures in aqueous electrolytes with multiple salt species. The methodologies integrate advanced characterization and simulation techniques, which bring multiple perspectives to the complex aqueous electrolyte phenomena.

Although little attention was paid to the cathode's role and the explicit interphase structure near anode, the authors elaborated several important questions in the multi-cation electrochemistry.

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Enclosed please find our revised manuscript after taking the reviewers' comments that were aimed at improving the quality of the presentation. Below please check for our **point-by-point responses to the reviewers' comments**, which is also incorporated into our revised manuscript.

Enumerated responses to comments from the reviewers.

Black italic: Reviewers' comments; **Blue type:** Our responses; **Red type:** Notable changes.

The corresponding update has been highlighted in Yellow in the revised manuscript.

Reviewer: 1 *In this work, the authors proposed the cation effect of Al^{3+} can simultaneously exert a deshielding effect on both H and O in water, which significantly weakens the water hydrogen bond and lowers T_i to $-117\text{ }^{\circ}\text{C}$ at a low salt concentration of 2.80 m. Additionally, dual-cation effects further facilitate the formation of an Al–Zn alloy layer for anode safeguarding. However, I think the novelty of this work is insufficient for the Nature series, some similar works on the effect of different cation–water interactions on T_i in aqueous solution has been reported previously (Nature Energy, 2024, 9, 839-848; Angew. Chem. Int. Ed. 2024, 63, e202407659; Sci. Adv. 2016, 2, e1600345). Enhancing the interaction of cation and water by introducing cations with high ionic potential to disrupt the hydrogen bond network is a rather common and intuitive strategy. Moreover, the mechanisms related to deshielding effect of both H and O on T_i of water is not clear and in-depth enough. The analysis and results presented in this work do not provide new insight into the intrinsic correlation among cation-effect and T_i . Overall, I don't think this manuscript is suitable for published in Nature Communications.*

Answer: We greatly appreciate the reviewer's critical comments, which is very helpful to improve the quality of our manuscript. To emphasize the significant and improve the quality of our work, we have

tried our best to revise the manuscript (highlighted in Yellow) to response your valuable and insightful suggestions, **readjust the structure** of the manuscript and **have done additional experiments** to better consolidate our conclusions. We deeply hope that, with the clarification of these issues which we did not address well in our previous manuscript, you could reconsider the publication of our work in *Nature Communications*.

a. The novelty of our work

We have carefully reviewed the references you mentioned regarding the effect of different cation–water interactions on T_f in aqueous solutions. However, we respectfully disagree with your comment that the novelty of our work is reduced by these publications.

First, we would like to clarify the key differences between our work and the studies you referenced. For the work in *Nature Energy*, 2024, 9, 839-848 and *Angew. Chem. Int. Ed.* 2024, 63, e202407659, while the authors explore the role of cation–water interactions in enhancing the antifreeze properties of aqueous electrolytes, **there are inconsistencies in their mechanistic explanations**, highlighting the need for further exploration in this field. Specifically, in the work of *Nature Energy*, 2024, 9, 839-848, the authors propose that the cations with high cation ionic potentials (such Al^{3+} and Ca^{2+}) enhance the interaction between the cation and water molecules, thereby disrupting the hydrogen bonding network in water and increasing entropy of the electrolyte to lower the eutectic temperature. This mechanism **emphasizes strong cation-water interactions**. In contrast, the work in *Angew. Chem. Int. Ed.* 2024, 63, e202407659 suggests that chaotropic ions (Ca^{2+}) exhibit weak binding interactions with water, leading to more water molecules entering the solvation structure, disrupting more hydrogen bonds, and thus lowering the freezing point. The latter work **emphasizes the relatively weak binding** between Ca^{2+}

and water molecules, which contradicts the stronger interaction between Ca^{2+} and water molecules with high ionic potential, as discussed in *Nature Energy*, 2024, 9, 839-848. Moreover, neither of the aforementioned studies delves deeply into the interactions between different cations and the H/O atoms in water molecules, and current antifreeze electrolytes based on inorganic salts still require high salt concentrations. Therefore, further exploration of the interactions between cations and water molecules remains valuable for future research.

In our work, we experimentally verify the strong antifreezing performance of Al^{3+} and identify the optimal antifreezing ratio. Importantly, through elaborate spectroscopic analyses (including NMR and Raman spectroscopy) and theoretical calculations, we demonstrate that Al^{3+} generates a strong deshielding effect for both O and H in water. This results in a significant antifreezing performance at lower salt concentrations. **Our novel approach not only provides new insights into the cation–water interactions but also offers an explanation for the antifreezing mechanism of Al^{3+} , which is distinct from the mechanisms proposed in existing literature.**

Additionally, regarding the study of *Sci. Adv.* 2016, 2, e1600345, which highlights how ion-specific effects influence ice nucleation at the polyelectrolyte brush (PB)/water interface, but its scope is largely within the context of material science and atmospheric chemistry. In contrast, our research is focused on different cations affect the shielding of H and O atoms in water molecules. Based on the cation effect, design aqueous electrolytes with superior electrochemical performance at ultralow temperatures, specifically for the energy storage applications. Therefore, while both studies address ion-water interactions, **they differ significantly in their application, research objectives, and methodologies.**

We then would like to highlight the novelty of our manuscript:

- (1) Our study presents a novel electrolyte design strategy based on the cation **deshielding effect**, advancing the understanding of antifreezing aqueous electrolytes and provides new insights into electrolyte design for extreme conditions, resulting in the **first observation** of a freezing point as low as -117 °C, achieved at a relatively low Al³⁺ concentration of 2.80 m.
- (2) Unlike previous approaches that focus on altering hydrogen bond network of water through salt or cosolvent modifications, our work reveals **a distinctive dual-cation interaction mechanism** that synergistically suppresses electrolyte crystallization and enhances ion transport kinetics.
- (3) Leveraging these cation effects, the dual-cation electrolyte extends the lifespan of Zn metal to over 10,340 hours at -60 °C (**>430 days**, and still stable in operation). This marks a **significant breakthrough** in the cycling life of Zn metal at ultralow temperatures, surpassing all previously reported Zn-based battery systems, including *Nat. Sustain.* 6, 325-335 (2023); *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); *Energy Environ. Sci.* 18, 713-727 (2025); *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); *Energy Environ. Sci.* 17, 8966-8977 (2024) and *et al* (Table R1). Additionally, the Zn/PANI full battery cycles more than 12,000 cycles at -60 °C and delivers a high reversible capacity of 115.5 mA h g at -80 °C. With superior cycling life, current density, and low-temperature performance, the Zn/PANI battery with our dual-cation electrolyte outperforms the majority of reported works to date, such as *Nat. Energy* 9, 839-848 (2024); *Nat. Commun.* 15, 6249 (2024); *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); *Energy Environ. Sci.* 18, 713-727 (2025); *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); *J. Am. Chem. Soc.* 146, 12743–

Table R1. The current density, areal capacity, cycling lifespan, cumulative capacity, DOD, Zn thickness and extreme operating temperatures of the symmetrical Zn cells with DCE41, compared with reported ultralow temperatures (≤ -40 °C) aqueous Zn-based systems.

Electrolyte	Current density (mA cm ⁻²)	Areal capacity (mA h cm ⁻²)	Cycling life (h)	T (°C)	Cumulative capacity (mA h cm ⁻²)	Depth of discharge (DOD,%), Zn thickness (μm)	Ref.	
DCE41	0.2	0.2	> 10,340 (shelving - recovery test, still running)	-60	> 1,378	1.6 (22)	This work	
			3,100			620		1.6 (22)
			> 1014 (still running)			> 202.8		4.7 (22)
	0.2	0.8	> 740 (still running)		> 148	6.2 (22)		
			> 718 (still running)					
			> 287.2			3.1 (22)		
	1	0.25	540	540	1.9 (22)			

	0.2	0.2	1,100	-70	220	1.6 (22)	
MSE-1D1W	0.2	0.2	2,000	-80	400	0.34 (100)	¹
Li ₂ ZnCl ₄ • 9H ₂ O	1	-	135	-70	135	-	²
7.5 ZnCl ₂	0.2	0.2	450	-70	90	-	³
1 M ZnCl ₂ +4 M CaCl ₂	0.5	0.5	480	-60	240	1.7 (50)	⁴
ZnCl ₂ +SF	1	1	1200	-60	1200	1.7 (100)	⁵
MIAE	0.5	0.5	700	-60	350	0.85 (100)	⁶
	1	10	800	-40	800	57 (30)	
BPE	0.2	0.2	1,370	-60	274	0.34 (100)	⁷
	0.5	0.5	2,300	-40	1,150	0.85 (100)	
TMP-40	0.4	0.4	7,000	-50	2,800	0.68 (100)	⁸
0.08 M C- ZnCl ₂ /PG- H ₂ O	0.2	0.1	2,200	-50	440	-	⁹
ZnCl ₂ +100 mM αDG	5	2.5	800	-40	4,000	43 (10)	¹⁰
LACA	0.25	0.25	2,000	-40	500	-	¹¹
3.0 M ZClO +0.3 M Zn(OAc) ₂	2.5	5	1,300	-40	3,250	32.5 (30)	¹²
ZHF50	0.5	0.25	770	-40	385	0.43 (100)	¹³
ACDE-3	0.5	0.5	1,100	-40	550	0.85 (100)	¹⁴

20% GVL/ ZnOTF	0.2	0.2	2,300	-40	460	-	15
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1 *Angew. Chem. Int. Ed.* 63, e202409986 (2024); **2** *Nat. Sustain.* 6, 325-335 (2023); **3** *Nat. Commun.* 11, 4463 (2020); **4** *Angew. Chem. Int. Ed.* 63, e202407659 (2024); **5** *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); **6** *J. Am. Chem. Soc.* 146, 31612-31623 (2024); **7** *Energy Environ. Sci.* 17, 8966-8977 (2024); **8** *Nat. Commun.* 14, 5443 (2023); **9** *Energy Storage Mater.* 70, 103524 (2024); **10** *Angew. Chem. Int. Ed.* 63, e202318496 (2024); **11** *Angew. Chem. Int. Ed.* 62, e202315834 (2023); **12** *Energy Environ. Sci.* 18, 713-727 (2025); **13** *Energy Environ. Sci.* 16, 5096-5107 (2023); **14** *Angew. Chem. Int. Ed.* 63, e202410210 (2024); **15** *Adv. Funct. Mater.* 35, 2413807 (2025).

Table R2. Comparison of the aqueous Zn-based batteries performance in this work with previously reported electrolytes at ultralow temperatures (≤ -40 °C).

Electrolyte	Cathode	Current density (A g ⁻¹)	Cycle number	Capacity retention (%)	T (°C)	Ref.
DCE41	PANI	0.5	788	100.0	-60	This work
		5	2,000	95.0		
			12,000	80.0		
		0.1	500	100.0	-70	
		0.5	700	90.0		
DCE42		0.2	85	100.0	-80	
Na-H ₂ O-Ca	NaFeMnH	0.1 C	20	93.1	-80	16
Na-H ₂ O-EG		0.5 C	70	85.1	-60	
MSE-1D1W	PANI	0.5	3,000	97.0	-80	1
5m Zn(ClO ₄) ₂	PANI	1	1,200	~85.0	-80	17
		1	5,000	~100.0	-70	
4 M Zn(BF ₄) ₂	TCBQ	0.1 C	20	70.0	-80	18

		0.1 C	50	94.7	-60	
3.5 M						
Mg(ClO ₄) ₂	PTO	0.2	100	~100.0	-70	19
+1 M						
Zn(ClO ₄) ₂						
Zn(BF ₄) ₂ -PAM	PANI	0.05	100	100.0	-70	20
7.5 m ZnCl ₂	PANI	0.2	2,000	100.0	-70	3
1 M ZnCl ₂	PTO	1	1,600	96.0	-60	4
+4 M CaCl ₂						
ZnCl ₂ +SF	VOH	0.5	1,500	100	-60	5
BPE	V ₂ O ₅	1	1,100	100	-60	7
3.0 M ZClO		1	16,500	~99.8	-60	
+ 0.3 M	I ₂ /AC	1	3,000	94.4	-40	12
Zn(OAc) ₂						
ZnCl ₂ +100mM	PANI	0.2	10,000	60.4	-50	10
αDG						
3ZC6LC	PANI	0.5	2,000	100	-50	21
0.08 M C-	PANI	0.05	1,000	100	-50	9
ZnCl ₂ /PG-H ₂ O						
7.6 m ZnCl ₂	VOPO ₄	1/3 C	200	95.0	-50	22
-0.05 m SnCl ₂						
60% G2	PANI	0.1	1,000	95.2	-45	23
	KVOH	0.1	4,000	82.9		
ZGBCP	PANI	10	30,000	85.4	-40	24
P20 (3 M	NaV ₃ O ₈ •	0.2	400	100	-40	25
Zn(OTf) ₂ +20	1.5H ₂ O					

%PC)						
8 m LiCl	PANI	1	4,000	95.7	-40	26
ZnAc ₂ +EDGFL	PANI	1	1,000	~52	-40	15
MIAE	PANI	0.5	12,000	~100	-40	6
		5	35,000	~56		
ZHF50	PANI	5	6,500	90	-40	13
8 M ZnCl ₂ /EG20	V ₂ O ₅	0.1	1,000	~87	-40	27
7P1W	TCBQ	0.1	700	76.3	-40	28
HE	NVO	0.1	~1,800	100	-40	29
ACDE-3	poly (1, 5- NAPD)	0.1	1,500	100	-40	14

1 *Angew. Chem. Int. Ed.* 63, e202409986 (2024); **3** *Nat. Commun.* 11, 4463 (2020); **4** *Angew. Chem. Int. Ed.* 63, e202407659 (2024); **5** *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); **6** *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); **7** *Energy Environ. Sci.* 17, 8966-8977 (2024); **9** *Energy Storage Mater.* 70, 103524 (2024); **10** *Angew. Chem. Int. Ed.* 63, e202318496 (2024); **12** *Energy Environ. Sci.* 18, 713-727 (2025); **13** *Energy Environ. Sci.* 16, 5096-5107 (2023); **14** *Angew. Chem. Int. Ed.* 63, e202410210 (2024); **15** *Adv. Funct. Mater.* 35, 2413807 (2025); **16** *Nat. Energy* 9, 839-848 (2024); **17** *Nat. Commun.* 14, 601 (2023); **18** *J. Mater. Chem. A* 9, 7042-7047 (2021); **19** *Nano-micro Lett.* 13, 204 (2021); **20** *Adv. Funct. Mater.* 2023, 33, 2214546; **21** *Nano-micro Lett.* 14, 98 (2022); **22** *Angew. Chem. Int. Ed.* 60, 18845-18851 (2021); **23** *Energy Environ. Sci.* 17, 4569-4581 (2024); **24** *Nat. Commun.* 15, 6249 (2024); **25** *Adv. Funct. Mater.* 32, 2111714 (2022); **26** *J. Am. Chem. Soc.* 146, 12743-12749 (2024);

27 *ACS Nano* 17, 17359-17371 (2023); **28** *ACS Energy Lett.* 9, 3380-3390 (2024); **29** *Nat. Commun.* 14, 2720 (2023).

b. The mechanisms research related to deshielding effect of Al^{3+} for both H and O on T_f of water

In our work, the mechanisms related to the deshielding effect of Al^{3+} on both H and O atoms in water, and its impact on the T_f , are primarily elucidated through **careful spectroscopic characterization combined with theoretical calculations**. Specifically, we compared the ^1H and ^{17}O NMR spectra of various electrolyte systems, including Li^+ , Na^+ , Mg^{2+} , Zn^{2+} , Ca^{2+} , and Al^{3+} , and demonstrated that only Al^{3+} induces a simultaneous deshielding effect on both the H and O atoms of water molecules. This deshielding effect lowers the resonance frequencies of both H and O, thereby reducing the ability of water molecules to form hydrogen bonds (which is linked to the larger q/r^2 value of Al^{3+} , as computed and shown in Fig. 1e). This leads to a significant reduction in the freezing point of the electrolyte. Furthermore, the larger shifts observed in the NMR spectra for both H and O in the Al^{3+} system highlight the stronger interaction between Al^{3+} and water molecules, distinguishing it from other cations (as shown in original Fig. 1d and Supplementary Figs. 1–4).

Additionally, we employed DFT calculations to examine the electrostatic potential (ESP) and Hirshfeld charge distributions between different cations and water molecules, which further confirm the influence of Al^{3+} on the electron cloud density of water (as illustrated in Fig. 1e and Supplementary Figs. 9–10). The binding energy calculations corroborate the stronger interaction between Al^{3+} and water molecules. Moreover, we compared the changes in the number of hydrogen bonds between water molecules at different temperatures in various electrolyte systems using molecular dynamics (MD) simulations

(original Fig. 1f and Supplementary Fig. 11), which emphasized that Al^{3+} significantly reduces HB formation due to its deshielding effect on both the H and O atoms of water.

Additionally, we greatly appreciate your valuable comments on our manuscript. In response to your suggestions, we have **further supplemented the manuscript with additional data** regarding the freezing points and hydrogen bond changes for various electrolyte systems. These updates are reflected in our detailed point-by-point responses below. We believe that the additional experimental data and explanations will further support our proposed mechanisms related to the deshielding effect of Al^{3+} on both H and O atoms in water, and we hope the revised manuscript will be suitable for publication in *Nature Communications*.

Below are our point-by-point responses to your comments:

1. The expression of T_t can easily bring confusion for readers since it is either common nor clear enough to correctly denote the specific solid–liquid transition point. Commonly T_f or T_m is utilized to express freezing point or melting point, respectively.

Response: Thank you for this very helpful comment. In the initial version of the manuscript, the use of T_t to denote the solid-liquid transition point was primarily based on the description in *Nat. Commun.* 11, 4463, (2020). However, we acknowledge your point that T_f or T_m is more commonly used to represent the freezing or melting point. To avoid any potential confusion, **we have revised the manuscript to replace “ T_t ” with “ T_f ” accordingly.**

2. The sequence order of cation deshielding effect on both H and O in water is different in this work. Which effect plays a dominant role and has a greater impact on the freezing point? What’s the relationship between the deshielding effect of H atom and the freezing point? The authors stress the core

point of this manuscript to the cation effect on low temperature performance of aqueous solutions. However, no solid experiments support the idea of Al^{3+} system possessing the lowest freezing point compared to other cation systems. The authors should supply these measurements (DSC or Raman) on freezing points of different cation systems and discuss the correlation with their corresponding deshielding effect of H atom.

Response: Thank you for your insightful suggestions. Both the deshielding effects for Al^{3+} on the H and O atoms of water play equally important roles in lowering the freezing point of the electrolyte. Previous related works (*Nat. Commun.* 11, 4463, (2020); *Angew. Chem. Int. Ed.* 63, e202407659, (2024)) generally indicate that positively charged cations strongly attract the highly electronegative O atoms in water molecules through hydration, thereby restricting their participation in HB formation. However, this perspective largely overlooks the impact of cations on H atoms, which also contribute to the formation of HB, particularly at lower temperatures. In contrast, although the sequence order of cation deshielding effect on both H and O in water may be different, this study emphasizes that both effects play equally significant roles in lowering the freezing point of aqueous electrolyte. In addition to demonstrating the deshielding effect of cations on O, our research also provides evidence of Al^{3+} -induced deshielding on H atoms by ^1H NMR spectra and Hirshfeld charge distributions of various electrolytes. The combined deshielding effects of Al^{3+} on both the O and H atoms significantly reduce their ability to form HBs, leading to a marked decrease in the freezing point of the electrolyte. Additionally, we appreciate your suggestion to include DSC or Raman data to support the idea that the Al^{3+} system possesses the lowest freezing point compared to other cation systems. To address this, we performed DSC measurements to compare the freezing points of different cation systems. As shown in

Figs. R1a and b, when the concentrations of both the cations and anions in the electrolyte were fixed at 0.9 m and 2.7 m, respectively, the Al^{3+} system exhibited the lowest freezing point compared to the other cation systems, confirming the superior antifreeze capability of the Al^{3+} system. This is primarily attributed to the strong deshielding effect of Al^{3+} on both the H and O atoms of water molecules, which significantly reduces their ability to form hydrogen bonds. We have added the DSC curves of different cation systems in the revised Supplementary information of Fig. 12, and discussed them in the revised manuscript in Pages 7, line 21-25.

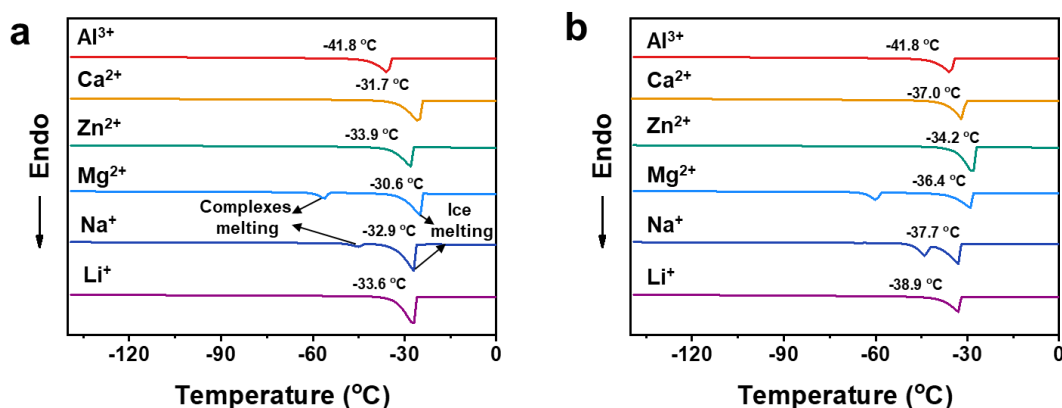


Fig. R1 DSC curves of different cation electrolytes with the anion of Cl^- . **a** The fixed cation concentration is 0.9 m and **b** the fixed Cl^- concentration is 2.7 m, respectively.

Further DSC measurements were conducted by fixing the concentrations of cations at 2.8 m across various systems. Notably, when the Al^{3+} concentration was 2.8 m, the system exhibited the best antifreeze performance, as previously established in the manuscript (Fig. R2a).

For further evaluation, the freezing points for Cl^- concentration set to 8.4 m were compared. As shown in Fig. R2b, when the Cl^- concentration was fixed at 8.4 m, the concentrations for Al^{3+} , Li^+ , Na^+ , Mg^{2+} , Zn^{2+} , and Ca^{2+} were 2.8 m, 8.4 m, 8.4 m, 4.2 m, 4.2 m, and 4.2 m, respectively, and the freezing point

of Al^{3+} system ($-117\text{ }^{\circ}\text{C}$, 2.8 m) was surpassed only by that of the Li^{+} system ($-123\text{ }^{\circ}\text{C}$, 8.4 m). This observation can be attributed to the total ion concentration in the solution, which varied across the systems.

It is important to note that this study emphasizes achieving superior antifreeze properties at low salt concentrations. Therefore, these results further substantiate the conclusion that the Al^{3+} system exhibits superior antifreeze capability compared to other cation systems.

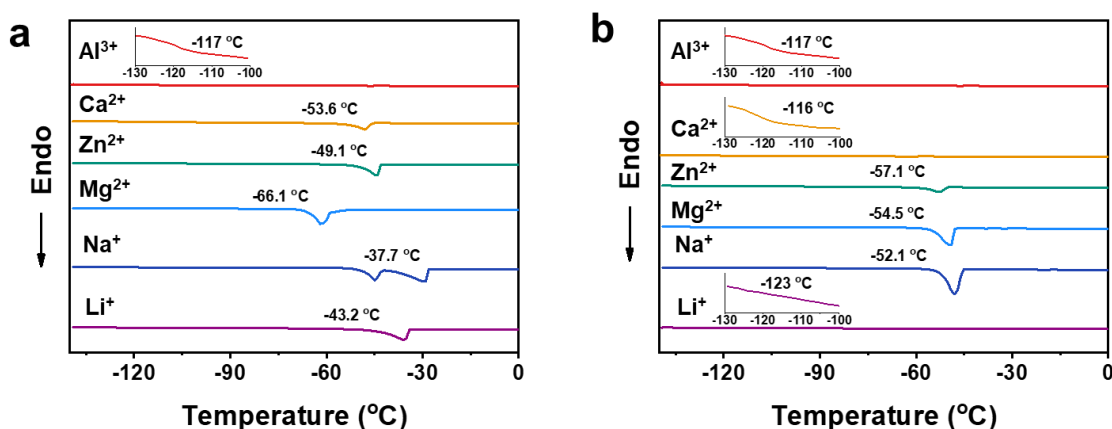


Fig. R2 DSC curves of different cation electrolytes with the constant anion of Cl^{-} . **a** The fixed cation concentration is 2.8 m and **b** the fixed Cl^{-} concentration is 8.4 m, respectively. Note: due to the solubility limit of NaCl being lower than 8.4 m, the DSC curve for the Na^{+} system in **b** represents the saturated concentration.

3. Due to the different valence state of different cations, how can the authors exclude the effect of the concentration of Cl^{-} on the freezing point?

Response: We thank the reviewer for raising this important question. To address the concern regarding the influence of Cl^{-} concentration on the freezing point, we carefully controlled the concentrations of both the cation and Cl^{-} in the DSC measurements, ensuring that the observed changes in the freezing

point were primarily governed by the cationic type, rather than fluctuations in Cl^- concentration.

In our experiments, the Cl^- concentration was fixed at 8.4 m, while the cation concentrations were varied across different cation systems. As shown in Fig. R2b, when the anion concentration was set to 8.4 m, the freezing point of the Al^{3+} system ($-117\text{ }^\circ\text{C}$) was second only to that of the Li^+ system ($-123\text{ }^\circ\text{C}$), with the Al^{3+} concentration at 2.8 m, much lower than that of the Li^+ system at 8.4 m. This indicates that the difference in freezing point was primarily due to the cation effect rather than variations in Cl^- concentration. To exclude the effect of Cl^- concentration on the freezing point, we have added the DSC curves (Fig. R2) of different cation systems in the revised Supplementary information of Fig. 15, and discussed them in the revised manuscript in Page 8, line 22-26, and Page 9, line 1-2.

4. Why the increased electron density on H implies a high proton activity of H atom to form HBs with O? H atom with lower electron density exhibits a more positive electrostatic potential and theoretically should more easily form HB with the O atom of adjacent water molecules.

Response: We appreciate the reviewer's insightful question. The explanation of how ion–water interactions influence the electron density of H and O atoms and affect hydrogen bond formation is primarily based on previous studies (*J. Chem. Soc. Faraday Trans. 94*, 3261-3269 (1998); *J. Am. Chem. Soc.* 146, 2257-2266 (2024)).

As described in previous studies, “if only PCA was contained in water, the ^2H peak would upshift to 4.6821 and 4.6907 ppm (for 0.5 and 1 m, respectively) because **less water was at a free state** compared with those in an environment containing H_2O . This is because the polar PCA molecule can **reduce the electron density of the water proton**, causing the H nucleus to **lose its shielding effect** and the **proton resonance frequency to move downward**. If different amounts of PCA (0.4–0.8 m) were further

included, the ^2H peak from water started to move forward to 4.726 and 4.741 ppm, respectively, proving that the **proton activity of free water is replaced by PCA** and part of the free water molecules in the solution is limited due to the polar PCA.”

Building on these findings, in our system, the strong electric field of Al^{3+} induces electron density transfer from the H nucleus to the vacant orbitals of Al^{3+} , leading to a reduction in electron density on H and a corresponding downshift in resonance frequency. This decreased shielding effect, arising from the interaction between Al^{3+} and the H nucleus, weakens the ability of H to act as HB donor for the information of HB. Therefore, the explanation based on proton resonance frequency provides a more accurate interpretation. To avoid potential misunderstanding, we have added the above discussion into the revised manuscript in Page 6, lines 2-8.

5. Higher deposition capacity ($>0.2 \text{ mAh cm}^{-2}$) test at room temperature and low temperature of symmetric Zn-Zn symmetric cells should be supplied.

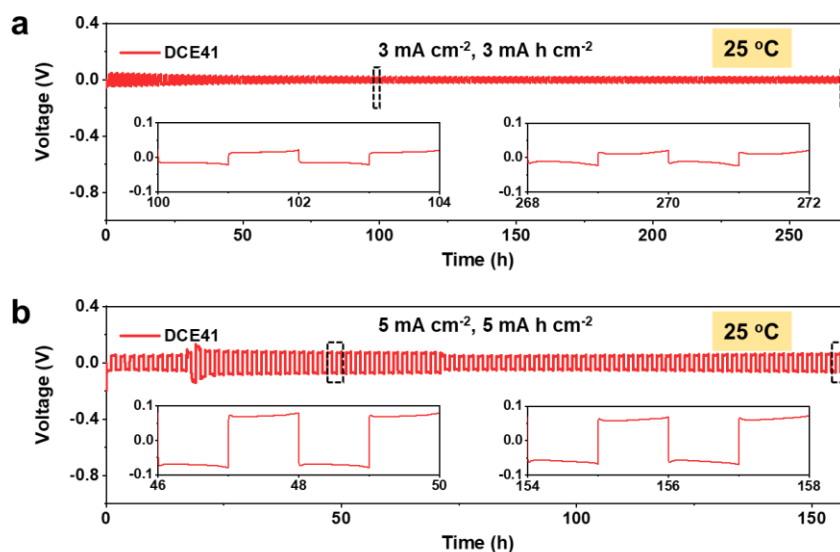


Fig. R3 Galvanostatic voltage profiles of the symmetrical Zn cells at **a** 3 mA cm⁻², 3 mA h cm⁻² and **b** 5 mA cm⁻², 5 mA h cm⁻² at 25 °C.

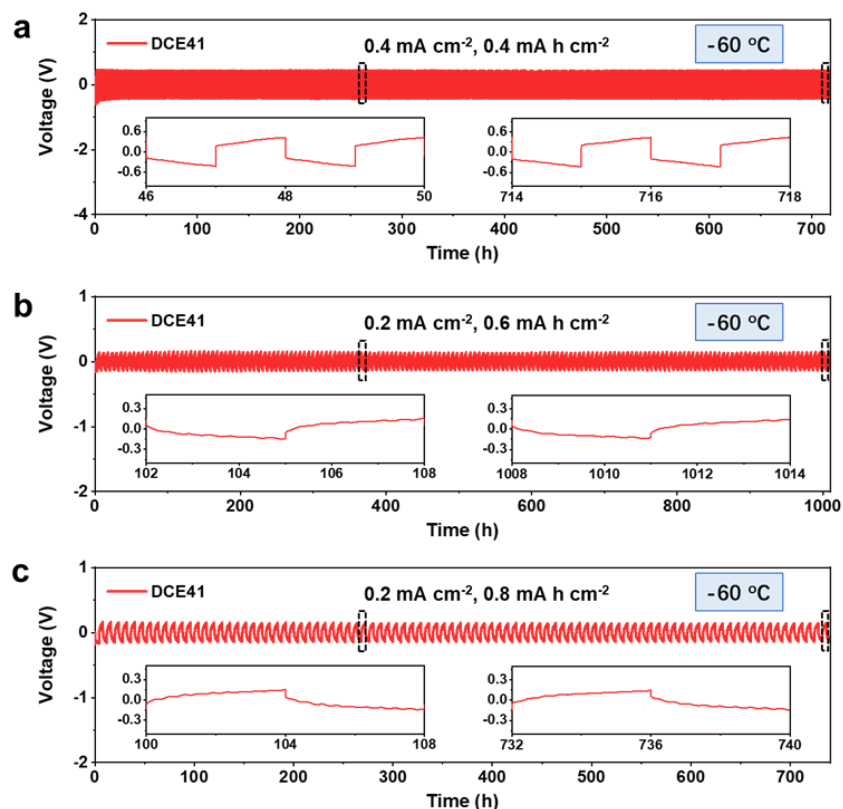


Fig. R4 Galvanostatic voltage profiles of the symmetrical Zn cells at **a** 0.4 mA cm^{-2} , 0.4 mA h cm^{-2} , **b** 0.2 mA cm^{-2} , 0.6 mA h cm^{-2} and **c** 0.2 mA cm^{-2} , 0.8 mA h cm^{-2} at -60°C .

Response: We acknowledge the reviewer for the important suggestion. The higher deposition capacity ($> 0.2 \text{ mA h cm}^{-2}$) test at room temperature and low temperature of symmetrical Zn cells are presented in Figs. R3 and R4. In the supplementary tests of the symmetrical Zn cells, $22 \mu\text{m}$ thin Zn metal was employed. As shown, at the high current density and area capacity of 3 mA cm^{-2} , 3 mA h cm^{-2} and 5 mA cm^{-2} , 5 mA h cm^{-2} , the cells with DCE41 presented reversible cycling for more than 270 h and 150 h, realizing the high depth of discharge (DOD) of Zn metal for 23.3% and 38.8%, respectively. Furthermore, the symmetrical cells were also performed at higher current density and area capacity at -60°C . As illustrated in Fig. R4, with DCE41, the symmetrical cell remained stable for more than 718 h (0.4 mA cm^{-2} , 0.4 mA h cm^{-2}), 1,014 h (0.2 mA cm^{-2} , 0.6 mA h cm^{-2}) and 740 h (0.2 mA cm^{-2} , 0.8 mA h cm^{-2})

cm⁻²). The above symmetrical cells at -60 °C are all still running.

Additionally, we have included the calculated DOD and cumulative capacity data in Table R1, and based on the combined analysis of current density, Zn metal thickness, cycle life, cumulative capacity, and DOD, we find that our cycling performance is highly competitive and surpasses many of the reported aqueous Zn-based battery systems, such as *Nat. Sustain.* 6, 325-335 (2023); *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); *Energy Environ. Sci.* 18, 713-727 (2025); *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); *Energy Environ. Sci.* 17, 8966-8977 (2024); *Angew. Chem. Int. Ed.* 63, e202409986 (2024); *Angew. Chem. Int. Ed.* 63, e202407659 (2024); *Angew. Chem. Int. Ed.* 63, e202318496 (2024); *Angew. Chem. Int. Ed.* 63, e202410210 (2024); *Nat. Commun.* 14, 5443 (2023); *Energy Environ. Sci.* 16, 5096-5107 (2023) and et al. We have added the above symmetrical Zn cells performance with DCE41 at -60 °C and 25 °C in Figs. S31 and S34, and discussed in revised manuscript in Page 15, line 1-4 and line 20-24.

6. The author mentions the viscosity of the electrolyte several times in the manuscript (page 8, lines 155 and 165, etc), and the relevant data should be provided.

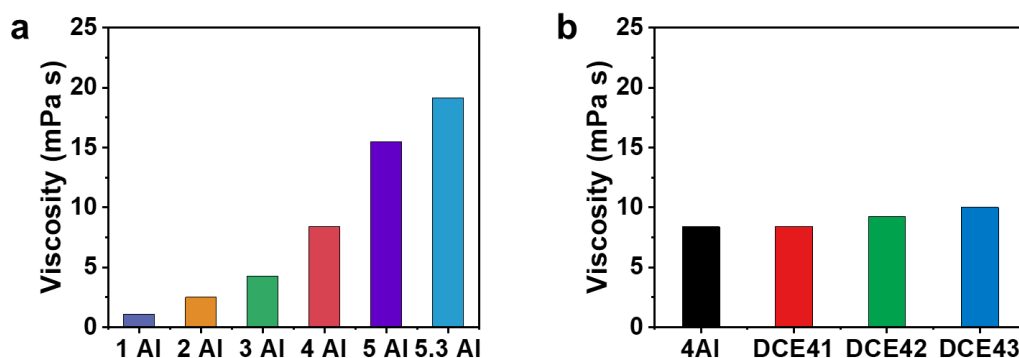


Fig. R5 Viscosities of **a** different AlCl₃ concentration electrolytes and **b** DCEs.

Response: We thank the reviewer for highlighting this important point. The viscosity of different AlCl_3 concentration electrolytes and DCEs was evaluated using a Rotary Rheometer (MARS 60), and the results are presented in Fig. R5. As shown, with increasing Al^{3+} concentration, the viscosity of the electrolyte gradually increases. This further verifies our statements in the manuscript: “However, when the concentration of Al salt exceeds 4 m, the electrolyte still freezes at -70°C . This is due to the stronger interaction between cations and anions, which makes the electrolytes more viscous and ultimately causes freezing.” and “The reduced intensity of the NMR spectra for ^{17}O and ^1H is related to the increased viscosity”.

Additionally, compared to 4Al, the viscosity of DCE41 slightly decreases, and no significant change in viscosity is observed with increasing concentration of ZnCl_2 . This suggests that the introduction of the ZnCl_2 does not significantly affect the viscosity of the electrolyte, which ensures the high ionic conductivity of the DCEs. We have added the above the results of viscosities in Figs. S14 and S22, and discussed in revised manuscript in Page 8, line 13-17 and Page 12, line 22-25.

7. In the Figure. 1g, please provide more comprehensive reasons to explain why the 4Al electrolyte system has the best anti-freezing performance.

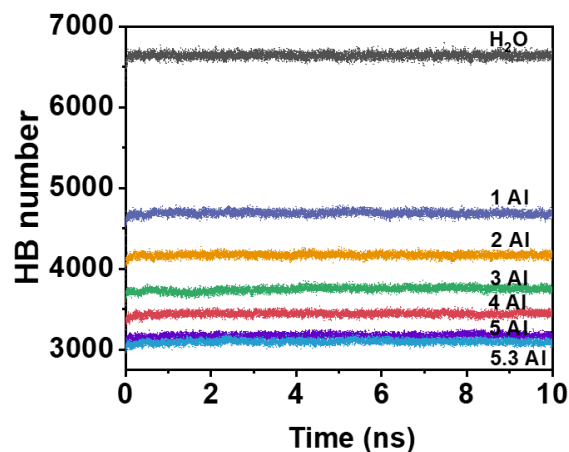


Fig. R6 The calculated HB number between water molecules in different AlCl₃ concentration electrolytes.

Response: We thank the reviewer for highlighting this important point. To provide a more comprehensive explanation for why the 4Al electrolyte system demonstrates best antifreezing performance, molecular dynamics (MD) simulations were further performed. As shown in Fig. R6, with increasing AlCl₃ concentration, the number of HBs between water molecules gradually decreases. However, in systems with lower AlCl₃ concentrations (1-3 m), the number of HBs remains relatively high. This observation indicates that at lower concentrations, the insufficient Al³⁺ concentration leads to an inadequate deshielding effect on the O and H atoms of water molecules, which results in freezing when the temperature is significantly reduced (as demonstrated by the inset images in Fig. 1g).

At higher concentrations, such as 5 m and 5.3 m, although the number of HBs between water molecules decreases significantly, Fig. R5a reveals a sharp increase in electrolyte viscosity when the AlCl₃ concentration exceeds 4 m. The elevated viscosity at these higher concentrations promotes salt crystallization at low temperatures, ultimately impairing the antifreezing performance of the electrolyte.

In contrast, the 4Al system achieves a substantial reduction in HB number while maintaining relatively

low viscosity, thereby allowing for superior antifreezing performance. We have added the MD simulation results for electrolytes with varying AlCl_3 concentrations in Fig. S13 and discussed in revised manuscript in Page 8, line 8-19.

8. Why are Zn^{2+} salts chosen to construct dual-cation electrolytes instead of other cation salts? If not for application to Zn-based batteries, are there other better options of cation to enhance the migration kinetics of electrolytes?

Response: We acknowledge the reviewer for these forward-thinking questions. The selection of Zn^{2+} salts to construct dual-cation electrolytes is primarily based on the following three considerations: (1) Compatibility with Zn metal anode and our research expertise: Zn metal is chosen as the anode due to its low redox potential (-0.763 V vs. standard hydrogen electrode), high theoretical capacity, intrinsic safety, and natural abundance. In aqueous Zn-ion batteries, the process of stripping/plating of Zn^{2+} is relatively stable. Moreover, our research group has extensive experience in aqueous Zn-based batteries, providing a strong foundation for optimizing and advancing this electrolyte system. (2) Improvement on Zn anode reversibility: Previous studies have shown that Zn-Al alloy formation on the Zn metal anode improves its reversibility. Based on this, we hypothesized that employing Zn^{2+} as the second cation could facilitate the formation of Zn-Al alloys on the Zn anode, thereby further improving the cycling performance of the battery. (3) Cost-efficiency and resource sustainability: Compared to other cation salts such as Li^+ or Na^+ , Zn^{2+} salts not only ensure good battery performance but also mitigate cost and environmental issues.

Regarding the reviewer's question, "If not for application to Zn-based batteries, are there other better options of cation to enhance the migration kinetics of electrolytes?" we acknowledge that while Zn^{2+} is

highly suitable for Zn-based batteries, other cations may offer enhanced migration kinetics in different electrolyte systems. For instance, aqueous Na^+ and Li^+ batteries have been extensively studied due to their smaller ionic radii, which are beneficial for improving ion migration rates. Research by Hu and Chen et al. (*Nat. Energy* 9, 839-848 (2024); *J. Am. Chem. Soc.* 146, 12743-12749 (2024)) on antifreeze electrolytes has demonstrated the potential of Na^+ and Li^+ systems in improving ion transport. In comparison to the strong interaction between Al^{3+} and water molecules, incorporating Na^+ or Li^+ into aqueous systems could lower the desolvation energy barrier through competitive ion-ion and ion-solvent interactions, thereby enhancing ion migration kinetics. Future work will focus on further optimizing these interactions to develop electrolyte systems with superior ion dynamics.

Reviewer: 2 *This paper designs an aqueous Zn battery electrolyte (DCE41) based on the dual-cation effect of Al^{3+} and Zn^{2+} , achieving high ionic conductivity and stability even under ultralow temperatures. The proposed strategy effectively reconfigures hydrogen bond networks and forms a corrosion-resistant Al-Zn alloy layer on the Zn anode, significantly enhancing battery performance at low temperatures. The systematic analysis of the deshielding effect and the mechanism for improved low-temperature performance based on cation effects is impressive. However, the study lacks sufficient data to elucidate the electrolyte structure and validate the mechanisms underlying performance improvement, as well as data proving its superiority compared to existing literature.*

Answer: We sincerely appreciate your positive remarks regarding the design of our dual-cation electrolyte and its enhanced low-temperature performance. We are also grateful for the recognition of our systematic analysis of the deshielding effect and the underlying mechanisms for improved performance. Regarding the concern about insufficient data to elucidate the electrolyte structure and

validate the mechanisms, we have carefully revised the manuscript to response your valuable and insightful suggestions, **readjust the structure** of the manuscript and **have done additional experiments** to better consolidate our proposed mechanisms underlying performance improvement. Moreover, we have **added more comparative data**, including the **latest published literature**, to demonstrate the breakthroughs of our dual-cation electrolyte system in aqueous Zn-based batteries under ultralow temperature conditions.

1. This study focused on the cation effect. Why was Cl^- selected as the constant anion among various anions?

Response: We thank the reviewer for rising this valuable question. Cl^- was selected as the constant anion for several key reasons. Firstly, Cl^- is widely used in aqueous electrolyte systems due to its low cost, good solubility, and ability to enhance ionic conductivity. Secondly, in studies investigating ion–water interactions, the antifreezing behavior of anions is often analyzed in relation to their influence on water molecular structure, as described by the **Hofmeister effect** (*Adv. Energy Mater.* **11**, 2002913 (2021)). To minimize anion–induced interference in the low-temperature performance, we chose Cl^- , which is positioned in the middle of the Hofmeister series. This strategic selection helps reduce its impact on freezing point depression, allowing a clearer focus on the cation effect in our study.

2. The inclusion of hetero-cation of Al^{3+} may cause unwanted competition for ion conduction with Zn^{2+} . The authors need to differentiate the diffusion behavior of Al^{3+} and Zn^{2+} . For example, the diffusion coefficient of Zn^{2+} should be measured both in the absence and presence of Al^{3+} .

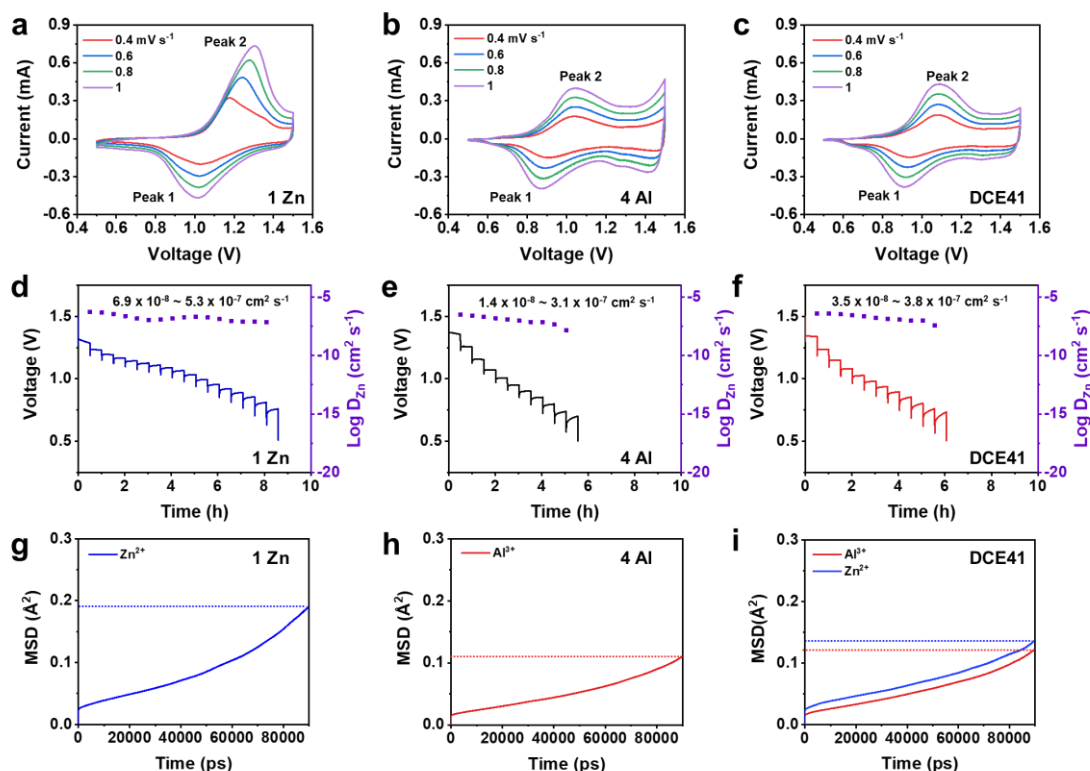


Fig. R7 CV curves of the Zn/PANI battery with **a** 1 Zn, **b** 4Al and **c** DCE41 at different scan rates. GITT tests of the Zn/PANI battery with **d** 1Zn, **e** 4Al and **f** DCE41. The results of simulated ion diffusion coefficient in **g** 1Zn, **h** 4Al and **i** DCE41.

Response: We express our gratitude to the reviewer for this expert suggestion. Cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT) were combined with molecular dynamics (MD) simulations to differentiate ion diffusion behavior across various electrolyte systems. Notably, in the DCE41 system, the presence of a unique solvation structure of $[\text{Al-Zn}(\text{H}_2\text{O})_x]^{5+}$ was confirmed (as shown in Figs. 3a and e), indicating that Zn^{2+} diffusion is influenced by Al^{3+} . This finding is further supported by CV results. As illustrated in Figs. R7a-c, the redox peak positions and shapes in DCE41 closely resemble those in the 4Al electrolyte rather than in 1Zn. To quantitatively assess ion diffusion, diffusion coefficients were calculated with Randles–Sevcik equation (*ACS Nano* 16, 8449-8460 (2022)).

For the 1Zn, 4Al, and DCE41 systems, the diffusion coefficients of the corresponding ions (peak 1) were determined to be 1.41×10^{-7} , 3.61×10^{-8} , and $6.00 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. These results indicate a possible reduction in Zn^{2+} diffusion coefficient in DCE41 compared to 1Zn (Figs. R7a-c), a trend that is further corroborated by the GITT results (Figs. R7d-f).

In our work, the design of our dual-cation electrolyte is predicated on introducing Zn^{2+} into the 4Al system to enhance Al^{3+} diffusion behavior. Therefore, **comparing the diffusion coefficient of Al^{3+} in the presence and absence of Zn^{2+} provides critical insight into the system.** Both CV and GITT results confirm that Al^{3+} exhibits an increased diffusion coefficient in DCE41 compared to 4Al. This enhancement is primarily attributed to the optimized solvation structure in the dual-cation electrolyte, which effectively lowers the desolvation energy (as demonstrated in Figs. 3d and e), thereby facilitating faster ion diffusion.

To more directly differentiate the diffusion behaviors of the ions, MD simulations were performed. As illustrated in Figs. R7g-i, in the presence of Al^{3+} (DCE41 electrolyte), the diffusion coefficient of Zn^{2+} is reduced, whereas the diffusion coefficient of Al^{3+} is increased compared to the 4Al system. This observation is consistent with the CV and GITT conclusions and further corroborates that the dual-cation electrolyte design effectively enhances the diffusion dynamics of Al^{3+} . **We have added the above CV, GITT and MD simulation results for different electrolytes in Figs. S44-46 and discussed in revised manuscript in Page 17, line 8-20.**

3. The study claims that progressive hydrogen bond (HB) disruption leads to an increase in entropy and contributes to Low T_g . However, no analysis of the electrolyte's entropy is provided.

Response: We appreciate the reviewer's insightful comment. Thermodynamic theory indicates that a

higher degree of disorder in the atomic coordination environment of an electrolyte corresponds to higher entropy, which in turn facilitates a lower freezing point (*Nano Res. Energy* 1, e9120003 (2022)). In our original manuscript, the entropy analysis of the electrolyte was primarily based on Raman spectroscopy. As shown in the Figs. 2d and e in the original manuscript, the O–H stretching region of water was deconvoluted into three components corresponding to network water (NW), intermediate water (IW), and multimer water (MW). With increasing AlCl_3 concentration, the O–H peaks shift to higher wavenumbers and become narrower, indicating a transition from strongly hydrogen-bonded NW to weakly bonded MW. This trend, evidenced by an increased MW ratio and decreased NW and IW ratios, signifies a progressive disruption of the HB network and an increase in the disorder of the electrolyte, which is consistent with a higher entropy state.

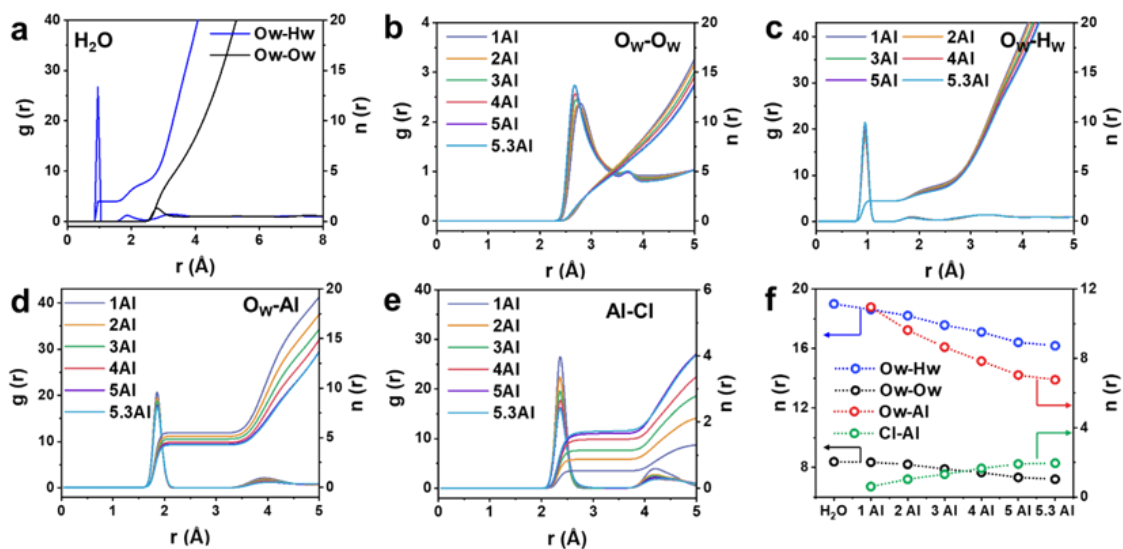


Fig. R8 MD stimulation results of aqueous solution and AlCl_3 electrolytes with varying concentrations.

a The corresponding RDF plots of $\text{O}_\text{w}\text{-H}_\text{w}$ and $\text{O}_\text{w}\text{-O}_\text{w}$ for aqueous solutions. The corresponding RDF plots of **b** $\text{O}_\text{w}\text{-H}_\text{w}$, **c** $\text{O}_\text{w}\text{-O}_\text{w}$, **d** $\text{O}_\text{w}\text{-Al}$ and **e** $\text{Al}\text{-Cl}$ for AlCl_3 electrolytes with different concentrations. **f**

The coordination numbers (n) of O_w-H_w , O_w-O_w , O_w-Al and $Al-Cl$ in aqueous solution and $AlCl_3$ electrolytes with different concentrations.

To provide complementary evidence, we conducted molecular dynamics (MD) simulations on water and $AlCl_3$ electrolytes with varying concentrations (Fig. R8). Previous studies suggest that the degree of disorder in an electrolyte can be reflected by the coordination species and coordination numbers of O atoms in water (*Nat. Energy* 9, 839-848 (2024)). MD simulations were performed with a 4 Å cutoff radius for coordination analysis. Compared to pure water, where O atoms are primarily coordinated by H (O_w-H_w) and other O (O_w-O_w), the coordination environment in $AlCl_3$ solutions becomes more complex, with the appearance of additional O_w-Al interactions and a progressive decrease in the coordination numbers of O_w-H_w and O_w-O_w . These simulation results corroborate the Raman data, indicating a reduced fraction of network water and a higher degree of disorder in the electrolyte, consistent with an elevated entropy state and a lower freezing point. We have added the MD simulation results of aqueous solution and $AlCl_3$ electrolytes with varying concentrations in Fig. S16 and discussed in revised manuscript in Page 10, line 11-16.

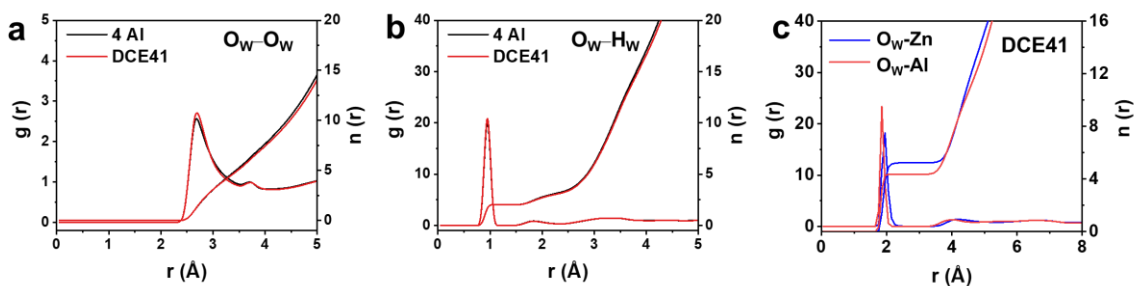


Fig. R9 MD stimulation results of 4Al and DCE41. **a** The corresponding RDF plots of O_w-O_w . **b** The corresponding RDF plots of O_w-H_w . **c** The corresponding RDF plots of O_w-Zn and O_w-Al in DCE41.

Moreover, in the dual-cation electrolyte system (DCEs), the incorporation of Zn^{2+} further diversifies the coordination environment by introducing Zn-O_w interactions (Fig. R9), resulting in even higher structural disorder relative to the 4Al system. We have added the MD simulation results MD stimulation results of 4Al and DCE41 in Fig. S21 and discussed in revised manuscript in Page 12, line 19-21.

4. The expressions used to indicate electrolyte concentrations are inconsistent and may cause confusion. Additionally, for an objective comparison, please provide the concentrations of DCE41~DCE43 in m units as well.

Response: We thank the reviewer's for rising this valuable question. We have provided the concentrations of DCE41, DCE42, and DCE43 in m units as 3.8 m, 4.8 m and 5.8 m, respectively. We have added this information in the revised manuscript in Page 11, line 26 and Page 12, line 1.

5. Fig. 2b: In the ^1H -NMR spectra, it is mentioned that H atoms in the electrolyte become increasingly deshielded with higher salt concentrations. However, the trend reverses as the peak shows shielding from 3 Al to 5.3 Al. Please provide an explanation for this phenomenon.

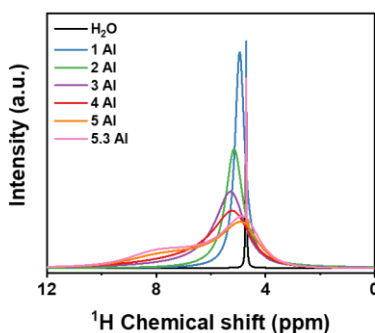


Fig. R10 ^1H NMR spectra of different AlCl_3 concentration electrolytes.

Response: We thank the reviewer's insightful observation regarding the ^1H -NMR chemical shift trend.

In the ^1H -NMR spectra of aqueous AlCl_3 solutions, as the concentration increases from 1 m to 3 m, an

obvious downfield shift is observed (Fig. R10). However, when the concentration further increases to 4 m, only a slight upfield shift occurs, suggesting that the deshielding effect reaches a maximum at this concentration. In addition, beyond 4 m, at 5 m and 5.3 m (saturation), a more noticeable upfield shift emerges, which can be attributed to the reorganization of the water coordination environment at high ion concentration (*J. Am. Chem. Soc.* 146, 2257–2266 (2024)). We have added the above discussion into the revised manuscript in Page 9, line 6-11.

6. Fig. 4a, Supplementary Fig. 32: Despite DCE41 exhibiting higher ionic conductivity and lower desolvation energy than 4 AI, it shows a higher symmetric cell overpotential. Provide a detailed discussion to explain this phenomenon.

Response: We thank the reviewer for academic suggestion. This phenomenon can also be detected in many previous literatures (*Angew. Chem. Int. Ed.* 2023, 62, e202302701; *Energy Environ. Sci.* 2023, 16, 4561). This occurrence has been noted even in electrolytes with higher ionic conductivity or lower desolvation energy, such as *J. Am. Chem. Soc.* 2022, 144, 11129-11137; *Angew. Chem. Int. Ed.* 2023, 62, e202310970.

Moreover, in aqueous Zn-based battery systems, previous studies have observed that the introduction of high-valent cations such as La^{3+} , Ce^{3+} , Sc^{3+} and Zr^{4+} often leads to an increase in overpotential in hybrid electrolytes (*Nat. Commun.* 13, 3252 (2022); *Adv. Mater.* 2022, 34, 2203104; *Angew. Chem. Int. Ed.* 2022, 61, e202211589; *Energy Environ. Sci.* 2023, 16, 4561). The literature attributes this phenomenon to the competitive adsorption between the dual cation on the electrode surface. Therefore, although DCE41 exhibits higher ionic conductivity and lower desolvation energy, the higher symmetrical cell overpotential is likely due to the competitive adsorption between Al^{3+} and Zn^{2+} ions

on the Zn metal surface. This suggests that the type of cations in the electrolyte and their interactions with the electrode surface can significantly influence the cell overpotential.

7. Fig. 5a-5c: Since the full cell data only represents the DCE41 electrolyte, it is difficult to assess its superiority. Please add the electrochemical performance of the comparative 4 Al electrolyte.

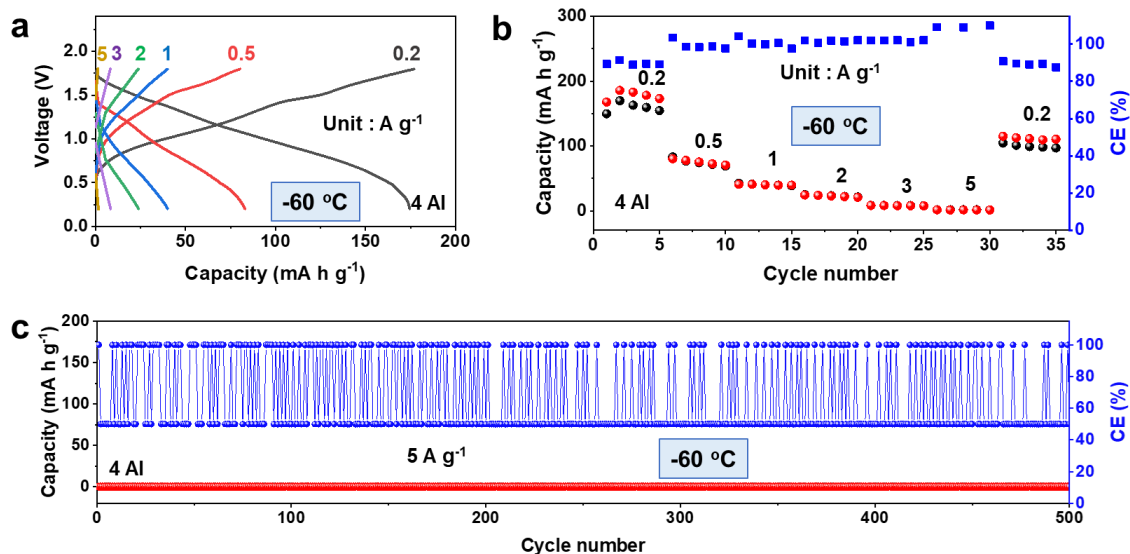


Fig. R11 **a** Galvanostatic charge/discharge curves of Zn/PANI battery with 4Al at different current densities at -60 °C. **b** Rate performance of Zn/PANI battery with 4Al at -60 °C. **c** Cycling performance at 5 A g⁻¹ at -60 °C.

Response: We thank the reviewer for the valuable suggestion. In response, we have included the electrochemical performance of the Zn/PANI full cell with the 4Al electrolyte for comparison. As shown in Fig. R11, the Zn/PANI battery with 4Al exhibits specific capacities of 164.3, 71.8, 40.5, 21.4, 7.8, and 3.9 mA h g⁻¹ at 0.2, 0.5, 1, 2, 3, and 5 A g⁻¹, respectively, at -60°C. Additionally, when the current density is cycled back from 5 A g⁻¹ to 0.2 A g⁻¹, only a capacity of 100.4 mA h g⁻¹ is retained, indicating poor rate performance. Furthermore, Fig. R11c illustrates that, due to the higher desolvation energy barrier, the capacity at a high current density of 5 A g⁻¹ for the 4Al electrolyte is only 2.9 mA h g⁻¹,

significantly lower than that of the DCE41 electrolyte (original Fig. 5b). We have added the electrochemical performance of the 4 Al electrolyte in the revised supporting information of Figs. S48 and S50, and discussed them in the revised manuscript in Page 17, line 25-26, Page 18, line 1-2, and 7-9.

8. Fig. S31-33: Comparing the performance of the 4Al electrolyte, which lacks Zn ions, with other systems appears to be an unfair comparison. It would be more appropriate to compare 1 m ZnCl₂ with DCE41 instead of 4Al.

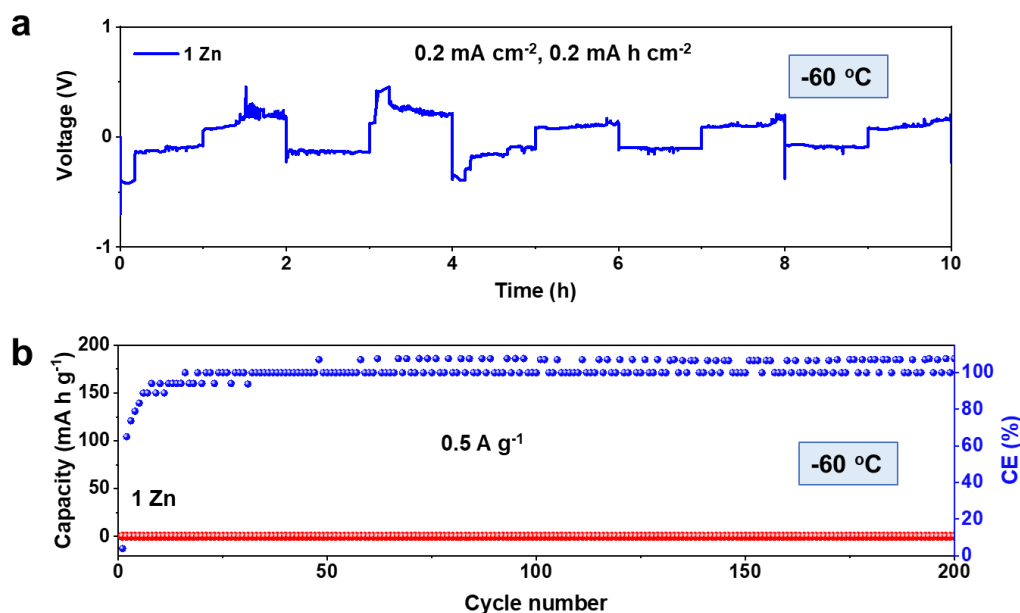


Fig. R12 a Galvanostatic voltage profiles of the symmetrical Zn cell with 1Zn at 0.2 mA cm⁻² and 0.2 mA h cm⁻² under -60 °C. **b** Rate performance of Zn/PANI battery with 1Zn at -60 °C.

Response: We sincerely appreciate the reviewer's valuable comment. Regarding the comparison in Figs. S31-33 (corresponding to the Figs. 40-42 in revised supplementary information), the main objective of comparing the performance of Zn metal in the 4Al electrolyte is to assess the cycling performance and the quality of the in situ formed Al-Zn alloy layer without the introduction of the second cation (Zn²⁺).

These experiments provide insights into the performance of the battery when Al^{3+} is the only cation present.

On the other hand, employing 1 m ZnCl_2 electrolyte for comparison would not be suitable, as it lacks Al^{3+} and cannot form the Al-Zn alloy layer, which would fail to highlight the advantage of introducing a second cation in the 4Al system. Additionally, as shown in Fig. R12, the 1Zn electrolyte does not function at -60°C , further demonstrating its limitations under ultralow temperature conditions and making it inappropriate for comparison with DCE41.

9. Table S1, Fig. 4a-3c: The areal capacity evaluated (0.2 mAh/cm^2) is too low compared to the $22\text{ }\mu\text{m}$ Zn metal, making it less meaningful to emphasize the cycle number or time. Therefore, please calculate the DOD and cumulative capacity for the evaluation and include them in Table S1.

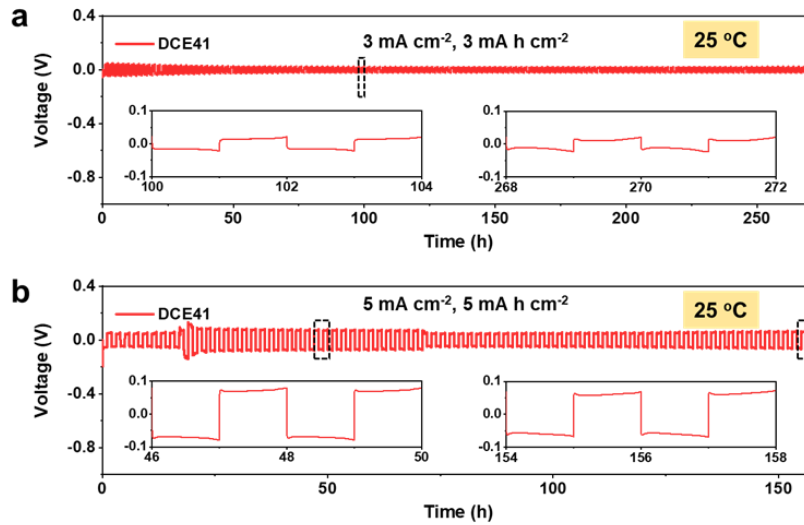


Fig. R13 Galvanostatic voltage profiles of the symmetrical Zn cells at **a** 3 mA cm^{-2} , 3 mA h cm^{-2} and **b** 5 mA cm^{-2} , 5 mA h cm^{-2} at 25°C .

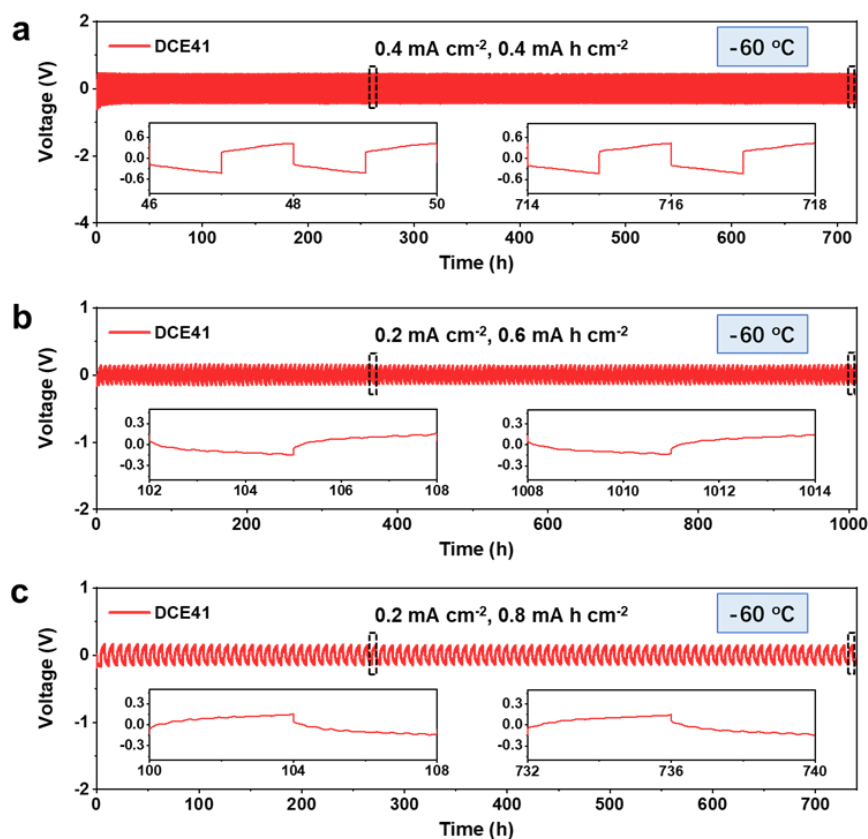


Fig. R14 Galvanostatic voltage profiles of the symmetrical Zn cells at **a** 0.4 mA cm^{-2} , 0.4 mA h cm^{-2} , **b** 0.2 mA cm^{-2} , 0.6 mA h cm^{-2} and **c** 0.2 mA cm^{-2} , 0.8 mA h cm^{-2} at $-60 \text{ }^{\circ}\text{C}$.

Table R3. The current density, areal capacity, cycling lifespan, cumulative capacity, DOD, Zn thickness and extreme operating temperatures of the symmetrical Zn cells with DCE41, compared with reported ultralow temperatures ($\leq -40 \text{ }^{\circ}\text{C}$) aqueous Zn-based systems.

Electrolyte	Current density (mA cm^{-2})	Area capacity (mA h cm^{-2})	Cycling life (h)	T ($^{\circ}\text{C}$)	Cumulative capacity (mA h cm^{-2})	Depth of discharge (%), Zn thickness (μm)	Ref.

			> 10,340				
			(shelving				
	0.2	0.2	-		> 1,378	1.6 (22)	
			recovery				
			test, still				
			running)				
	0.2	0.2	3,100		620	1.6	
						(22)	
			> 1014				
DCE41	0.2	0.6	(still	-60	> 202.8	4.7 (22)	This
			running)				work
			> 740				
	0.2	0.8	(still		> 148	6.2 (22)	
			running)				
			> 718				
	0.4	0.4	(still		> 287.2	3.1 (22)	
			running)				
	1	0.25	540		540	1.9 (22)	
	0.2	0.2	1,100	-70	220	1.6 (22)	
MSE- 1D1W	0.2	0.2	2,000	-80	400	0.34 (100)	¹
Li ₂ ZnCl ₄ • 9H ₂ O	1	-	135	-70	135	-	²
7.5 ZnCl ₂	0.2	0.2	450	-70	90	-	³
1 M ZnCl ₂ +4 M CaCl ₂	0.5	0.5	480	-60	240	1.7 (50)	⁴
ZnCl ₂ +SF	1	1	1200	-60	1200	1.7 (100)	⁵

MIAE	0.5	0.5	700	-60	350	0.85 (100)	6
	1	10	800	-40	800	57 (30)	
BPE	0.2	0.2	1,370	-60	274	0.34 (100)	7
	0.5	0.5	2,300	-40	1,150	0.85 (100)	
TMP-40	0.4	0.4	7,000	-50	2,800	0.68 (100)	8
0.08 M C- ZnCl ₂ /PG- H ₂ O	0.2	0.1	2,200	-50	440	-	9
ZnCl ₂ +100 mM αDG	5	2.5	800	-40	4,000	43 (10)	10
LACA	0.25	0.25	2,000	-40	500	-	11
3.0 M ZClO + 0.3 M Zn(OAc) ₂	2.5	5	1,300	-40	3,250	32.5 (30)	12
ZHF50	0.5	0.25	770	-40	385	0.43 (100)	13
ACDE-3	0.5	0.5	1,100	-40	550	0.85 (100)	14
20% GVL/ ZnOTF	0.2	0.2	2,300	-40	460	-	15

1 *Angew. Chem. Int. Ed.* 63, e202409986 (2024); **2** *Nat. Sustain.* 6, 325-335 (2023); **3** *Nat. Commun.* 11, 4463 (2020); **4** *Angew. Chem. Int. Ed.* 63, e202407659 (2024); **5** *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); **6** *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); **7** *Energy Environ. Sci.* 17, 8966-8977 (2024); **8** *Nat. Commun.* 14, 5443 (2023); **9** *Energy Storage Mater.* 70, 103524 (2024); **10** *Angew. Chem. Int. Ed.* 63, e202318496 (2024); **11** *Angew. Chem. Int. Ed.* 62, e202315834 (2023); **12** *Energy Environ. Sci.* 18, 713-727 (2025); **13** *Energy Environ. Sci.* 16, 5096-5107 (2023); **14** *Angew. Chem. Int. Ed.* 63, e202410210 (2024); **15** *Adv. Funct. Mater.* 35, 2413807 (2025).

Response: We express our gratitude to the reviewer for pointing out this aspect. As previous studies have shown, side reactions and dendrite formation significantly degrade the cycling performance of Zn-based batteries, **particularly at low current densities**. For instance, the studies referenced in papers (*Adv. Energy Mater.* 13, 2204092 (2023); *Adv. Funct. Mater.* 32, 2112609 (2022) and et al) have evaluated the symmetrical Zn cells performance at low current densities and demonstrated the excellent performance of the designed electrolytes in suppressing side reactions. Based on these findings, we believe that a symmetrical cell employing ultra-thin 22 μm Zn foil, cycled at 0.2 mA cm^{-2} and 0.2 mA h cm^{-2} for over 10,340 h (430 days), can effectively demonstrate the superior performance of our dual-cation electrolyte in side reaction suppression.

Nevertheless, we fully agree with the reviewer's point regarding the importance of high-capacity symmetrical cell performance for practical applications. Therefore, **we provided on the performance of symmetrical cells at the current density and area capacity of 3 mA cm^{-2} , 3 mA h cm^{-2} , and 5 mA cm^{-2} , 5 mA h cm^{-2} at $25\text{ }^{\circ}\text{C}$. We also further tested the symmetrical cell performance at low temperatures with lower current densities and higher areal capacities, including 0.4 mA cm^{-2} , 0.4 mA h cm^{-2} ; 0.2 mA cm^{-2} , 0.6 mA h cm^{-2} ; and 0.2 mA cm^{-2} , 0.8 mA h cm^{-2} . As shown in Figs. R13a and b, at high current densities and areal capacities of 3 mA cm^{-2} , 3 mA h cm^{-2} , and 5 mA cm^{-2} , 5 mA h cm^{-2} , the cells with DCE41 exhibited reversible cycling for more than 270 hours and 150 hours, respectively, achieving a high depth of discharge (DOD) of 23.3% and 38.8%. Furthermore, with DCE41 under $-60\text{ }^{\circ}\text{C}$, the symmetric cells remained stable for more than 400 h at 0.4 mA cm^{-2} , 0.4 mA h cm^{-2} ; 600 hours at 0.2 mA cm^{-2} , 0.6 mA h cm^{-2} ; and 500 hours at 0.2 mA cm^{-2} , 0.8 mA h cm^{-2} , achieving DODs of 3.1%, 4.7%, and 6.2%, respectively (Figs. R14). The above symmetrical cells at $-60\text{ }^{\circ}\text{C}$ are all still running.**

Additionally, we have included the calculated DOD and cumulative capacity data in Table R3, and based on the combined analysis of current density, Zn metal thickness, cycle life, cumulative capacity, and DOD, we find that our cycling performance is highly competitive and surpasses many of the reported aqueous Zn-based battery systems, such as *Nat. Sustain.* 6, 325-335 (2023); *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); *Energy Environ. Sci.* 18, 713-727 (2025); *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); *Energy Environ. Sci.* 17, 8966-8977 (2024); *Angew. Chem. Int. Ed.* 63, e202409986 (2024); *Angew. Chem. Int. Ed.* 63, e202407659 (2024); *Angew. Chem. Int. Ed.* 63, e202318496 (2024); *Angew. Chem. Int. Ed.* 63, e202410210 (2024); *Nat. Commun.* 14, 5443 (2023); *Energy Environ. Sci.* 16, 5096-5107 (2023) and et al (Table R3).

10. Table S2: It seems that recently published papers on low-temperature ZMBs have not been included. Please add the following papers and provide a comparison.

Response: We express our gratitude to the reviewer for pointing out this aspect. However, we did not receive the specific papers that you mentioned in the correspondence. As a result, we conducted a comprehensive review of the latest publications on low-temperature ZMBs and have included the relevant performance data in Table R3 and Table R4 for comparison (The newly added references have been highlighted in yellow). In addition to the performance comparisons already made in Table R3, we found that the full-battery cycling performance achieved with our dual-cation electrolyte still outperforms some of the most recent studies published on this topic, such as *Nat. Energy* 9, 839-848 (2024); *Nat. Commun.* 15, 6249 (2024); *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); *Energy Environ. Sci.* 18, 713-727 (2025); *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); *J. Am. Chem. Soc.* 146, 12743-12749 (2024); *Angew. Chem. Int. Ed.* 63, e202409986 (2024); *Angew. Chem. Int. Ed.*

63, e202407659 (2024); *Angew. Chem. Int. Ed.* 63, e202318496 (2024); *Angew. Chem. Int. Ed.* 63, e202410210 (2024); *Energy Environ. Sci.* 17, 4569-4581 (2024); *Energy Environ. Sci.* 17, 8966-8977 (2024); *Nat. Commun.* 14, 601 (2023); *Nat. Commun.* 14, 2720 (2023); *Energy Environ. Sci.* 16, 5096-5107 (2023) and *et al.* We have updated the Supplementary Tables 1 and 2 in the revised supplementary information with the latest comparative data.

Table R4. Comparison of the aqueous Zn-based batteries performance in this work with previously reported electrolytes at ultralow temperatures (≤ -40 °C).

Electrolyte	Cathode	Current density (A g ⁻¹)	Cycle number	Capacity retention (%)	T (°C)	Ref.
DCE41	PANI	0.5	788	100.0	-60	This work
		5	2,000	95.0		
			12,000	80.0		
		0.1	500	100.0	-70	
		0.5	700	90.0		
DCE42		0.2	85	100.0	-80	
Na-H ₂ O-Ca	NaFeMnH	0.1 C	20	93.1	-80	16
Na-H ₂ O-EG		0.5 C	70	85.1	-60	
MSE-1D1W	PANI	0.5	3,000	97.0	-80	1
5m Zn(ClO ₄) ₂	PANI	1	1,200	~85.0	-80	17
		1	5,000	~100.0	-70	
4 M Zn(BF ₄) ₂	TCBQ	0.1 C	20	70.0	-80	18
		0.1 C	50	94.7	-60	
3.5 M Mg(ClO ₄) ₂	PTO	0.2	100	~100.0	-70	19

+1 M						
Zn(ClO ₄) ₂						
Zn(BF ₄) ₂ -PAM	PANI	0.05	100	100.0	-70	20
7.5 m ZnCl ₂	PANI	0.2	2,000	100.0	-70	3
1 M ZnCl ₂ +4 M CaCl ₂	PTO	1	1,600	96.0	-60	4
ZnCl ₂ +SF	VOH	0.5	1,500	100	-60	5
BPE	V ₂ O ₅	1	1,100	100	-60	7
3.0 M ZClO + 0.3 M Zn(OAc) ₂	I ₂ /AC	1	16,500	~99.8	-60	12
ZnCl ₂ +100mM αDG	PANI	0.2	10,000	60.4	-50	10
3ZC6LC	PANI	0.5	2,000	100	-50	21
0.08 M C- ZnCl ₂ /PG-H ₂ O	PANI	0.05	1,000	100	-50	9
7.6 m ZnCl ₂ -0.05 m SnCl ₂	VOPO ₄	1/3 C	200	95.0	-50	22
60% G2	PANI	0.1	1,000	95.2	-45	23
	KVOH	0.1	4,000	82.9		
ZGBCP	PANI	10	30,000	85.4	-40	24
P20 (3 M Zn(OTf) ₂ +20 %PC)	NaV ₃ O ₈ • 1.5H ₂ O	0.2	400	100	-40	25
8 m LiCl	PANI	1	4,000	95.7	-40	26
ZnAc ₂ +EDGF	PANI	1	1,000	~52	-40	15

L						
MIAE	PANI	0.5	12,000	~100	-40	6
		5	35,000	~56		
ZHF50	PANI	5	6,500	90	-40	13
8 M	V ₂ O ₅	0.1	1,000	~87	-40	27
ZnCl ₂ /EG20						
7P1W	TCBQ	0.1	700	76.3	-40	28
HE	NVO	0.1	~1,800	100	-40	29
ACDE-3	poly (1, 5-	0.1	1,500	100	-40	14
	NAPD)					

1 *Angew. Chem. Int. Ed.* 63, e202409986 (2024); **3** *Nat. Commun.* 11, 4463 (2020); **4** *Angew. Chem. Int. Ed.* 63, e202407659 (2024); **5** *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.202500434 (2025); **6** *J. Am. Chem. Soc.* 146, 46, 31612-31623 (2024); **7** *Energy Environ. Sci.* 17, 8966-8977 (2024); **9** *Energy Storage Mater.* 70, 103524 (2024); **10** *Angew. Chem. Int. Ed.* 63, e202318496 (2024); **12** *Energy Environ. Sci.* 18, 713-727 (2025); **13** *Energy Environ. Sci.* 16, 5096-5107 (2023); **14** *Angew. Chem. Int. Ed.* 63, e202410210 (2024); **15** *Adv. Funct. Mater.* 35, 2413807 (2025); **16** *Nat. Energy* 9, 839-848 (2024); **17** *Nat. Commun.* 14, 601 (2023); **18** *J. Mater. Chem. A* 9, 7042-7047 (2021); **19** *Nano-micro Lett.* 13, 204 (2021); **20** *Adv. Funct. Mater.* 2023, 33, 2214546; **21** *Nano-micro Lett.* 14, 98 (2022); **22** *Angew. Chem. Int. Ed.* 60, 18845-18851 (2021); **23** *Energy Environ. Sci.* 17, 4569-4581 (2024); **24** *Nat. Commun.* 15, 6249 (2024); **25** *Adv. Funct. Mater.* 32, 2111714 (2022); **26** *J. Am. Chem. Soc.* 146, 12743-12749 (2024); **27** *ACS Nano* 17, 17359-17371 (2023); **28** *ACS Energy Lett.* 9, 3380-3390 (2024); **29** *Nat. Commun.* 14, 2720 (2023).

Reviewer: 3 *The authors presented an interesting Zn-based aqueous battery system with promising low-temperature performance. The authors focused on the cations' roles in the solvation shell and water cluster reconstructions, evaluated and characterized the electrochemistry with different instrumental techniques and atomistic simulations. In general, the experimental portion suggests that the authors conducted comprehensive studies on how the dual cation effects from Al-Zn-water interactions contribute to cell performance. However, the following problems, especially regarding the simulation studies, should be addressed prior to publication.*

Answer: We sincerely appreciate the reviewer's positive evaluation of our work and their recognition of the significance of our research. The constructive comments, particularly those concerning the simulation studies, are highly valuable for further strengthening our analysis. In the following point-by-point responses, we have carefully addressed each concern and provided additional clarifications and supporting data.

1. *In the introduction section, "The dissociated metal cations interact with the O atoms of water molecules via electrostatic interactions, leading to a reduction in the electron density around O": The interactions between metal ions and H₂O molecules are not just electrostatic interactions. The nature of M-O bonding is more complex than simple ionic bonding.*

Response: We sincerely thank and agree with the reviewer's comment. Our original description of dissociated metal cation–water interactions was based on the previous reported literature (*Nat. Commun.* **11**, 4463 (2020)): "With multiple-valence charge and small radius, Zn²⁺ owns a large electric field, and generates strong **electrostatic interactions** with the dipolar water molecule, and thus rearranges the coordination structures of water molecules around metal ions."

However, after extensive literature review, we fully concur that the nature of M–O bonding is more complex than simple ionic bonding. For example, previous studies have noted that “electrolytes dissolved in water dissociate into ions that are hydrated. The large electric field around the (smaller) ions **causes the dipolar water molecules to rearrange themselves in the hydration shell(s)** around the ions with structures differing from that in bulk water” (*Chem. Rev.* 109, 1346–1370 (2009)). In addition, it has been reported that “the electrical field around the ion (as determined by its strength) causes the restructuring of the water hydrogen bonded network (matrix) and reorientation of water molecules around the ion, as well as some change of the electron density on the hydrogen and oxygen atoms of the water molecules near it (**ion-dipole interactions**); and Analysing the measured $\delta(^{17}\text{OH}_2)$ and $\delta(^1\text{H}_2\text{O})$ values for various salts leads to the somewhat unexpected conclusion that the disruption or extension of the hydrogen bond by the ion on the oxygen atom of the tetra-coordinated water molecule and the subsequent **reorientation and polarization** of it by the electric field of the ion causes a **downfield (deshielding)** rather than an upfield (shielding) shift for the water oxygen atom” (*J. Chem. Soc., Faraday Trans.* 94, 3261–3269 (1998)).

Thus, the dissociated metal cations interact with the electronegative O atoms of water not solely through electrostatic interactions but via ion–dipole interactions that are also affected by dipole orientation and field-induced polarization. Consequently, the nature of M–O bonding is far more complex than simple ionic bonding.

Based on these considerations, we have corrected the discussion in our revised manuscript to “The electric field generated by dissociated metal cations interacts with the highly electronegative O atoms of water molecules, leads to a reduction in the electron density around O (deshielding effect (DSE)).”

2. For Fig. 2h, I couldn't understand why the MSD vs time is such a perfect linear relationship.

Explanation is needed.

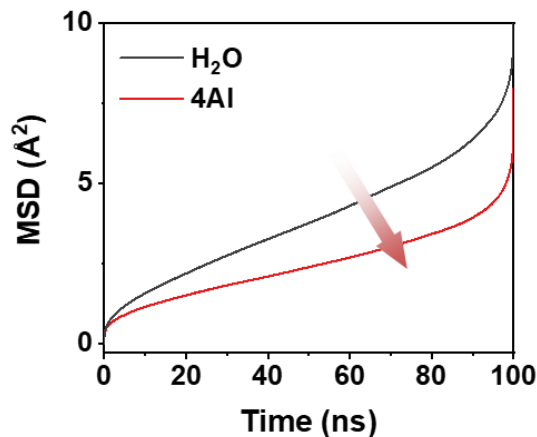


Fig. R15 Recalculated MSD versus time profiles of the water.

Response: We appreciate your insightful comment. In our previous theoretical calculations, the nearly perfect linearity observed in the MSD vs. time curve is attributable to the relatively short duration of the trajectory data used for statistical analysis. Additionally, as raised in your sixth comment, the TIP3P water model may not be ideally suited for this system. Consequently, we adopted the TIP4P-Ew water model and re-conducted the calculations. Analysis of the first 100 ns of the simulation continues to support our conclusion that the diffusion coefficient of water in the 4Al electrolyte is significantly reduced, although, as you mentioned, the MSD versus time curves are not perfectly linear (Fig. R15).

We have updated the recalculated MSD versus time profiles of water in our revised manuscript in Fig. 2h.

3. For the claim “Nevertheless, in 4Al, Al^{3+} coordinates with four water molecules and two Cl^- ions in the first solvation shell (Fig. 3d). After the introduction of $ZnCl_2$, the snapshot reveals that Al^{3+} is coordinated by four water molecules and two Cl^- ions, whereas Zn^{2+} is coordinated by five water

molecules and one Cl^- ion.”: Although it is presumably backed by the energetics calculated at the PBE level of theory, the snapshots of a few salvation structures are not representative enough to reflect global behavior. The evolutions or means of water ion and ion-ion counts would be more solid evidence.

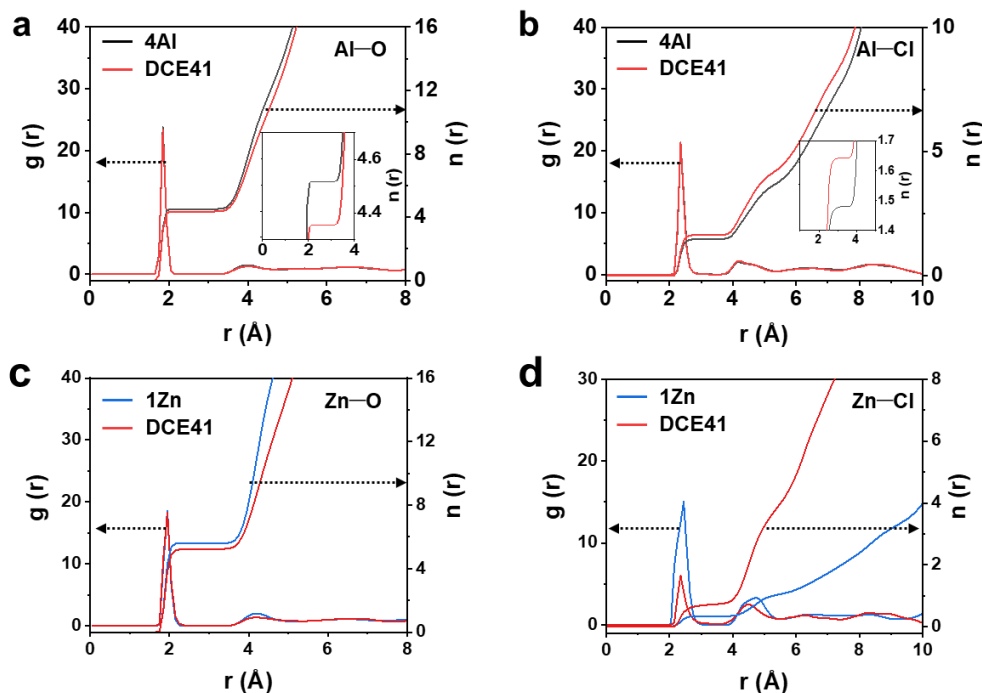


Fig. R16 MD stimulation results of different electrolytes. The corresponding RDF plots of **a** Al-O and **b** Al-Cl for 4Al and DCE41. The corresponding RDF plots of **c** Zn-O and **d** Zn-Cl for 1Zn and DCE41.

Response: We thank the reviewer for the valuable comment. We would like to clarify that, in addition to the snapshots of the solvation structure presented in Fig. 3d, Supplementary Figs. 19 and 21 in the original manuscript also display the averaged radial distribution functions (RDFs) for $\text{Al}^{3+}\text{-O}$, $\text{Al}^{3+}\text{-Cl}^-$, $\text{Zn}^{2+}\text{-O}$, and $\text{Zn}^{2+}\text{-Cl}^-$. Therefore, our determination of the ion coordination numbers is based on the evolutions or mean values of water - ion and ion - ion counts.

Furthermore, given your concerns about the water model selection and the system equilibrium, we replaced the water model as recommended and added NPT simulations. Based on this adjustment, we

reanalyzed the complete trajectory data of water molecules and ions generated over 100,000 ps (100 ns) in NVT simulations for the 1Zn, 4Al, and DCE41 systems. We then recalculated the average RDFs for $\text{Al}^{3+}\text{-O}$, $\text{Al}^{3+}\text{-Cl}^-$, $\text{Zn}^{2+}\text{-O}$, and $\text{Zn}^{2+}\text{-Cl}^-$. As shown in Fig. R16, the recalculated results are consistent with the trends observed in our original manuscript, and the coordination numbers are very similar. Specifically, the average coordination numbers (ACNs) for water molecules and Cl^- in the Al^{3+} solvation structure are 4.52 and 1.48 in the 4Al electrolyte, respectively. In the DCE41 system, the ACN for $\text{Al}\text{-O}$ slightly decreases from 4.52 to 4.36, while the ACN for $\text{Al}\text{-Cl}$ increases from 1.48 to 1.64. This change is attributed to the interactions between Cl^- (in the Zn^{2+} solvation shell) and water (in the Al^{3+} solvation shell). Similarly, in the Zn^{2+} solvation shell, the ACNs for water decreases from 5.64 (1Zn) to 5.23 (DCE41), whereas that for Cl^- increases from 0.36 (1Zn) to 0.77 (DCE41).

Additionally, to better illustrate the changes in coordination number and species in the DCE41 system, we initially analyzed the coordination number of ions in the solvation structure based on snapshots. Following this, we provided a more accurate description of the coordination number through RDF curves. However, to prevent potential misunderstandings, we have revised the original description as follows: “Nevertheless, in 4Al, Al^{3+} coordinates with water molecules and Cl^- ions in the first solvation shell (Fig. 3d). After the introduction of ZnCl_2 , the snapshot reveals that Al^{3+} is coordinated by water molecules and Cl^- ions, whereas Zn^{2+} is coordinated by water molecules and Cl^- ion. Moreover, the Cl^- in the Zn solvation shell interacts with the H_2O in the Al^{3+} solvation shell, resulting in a unique dual-cation coordination solvation structure (Fig. 3e)”

Meanwhile, we have added the newly recalculated results in Figs. S26 and S28 in the revised Supplementary Information, and our improved computational methods are described in detail in the

experimental section.

4. The DFT calculation in this study was conducted with the Material Studio package, which I do not believe is the best option. There are many other open-source DFT packages including ORCA, that offer more reliable molecular modeling than Materials Studio.

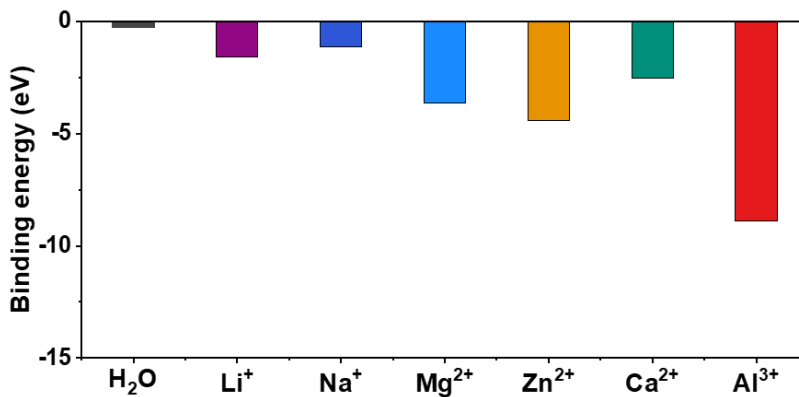


Fig. R17 The recalculated binding energies for water with water and water with different cations by DFT.

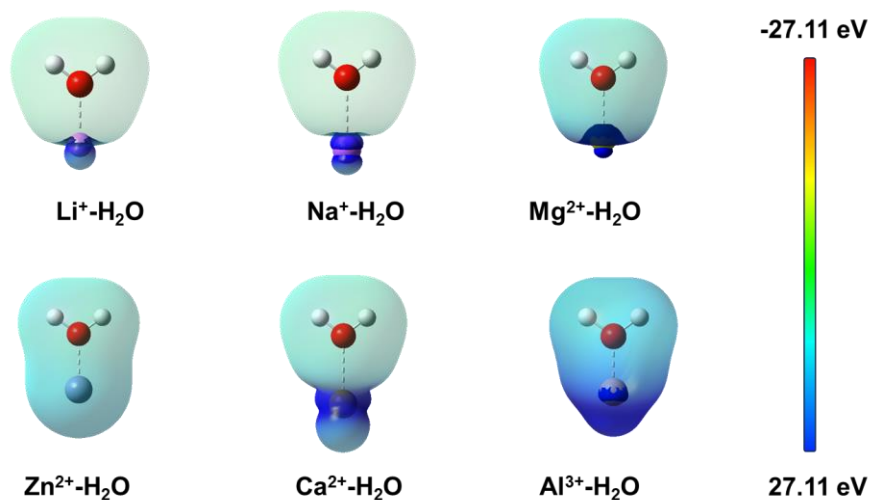


Fig. R18 The recalculated ESP distributions for the structure of the cation-water mixture by DFT.

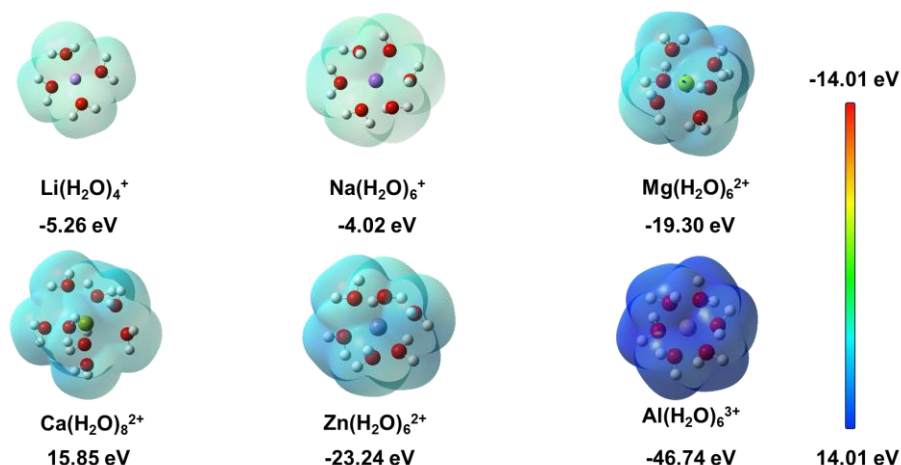


Fig. R19 The recalculated ESP distributions and binding energies for solvation structures with different cations by DFT.

Response: We appreciate the reviewer's valuable comment. Given your concerns about the DFT calculation with the Material Studio package, we have re-performed our DFT calculations employing the open-source package ORCA, which is widely recognized for its robust molecular modeling capabilities. Specially, DFT calculations were conducted using the B3LYP functional with Grimme's D4 dispersion correction (B3LYP-D4). The def2-TZVP basis set was employed for all atoms, along with the def2/J auxiliary basis set to accelerate Coulomb integrals within the resolution of identity (RIJCOSX) approximation. A very tight SCF convergence criterion was applied to ensure high accuracy in the self-consistent field (SCF) procedure. Harmonic vibrational frequency calculations were conducted to verify the nature of the optimized structures (confirmed as minima by the absence of imaginary frequencies) and to compute thermal corrections to Gibbs free energy at 298.15 K and 1 atm. These thermal corrections include contributions from translational, rotational, and vibrational partition functions, as well as the zero-point energy (ZPE) correction. Single-point energy calculations were performed using range-separated hybrid meta-GGA functional ω B97M-V, which includes VV10 nonlocal correlation.

The def2-TZVP basis set was employed for all atoms, with the def2/J auxiliary basis set used to accelerate Coulomb integral evaluations under the resolution of identity (RIJCOSX) approximation. The strong SCF keyword was applied to enhance SCF convergence, and the no auto start option was applied to disable automatic initial guess generation.

Figs. R17-19 presents the ORCA-based DFT calculation results including binding energies, and ESP distributions, which effectively support our conclusions. We have updated these recalculated results in the revised manuscript and Supplementary Information, and our improved computational methodology is detailed in the experimental section.

5. This study used the PBE functional to perform molecular orbital calculations, which usually have unacceptable error ranges, especially the obtained energetics. Without systematic benchmarks against higher level of theory, the results cannot be published. This point is related to the validness of Fig. 3d, 3e, Supplementary Fig. 7, and Supplementary Fig. 9.

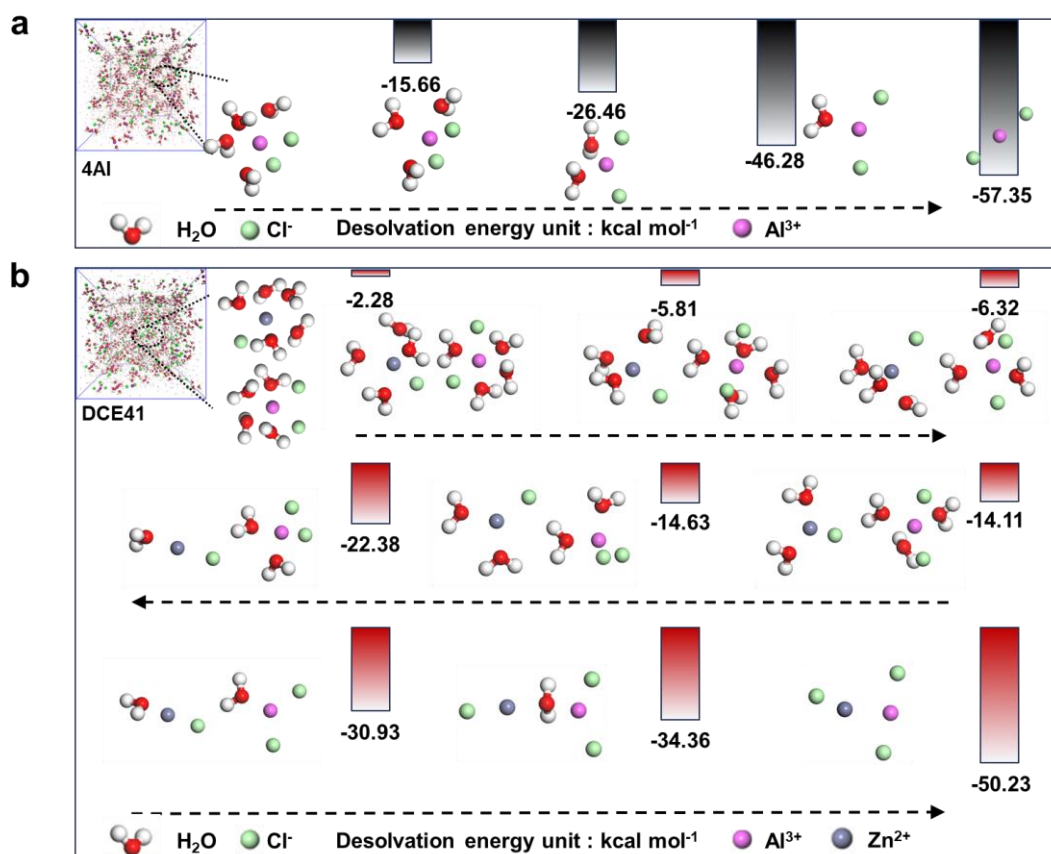


Fig. R20 The recalculated E_a values of 4Al and DCE41. Snapshots of the MD simulation cell and the desolvation processes of cations for **a** 4Al and **b** DCE41.

Response: Thank you for your valuable comment. In our study, the energetics were calculated with the PBE functional, in line with previously published works that have employed this functional for energy-related calculations, such as *Energy Environ. Sci.* 17, 8966 (2024); *Angew. Chem. Int. Ed.* 2025, DOI:10.1002/anie.202500434. However, given your concerns about potential inaccuracies with the PBE functional, we recalculated the desolvation energies (Figs. R20a and R20b, corresponding to Figs. 3d and 3e in the original manuscript) and binding energies (Fig. R17, corresponding to Supplementary Fig. 7 in the original Supplementary information) by the ORCA software package. We also performed electrostatic potential calculations using Gaussian16 software package (Figs. R18 and R19,

corresponding to the inset images in Fig. 1e and Supplementary Fig. 9 in the original manuscript and Supplementary information). These revised results support our conclusions and are incorporated into the revised manuscript.

6. *The water model implemented in this study is TIP3P. ff19SB with OPC model was reported to have much better performance than TIP3P model. At least a benchmark between these two models or against DFT should be provided to support the simulation results.*

Response: We appreciate the reviewer's expert suggestion. Indeed, the ff19SB with OPC models perform better than the TIP3P model. However, in our system, we selected the TIP3P water model based on previous literature regarding molecular dynamics simulations of AlCl_3 aqueous solutions (*Energy Storage Mater.* 44, 497-507 (2022)).

In response to your suggestion, we also examined the effect of different water models on our simulation results. Since GROMACS package does not include an OPC water model, we selected the TIP4P-Ew water model, which is considered to provide better performance, and reconduted MD simulations for the 1Zn, 4Al, and DCE41 systems, and the results are displayed in Fig. R16.

The comparison of the TIP4P-Ew and previous TIP3P simulations shows consistent trends in ion-ion and ion-water coordination numbers. These results reinforce our conclusions and we have added the updated results of Fig. R16 in the revised Supplementary Information.

7. *In the MD simulations of "different cation systems", Abmer99sb-ildn may be reasonably good for simulating Zn-water interactions, according to the literature. However, for other metal ion cases including Al and Ca, additional evaluation of this FF is needed to support these results.*

Response: We thank the reviewer for raising this valuable question. Your scrutiny regarding the

computational parameters is greatly appreciated. We have neglected to explain the source of the force field of ions not contained in the AMBER99SB-ILDN force field. We employed the General Amber Force Field (GAFF) in the AMBER software to generate the missing ion parameter files for the Amber99SB-ILDN force field and utilized ACPYPE to convert the AMBER topology files into the GROMACS format. Based on this, we simulated the interactions between ions and water. We have added the above parameter details to the Computational methods section in revised manuscript in Page 22, line 15-18.

8. Related to question 2, no evidence suggests that the system reached equilibration in any MD simulations. In the model initiation step, instead of using nPT to allow simulation cell, the authors relaxed the system with the conjugate gradient minimization method, without considering any intermolecular collisions at the corresponding temperature. Without a comparison of the obtained density with experimental values, this simulation approach cannot prove its efficacy, especially since temperature effects are of major research interest. Additionally, for those of single salt systems, only 0.5 ns of nVT simulation was performed, which is far from reaching any statistically meaningful conclusions.

Response: We appreciate the reviewer's insightful comment regarding equilibration in our MD simulations. In response, our simulation protocol has been substantially refined. Rather than solely relying on conjugate gradient minimization for system relaxation, we now begin with energy minimization using the steepest descent algorithm (with a convergence criterion of 1000.0 kJ/mol·nm (emtol) and a maximum step size of 0.002 nm over 2,500,000 steps). Following minimization, an isothermal-isobaric (NPT) ensemble simulation was conducted to equilibrate the system. The NPT simulation used the molecular dynamics algorithm with a total of 5,000,000 steps and a time step of 2

fs (dt), corresponding to a total simulation time of 10 ns. Temperature was controlled at 293.15 K via the V-rescale method with a coupling time constant of 0.1 ps and reference temperatures of 293.15 K. The systems were pressurized to 1.0 bar for density stabilization. Equilibration involved the Berendsen and V-rescale methods for pressure and temperature control with a time constant of 1.0 ps and a compressibility of $4.5 \times 10^{-5} \text{ bar}^{-1}$. Electrostatic interactions were treated employing the particle mesh Ewald (PME) method with a Fourier spacing of 0.12 nm, and van der Waals (vdW) interactions were modeled with a cutoff of 1.0 nm. Periodic boundary conditions (PBC) were applied in all directions. Notably, the density obtained from NPT simulations exhibits excellent agreement with experimental measurements. The experimentally determined density of 4Al is 1.27 g cm^{-3} , while the simulated density is 1.21 g cm^{-3} . Subsequently, a canonical (NVT) ensemble simulation was performed to further equilibrate the system. The simulation ran for 50,000,000 steps (totaling 100 ns) with a time step of 2 fs. The system temperature was maintained at 293.15 K using the V-rescale thermostat with a coupling time constant of 0.1 ps. A grid-based neighbor list approach was employed, with a neighbor list cutoff of 1.0 nm and updates performed every 20 steps. The hydrogen bonds were recognized if the donor–acceptor distance was $\leq 0.35 \text{ nm}$ and the donor–hydrogen–acceptor angle was $\geq 30^\circ$ in the simulated systems. A 10 ns statistical analysis was conducted for different cationic systems. The same method were applied at 253.15 K and 273.15 K.

We employed this optimized method to statistically analyze the average number of HBs in different cationic systems over 10 ns (compared to 0.5 ns in our original manuscript) at various temperatures, as presented in Fig. R21. As shown, the average number of HBs among water molecules in Al^{3+} systems experience minimal changes as the temperature decreases from 25 to 0 °C and further to -20 °C. This

observation is consistent with our original manuscript and further reinforces our conclusions.

We believe that these improvements adequately address the reviewer's concerns regarding system equilibration and the validity of our simulation approach. We have added all modifications and detailed computational protocols in the Computational methods section and updated recalculated results in Fig. 1f and Supplementary Fig. 11.

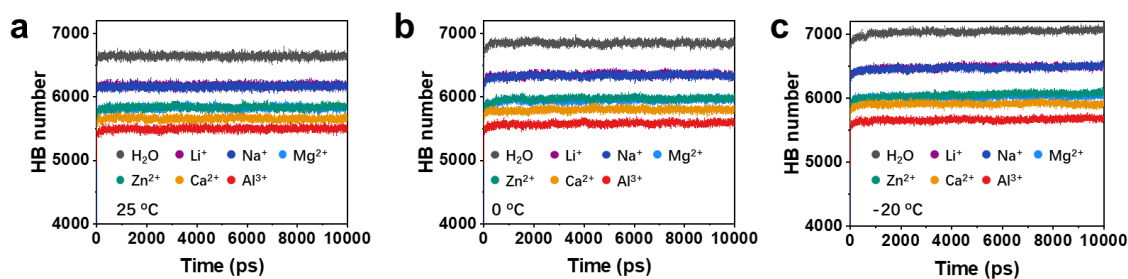


Fig. R21 The recalculated HB number between water molecules in different cationic systems at **a** 25 °C, **b** 0 °C and **c** -20 °C.

9. In the investigation of electrolyte systems, the authors switched the force field and timestep without explanation or benchmark.

Response: We express our gratitude to the reviewer for pointing out this aspect. Considering the concerns raised in the previous comments, including the water model and the equilibration process in MD simulations, we have performed revised molecular dynamics simulations with a standardized force field, timestep, and simulation protocol. The detailed simulation procedure and parameters have been comprehensively described in our response to Comment 8.

10. The authors performed many batches of MD simulations of the electrolyte systems with decently long lengths. Ionic transport properties such as ion diffusivity/conductivity could be provided based on these simulations to provide more intriguing conclusions.

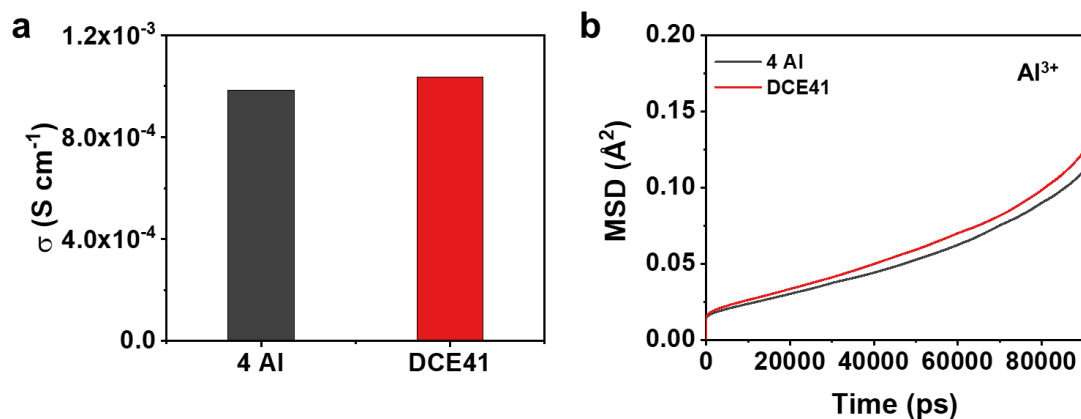


Fig. R22 **a** The results of simulated ionic conductivities in 4Al and DCE41. **b** The results of simulated Al³⁺ diffusion coefficient in 4Al and DCE41.

Response: We thank the reviewer's valuable suggestions. To further analyze the molecular dynamics simulation results, we have evaluated the effect of introducing the secondary cation Zn²⁺ on the ionic conductivity and diffusion coefficients of the system. The ionic conductivities of the 4Al and DCE41 systems were calculated with the equation of Green-Kubo (*Nat. Phys.* 15, 967 – 972 (2019)). As shown in Fig. R22a, at 25 °C, the ionic conductivity of DCE41 is slightly higher than that of 4Al with comparable values, which aligns well with our experimental findings (Supplementary Fig. 23).

Additionally, we performed a statistical analysis of the diffusion coefficients for the 4Al and DCE41 systems. As illustrated in Fig. R22b, the introduction of Zn²⁺ in the DCE41 system enhances the diffusion coefficient of Al³⁺. This result is consistent with our experimental data obtained from cyclic voltammetry (CV) and galvanostatic intermittent titration technique (GITT) (Supplementary Figs. 17-18), further supporting our conclusions that the introduction of the secondary cation optimizes the solvation structure of ions in the DCE41 system, thereby reducing the desolvation energy of ions and improving their diffusion behavior.

11. For Supplementary Fig. 7, it seems that no effort was put into eliminating the bias from different numbers of HBs among water molecules in the solvation shell. In addition, since the study of binding energy is mainly of kinetics interests, thermal corrections should be applied to obtain free energy instead of total electronic energy (presumably).

Response: We appreciate the reviewer for pointing out these aspects. First, we would like to clarify that Supplementary Fig. 7 does not involve the influence of different solvation shells. We suspect that you may be referring to Supplementary Fig. 9, which analyzes the solvation structures of cations with different numbers of water molecules.

Regarding the solvation energy calculations, the solvation structures of different metal cations in water have been reported in the literature (*Chem. Rev.* 93, 1157-1204 (1993)). In our previous solvation energy calculations employing *Material Studio*, thermal corrections were considered; however, we did not explicitly specify this in the computational parameters. We appreciate your reminder.

Furthermore, considering your concerns regarding the accuracy of our theoretical calculations with the PBE functional in *Material Studio*, we have recalculated the solvation energies with *ORCA*, incorporating thermal corrections. The updated results, presented in Fig. R19, confirm that Al^{3+} exhibits the highest solvation energy and supports our conclusions.

We have updated the solvation energy results in Supplementary Fig. S9 and added the relevant computational parameter details in the Computational methods section of the revised manuscript.

In summary, the above are our clarifications and point-by-point responses for the misunderstandings and comments raised by the reviewers. We also acknowledge that further

clarifications and modifications on these critical aspects are necessary to improve the quality of our manuscript. We sincerely wish that **you can reconsider the publication of our revised manuscript** in *Nature Communications*.

We look forward to receiving your reassessment of this work. Thank you for your kind consideration.

Sincerely Yours,

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Response to Reviewers

Reviewer #1: *We can see the authors have paid great effort to illustrate the main novelty of this work. Regrettably, I still retain my original opinion that the manuscript fails to meet the criteria for publication in Nature Communications. The reasons for this are as follows:*

Answer: We sincerely thank the reviewer for the thoughtful evaluation of our work and for acknowledging our efforts in clarifying its novelty. While we regret that the manuscript does not yet meet your expectations, we appreciate your constructive feedback. The following is the point-by-point response to all the questions. We hope that we have satisfactorily addressed your concerns, and will be glad if you could re-review our revised manuscript.

1. Novelty is still the main reason. Actually the deshielding effect of cations is essentially the same as the cation ionic potentials since their effect on water molecules shows no difference. Besides, in addition to the previously mentioned studies on cation-water interactions, a number of cation-regulated hydrogen bonding mechanisms have been reported. Specifically, the deshielding effect of several cations (especially "super-hydration structure" effect of Ca^{2+}) on both H and O of water have also been proposed and confirmed in previous research (Angew. Chem. Int. Ed. 2024, 63, e202407659). Therefore, this work can only supply some support on this effect, thus not reaching the high standard of Nature Communications.

Response: We sincerely appreciate the reviewer's thoughtful evaluation of our work and the critical comments raised. In response to the concern regarding the novelty of our study and its potential overlap with the findings in *Angew. Chem. Int. Ed.* 2024, 63, e202407656, we would like to clarify the originality and scientific contribution of our work from the following perspectives:

(1) The difference between the deshielding effect and cation ionic potentials: (aim to "Actually the deshielding effect of cations is essentially the same as the cation ionic potentials since their effect on water molecules shows no difference")

We believe that the shielding or deshielding effects of cations on the H and O atoms in water molecules are primarily governed by their electrostatic field strength, which can be quantitatively described by the q/r^2 , where q and r are the charge density and ionic radius of ions, respectively. As reported in the

literature (*J. Chem. Soc. Faraday Trans. 1998, 94, 3261-3269*), cations with a high q/r^2 exert a strong electric field that can effectively reorient and polarize surrounding water molecules, leading to a reconstruction of the hydrogen-bonding (HB) network and the simultaneous deshielding effect (DSE) on both O and H atoms. Based on this principle, our work introduces a meaningful metric to quantify the extent of such deshielding effects and elucidate the specific interactions between various cations and water molecules. It is important to note that while ionic potential has been discussed in prior studies, the specific and differential impacts of high-valent cations on both H and O atoms have not been comprehensively addressed, which underscores the significance of our investigation.

(2) The contradictory between the previously mentioned studies on cation-water interactions: (aim to “*Besides, in addition to the previously mentioned studies on cation-water interactions, a number of cation-regulated hydrogen bonding mechanisms have been reported*”)

In the previous report on ionic potential (*Nature Energy, 2024, 9, 839-848*), Ca^{2+} has been categorized as a high ionic-potential cation, similar to Al^{3+} , and thus is generally expected to exhibit strong interactions with water molecules. However, in the recent study published in *Angew. Chem. Int. Ed. 2024, 63, e202407656*, experimental results reveal that Ca^{2+} actually exhibits relatively weak interactions with water, leading to the formation of a “super-hydration structure”. This observation highlights the limitations of using ionic potential alone to evaluate the interaction strength between cations and water molecules. Our work thus places particular emphasis on the differential interactions of high ionic-potential cations with both H and O atoms. Through temperature-dependent simulations of HB number (as shown in original Fig. 1f), we further demonstrate that Ca^{2+} exhibits weaker interactions with water compared to Al^{3+} , which interacts much more strongly. This contributes to a new mechanistic perspective on how high ionic-potential cations influence the HB network.

(3) The misunderstanding of Ca^{2+} deshielding behavior: (aim to “*Specifically, the deshielding effect of several cations (especially “super-hydration structure” effect of Ca^{2+}) on both H and O of water have also been proposed and confirmed in previous research (Angew. Chem. Int. Ed. 2024, 63, e202407659)*”)

The *Angew.* article reports that Ca^{2+} exhibits a deshielding effect on the O atom but a shielding effect on the H atom of water molecules, as evidenced by the ^{17}O and ^1H NMR spectra in *Angew. Chem. Int.*

Ed. 2024, 63, e202407656. Therefore, the statement that Ca^{2+} exhibits simultaneous deshielding effects on both H and O is inconsistent with the actual findings. In contrast, our study systematically analyzes and categorizes the effects of different cations on H and O atoms, introducing the concept of “deshielding effect cation” (DSEC) and “shielding effect cation” (SEC). This classification offers a new framework for understanding the multidimensional interactions between cations and water molecules.

(4) On the distinction and innovation of our work compared to the *Angew. Chem. Int. Ed. 2024, 63, e202407656* article: (aim to “*Therefore, this work can only supply some support on this effect, thus not reaching the high standard of Nature Communications*”)

Our work is not a direct extension or support of the *Angew.* study, but rather offers independent insights and innovations. Specifically, we systematically compare the distinct effects of a series of cations (Na^+ , Li^+ , Ca^{2+} , Zn^{2+} , Mg^{2+} , Al^{3+}) on both H and O atoms in water molecules—an analysis not covered in the *Angew. Chem. Int. Ed. 2024, 63, e202407656* article, which focuses primarily on the effects of Ca^{2+} , Zn^{2+} , and Mg^{2+} on O atoms only.

Another key innovation of our study lies in the discovery of a **dual-cation synergistic and competitive coordination–co-deposition effect** under ultralow temperature conditions. This effect promotes the formation of an Al-Zn alloy at the Zn metal anode surface and significantly enhances interfacial cation kinetics. While *Angew. Chem. Int. Ed. 2024, 63, e202407656* primarily emphasizes hydration structure in bulk solution, our focus is on the microscopic synergistic/competitive behavior of Al^{3+} and Zn^{2+} at the electrolyte/electrode interface and its impact on cation deposition kinetics behavior, particularly under low temperature conditions. Through detailed spectroscopic evidence and theoretical calculations, we confirm the formation of Al-Zn alloy, showing that dual cation coordination not only facilitates the reversible co-deposition of Al^{3+} and Zn^{2+} but also greatly extends the cycling life of the Zn anode. In our system, the Zn anode maintains stable operation at $-60\text{ }^{\circ}\text{C}$ for over 10,340 hours (>430 days). To the best of our knowledge, such long-term reversible deposition of Al^{3+} and Zn^{2+} , and stable Zn metal operation under subzero temperatures have not been previously reported.

In summary, the scientific value and novelty of our study lie in the following aspects:

- a. Systematic comparison of different cations in terms of their distinct interactions with both H and O atoms in water molecules;
- b. Introduction of a classification framework (DSECs vs. SECs) that enhances the mechanistic understanding of cation-induced effects;
- c. Elucidation of a dual-cation coordination–co-deposition mechanism through spectroscopic and theoretical analyses;
- d. Demonstration of ultralong reversible deposition of dual cation and stable Zn anode cycling at ultralow temperatures.

2. The authors mention that the deshielding effect of Al^{3+} on H atoms and O atoms also plays a role in lowering the freezing point in Respond manuscripts. Is it possible to establish a metric to quantify this?

Response: We sincerely thank the reviewer for raising this important question regarding the possibility of quantifying the deshielding effect of Al^{3+} on the H and O atoms in water molecules. This issue is indeed crucial for a deeper understanding of how cations interact with water molecules and thereby enhance antifreezing performance.

In this study, we attempt to evaluate the electrostatic perturbation ability of different cations using a classical physical descriptor—electrostatic field strength (q/r^2). As previously reported (*J. Chem. Soc. Faraday Trans. 1998, 94, 3261-3269*), cations with higher q/r^2 values typically exhibit stronger polarizing abilities, which enable significant reconstruction of the HB network. This reorientation and polarization of surrounding water molecules lead to simultaneous deshielding effects on both H and O atoms.

To correlate this effect with experimental observations, we systematically analyzed the ^1H and ^{17}O NMR spectra of electrolyte systems containing different cations (as shown in original Fig. 1d and Supplementary Figs. 1–4). In the case of Al^{3+} , we observed pronounced downfield shifts for both H and O signals (deshielding effect), suggesting strong polarization and structural reorganization of the water molecules. The concurrent broadening of the line width for both ^1H and ^{17}O NMR peaks further supports the intensified interaction between Al^{3+} and the corresponding atmos. This experimental evidence is corroborated by DSC measurements (as shown in original Supplementary Figs. 12 and 15), which reveal

a marked depression in the freezing point of the Al^{3+} containing electrolyte, highlighting the link between deshielding effects and enhanced antifreezing properties.

To further support these findings, we conducted molecular dynamics simulations to quantify hydrogen bond number at different temperatures (as shown in original Fig. 1d). The simulations confirm that Al^{3+} substantially disrupts the HB network and increases interaction with water molecules, offering theoretical validation of the experimentally observed deshielding behavior.

Based on these studies, we propose a multi-dimensional evaluation framework to systematically quantify the deshielding effect of cations. This framework integrates: (i) the intrinsic q/r^2 value of the cation as a descriptor of its polarizing capability; (ii) the downfield shifts in ^1H and ^{17}O NMR signals relative to pure water, along with line width broadening; and (iii) reductions in freezing point observed by DSC, complemented by structural parameters such as hydrogen bond numbers from simulations. This combined approach enables comparative evaluation of the deshielding abilities of different cations, particularly high charge density species like Al^{3+} .

3. Is there a direct relationship between the deshielding effect of cations and the ionic conductivity of their electrolyte systems?

Response: We thank the reviewer for raising this professional question. We believe that the deshielding effect of cations is indeed correlated with the ionic conductivity of electrolyte systems, but it is not the sole determining factor. Ionic conductivity is influenced by a combination of factors, including electrolyte viscosity, cation coordination structures, and ion aggregation behaviors.

In our system, the proposed deshielding effect mainly reflects the interactions between cations and water molecules, particularly the perturbation of the local environments of H and O atoms in water. This perturbation indicates the extent to which the HB network is disrupted. A greater disruption of this network generally suppresses electrolyte freezing at low temperatures, which is beneficial for improving ionic conductivity under such conditions.

However, our study also reveals that increasing the concentration of deshielding effect cations (such as Al^{3+}) leads to a gradual rise in viscosity (as shown in original Supplementary Fig. S14). Notably, when the Al^{3+} concentration exceeds 4 m, the viscosity increases significantly, suggesting that an overly strong

deshielding effect restricts the mobility of water molecules. This is further supported by low-field nuclear magnetic resonance (LF-NMR) results in original Supplementary Fig. S17. Correspondingly, as shown in original Supplementary Fig. S23, the ionic conductivity of the 4Al system decreases markedly at temperatures below -60 °C.

To mitigate the adverse impact of an excessively strong deshielding effect on low temperature conductivity, we introduced a second cation to moderate the interaction strength between Al^{3+} and water molecules. Nuclear magnetic resonance (NMR) and LF-NMR results (as shown in original Figs. 3a and b) show that the presence of the second cation alleviates the deshielding intensity through a competitive effect while maintaining Al^{3+} as the dominant contributor. This adjustment effectively enhances the ionic conductivity at ultralow temperatures.

Therefore, we conclude that ionic conductivity arises from the interplay of multiple factors. While the deshielding effect of cations contributes to conductivity behavior, it is not linearly correlated and cannot be regarded as the sole governing parameter.

Reviewer #2: *The authors have appropriately addressed the raised concerns by providing clear explanations and referencing relevant literature. Overall, the revised manuscript demonstrates improved clarity, added experimental depth, and presented strong evidence for its superior low-temperature performance. The following comments need to be addressed.*

Answer: We greatly thank the respected Reviewer for the time and effort dedicated to evaluating our revised manuscript, as well as for the positive and constructive comments. We are pleased to know that the improved clarity, enhanced experimental depth, and the strong evidence supporting the low-temperature performance of our system were well recognized. Following the Reviewer's valuable suggestions, we have carefully addressed all remaining comments. The point-by-point responses are detailed below. We hope that we have satisfactorily addressed your concerns, and will be glad if you could re-review our revised manuscript.

1. This study introduced a dual-cation electrolyte system (DCE) based on Al^{3+} and Zn^{2+} , where Al^{3+} induces strong deshielding effects on water molecules by disrupting hydrogen bonding networks. In

addition to bulk ionic conductivity, which is enhanced by the disruption of hydrogen bonding networks, charge transfer at the anode-electrolyte interface (which is affected by deshielding) is important for low temperature performance. A detailed discussion, together with the relevant results, should be added.

Response: We acknowledge the reviewer for this professional recommendation. We fully agree that, in addition to bulk ionic conductivity, charge transfer behavior at the anode–electrolyte interface also plays a critical role in determining low temperature electrochemical performance.

In our study, the strong deshielding effect induced by Al^{3+} ensures efficient ion transport at low temperatures. Moreover, by introducing Zn^{2+} as a secondary cation, the desolvation energy in the dual-cation system is significantly reduced compared to that in the 4Al system (as demonstrated in origin manuscript Fig. 3c). This trend is further supported by the calculated desolvation energies in Fig. 3d. These improvements are attributed to the introduction of Zn^{2+} , which mitigates the overly strong deshielding effect of Al^{3+} on water molecules and tunes the cation coordination environment, thereby facilitating charge transfer at the anode–electrolyte interface.

To provide more direct evidence of the improved anode–electrolyte interfacial kinetics at low temperatures, we performed in situ Electrochemical impedance spectroscopy (EIS) measurements on Zn/Zn symmetrical cells assembled with different electrolytes across a wide temperature range (Figs. R1a and b). We further analyzed the impedance data using the distribution of relaxation time (DRT) method (Figs. R1c and d), which enables the deconvolution of electrochemical processes with distinct relaxation characteristics (*Nat. Commun.* 2024, 15, 6249; *Angew. Chem. Int. Ed.* 2023, 62, e202301192; *Adv. Funct. Mater.* 2024, 34, 2407262). As shown in Figs. R1c and d, both the 4Al and DCE41 electrolytes exhibit an increase in charge transfer resistance (R_{ct}) with decreasing temperature. However, at all tested temperatures, the DCE41 electrolyte consistently displays a lower R_{ct} compared to the 4Al system, indicating more efficient interfacial charge transfer kinetics. This result further confirms that the dual-cation electrolyte design effectively improves charge transfer processes at the electrode–electrolyte interface under low-temperature conditions, thereby promoting faster interfacial kinetics.

We have added the EIS and DRT curves with different electrolytes in the revised Supplementary Information in Fig. S25, and discussed them in the revised manuscript in Page 12, line 25-26, Page 13,

line 1-4.

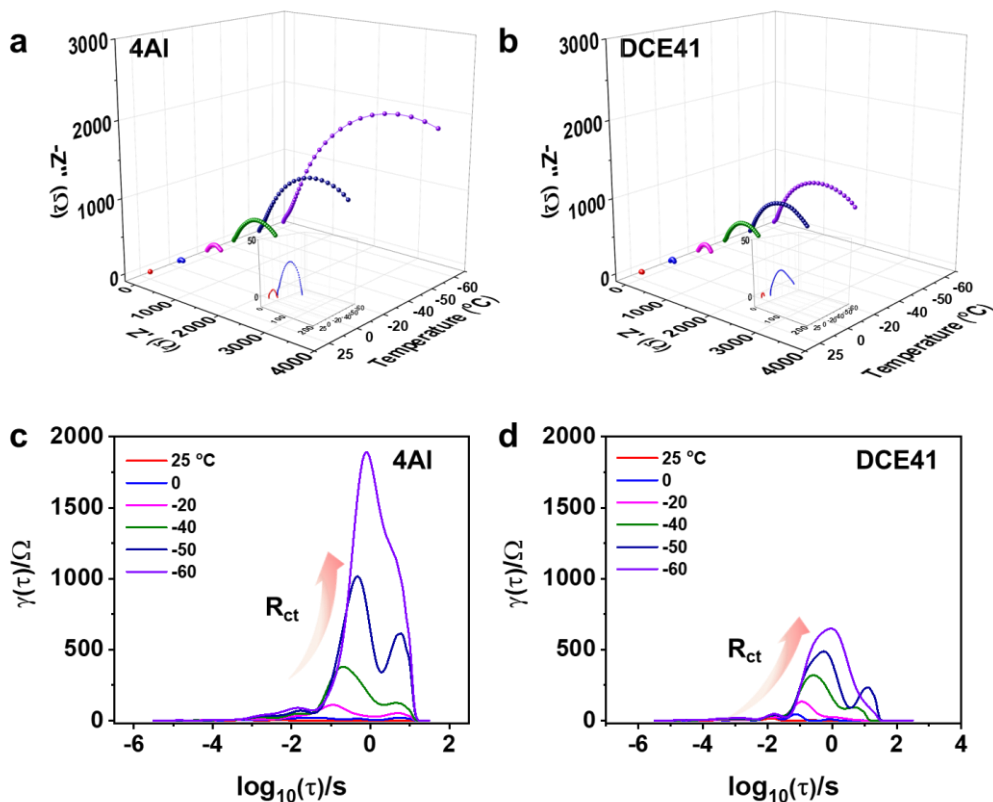


Fig. R1 EIS curves for the symmetrical Zn batteries with **a** 4Al and **b** DCE41 from 25 °C to -60 °C. The corresponding DRT curves for the symmetrical Zn batteries with **c** 4Al and **d** DCE41 from 25 °C to -60 °C.

2. PANI was used as a cathode material. The versatility of this approach should be discussed. Is this approach applicable to other cathode systems?

Response: We thank the reviewer for rising this valuable question. As a representative organic cathode material, PANI exhibits distinct advantages under low temperature conditions compared to conventional inorganic cathodes, especially in terms of its energy storage mechanism. In contrast, inorganic cathodes often suffer from sluggish ion intercalation/deintercalation kinetics at low temperatures, severely limiting their performance. Interestingly, in our system the dual-cation strategy we proposed can effectively enhance ion transport kinetics even under ultra-low-temperature conditions.

To further evaluate the universality of this strategy, we tested the battery performance with inorganic cathode. Specifically, we synthesized a representative vanadium-based cathode material, Zn_{0.25}V₂O₅,

via a hydrothermal method, and compared its electrochemical performance in different electrolytes. As shown in Fig. R2, at $-60\text{ }^{\circ}\text{C}$ and a current density of 0.2 A g^{-1} , the $\text{Zn}/\text{Zn}_{0.25}\text{V}_2\text{O}_5$ battery with 4Al electrolyte delivers a capacity of 65.2 mA h g^{-1} after 200 cycles. In contrast, when using DCE41, the battery still maintains a capacity of 181.5 mA h g^{-1} after 200 cycles. The initial increase in capacity observed during early cycles is attributed to the gradual activation of the cathode material (*J. Am. Chem. Soc.* 2024, 146, 31612–31623). The relatively higher capacity achieved in the DCE41 system further supports the positive role of our dual-cation strategy in enhancing cation transport kinetics under low-temperature conditions.

We have added the electrochemical results of $\text{Zn}/\text{Zn}_{0.25}\text{V}_2\text{O}_5$ with different electrolytes to the revised Supplementary Information in Fig. S55 and discussed the performance in the revised manuscript in Page 18, lines 7-8. The synthesis details of $\text{Zn}_{0.25}\text{V}_2\text{O}_5$ have also been included in the revised manuscript.

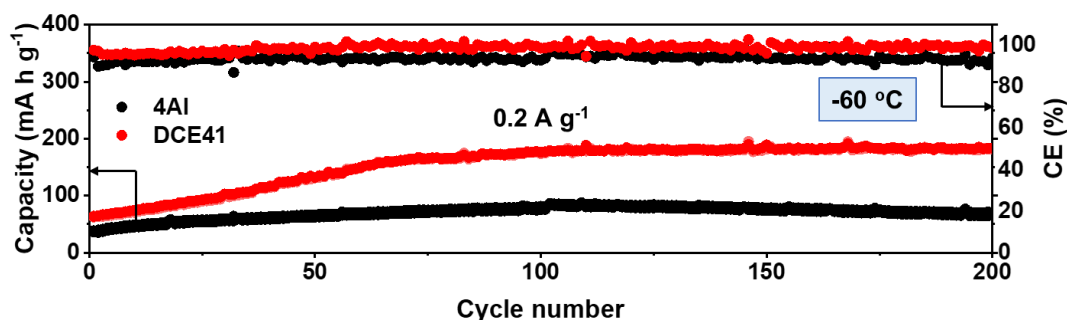


Fig. R2 Cycling performance of $\text{Zn}/\text{Zn}_{0.25}\text{V}_2\text{O}_5$ with different electrolytes at 0.2 A g^{-1} at $-60\text{ }^{\circ}\text{C}$.

Reviewer #3: *Although an additional author is included, it is impressive that the simulation work can be revised from a novice level to a reasonably systematic degree within such a short time period. Personally, I tend to believe Yanchun Xie deserves to be treated as a co-first author; but that's up to the corresponding authors' discretion.*

Answer: We sincerely appreciate the Reviewer's recognition of the progress made in the simulation work. The constructive feedback during the review process has been instrumental in guiding us to enhance the theoretical analysis. In view of Yanchun Xie's substantial contribution to the theoretical calculations, we have updated the author list to include him as a co-first author in the revised manuscript.

We are grateful for the Reviewer's thoughtful suggestion and kind encouragement. Following the Reviewer's valuable suggestions, we have carefully addressed all remaining comments. The point-by-point responses are detailed below. We hope that we have satisfactorily addressed your concerns, and will be glad if you could re-review our revised manuscript.

1. An additional requirement for the simulation part: a detailed energy table of all computed species should be included in SI. The atomic coordinates could be optional but should be available upon reasonable request. All the open-source packages and repositories involved in data analysis should also be cited and acknowledged.

Response: We acknowledge the reviewer for this professional recommendation. We have added a comprehensive table (Tables R1 and R2) summarizing the total energies and solvation energies of all computed species in the revised Supplementary Information (Supplementary Tables 3 and 4). The optimized atomic coordinates of all relevant species have been saved and are now provided as an attached file. In addition, all open-source packages and tools used for simulation and data analysis, including def2-TZVP basis and General Amber Force Field (GAFF) force field, have been properly cited and acknowledged in the revised manuscript. We hope these additions adequately address the reviewer's concerns.

Table R1 Total electronic energies of individual components involved in binding energy calculations.

Structure	Energy (Ha)	Structure	Energy (Ha)
H ₂ O	-76.43	H ₂ O-H ₂ O	-152.8711790
Al ³⁺	-240.4021947	Al ³⁺ -H ₂ O	-317.1599228
Zn ²⁺	-1778.333368	Zn ²⁺ -H ₂ O	-1854.926665
Ca ²⁺	-676.8832233	Ca ²⁺ -H ₂ O	-753.4077311
Mg ²⁺	-199.2261975	Mg ²⁺ -H ₂ O	-275.7907659
Na ⁺	-162.0709867	Na ⁺ -H ₂ O	-238.5436533
Li ⁺	-7.275950535	Li ⁺ -H ₂ O	-83.76521811

Table R2 Total electronic energies of relevant species involved in desolvation energy calculations.

Structure	Gibbs Free Energy (Ha)	Structure	Gibbs Free Energy(Ha)
[Al ₂ Cl(4H ₂ O)]	-1468.75	[Al ₂ Cl(3H ₂ O)]	-1392.28
[Al ₂ Cl(2H ₂ O)]	-1315.80	[Al ₂ Cl(1H ₂ O)]	-1239.29
[Al ₂ Cl]	-1162.75	H ₂ O	-76.46
[AlCl(4H ₂ O)]Cl[Zn(5H ₂ O)]	-4090.85	[AlCl(2H ₂ O)]Cl[Zn(2H ₂ O)]	-3708.48
[AlCl(4H ₂ O)]Cl[Zn(4H ₂ O)]	-4014.38	[AlCl(2H ₂ O)]Cl[Zn(H ₂ O)]	-3631.98
[AlCl(4H ₂ O)]Cl[Zn(3H ₂ O)]	-3937.91	[AlCl(H ₂ O)]Cl[Zn(H ₂ O)]	-3555.47
[AlCl(3H ₂ O)]Cl[Zn(3H ₂ O)]	-3861.44	[AlCl(H ₂ O)]Cl[Zn]	-3478.95
[AlCl(2H ₂ O)]Cl[Zn(3H ₂ O)]	-3784.95	[AlCl]Cl[Zn]	-3402.40

2. Despite the significantly enhanced simulation work quality, I have to point out that the writing quality is still below the average of Nat Comm. A more concise and concentrated paper can benefit more researchers in the scientific community. Redundant phrasing and detailed technical descriptions can be reserved for SI.

Response: We sincerely thank the reviewer for the critical and constructive feedback regarding the manuscript writing. We fully agree that a more concise and focused main text can enhance readability and benefit a broader scientific audience. In the revised manuscript, we have carefully polished the language and streamlined several paragraphs to improve clarity. In particular, certain technical descriptions and detailed simulation discussions have been relocated to the Supplementary Information to ensure the main text remains concise and coherent. We hope the revised version better meets the standards of Nat. Commun.

Response to Reviewers

Reviewer #1:

I acknowledge the author's effort in revising the manuscript and clarify its novelty. However, after careful evaluation, I still find that the core contribution of this work largely consists of integrating and extending previously reported observations rather than establishing a genuinely novel mechanism or principle. Therefore, I do not consider the work suitable for publication in Nature Communications.

Reply: We sincerely thank the reviewer for acknowledging our efforts in revising the manuscript and clarifying its novelty. We would like to further emphasize that the contribution of our work lies not in incremental improvement, but in establishing a new mechanism for understanding and exploiting cation effects in aqueous systems:

1) Distinct deshielding effect principle:

Previous studies have individually discussed ionic potential or selective cation interactions with either O or H atoms individually. However, our work is the first to demonstrate and validate the simultaneous deshielding effect (DSE) on both H and O atoms as a unified principle, supported by comprehensive spectroscopic and theoretical analyses. This principle provides a mechanistic clarity that resolves contradictions among prior studies (e.g., strong vs. weak cation–water interactions) and offers a new guideline for the rational design of antifreezing electrolytes.

2) Dual-cation effect:

Beyond bulk hydration, we identify a synergistic and competitive dual-cation coordination and codeposition effect, which differs fundamentally from prior reports focusing solely on hydration structures. This mechanism enables long-term stabilization of Zn electrodes at -60 °C for over 10,340 h, exceeding previously reported lifetimes of Zn electrodes under ultralow temperature conditions. Furthermore, Zn||PANI full cells achieve more than 12,000 cycles at -60 °C and deliver 115.5 mA h g⁻¹ at -80 °C, demonstrating both durability and practical relevance. Importantly, this dual-cation strategy also suggests a new direction for ion transport kinetics and interfacial engineering and in aqueous batteries under extreme conditions.

Taken together, our work does not simply integrate previous findings, but establishes the cation effect as a distinct principle for regulating water structure (via simultaneous deshielding effect of H and O atoms) and enabling low-temperature aqueous electrochemistry (through dual-cation competition and synergy effect), and a breakthrough in electrochemical performance. We believe these contributions provide fresh conceptual and practical insights for the broader field of aqueous electrolytes.

Reviewer #2:

The revised manuscript has sufficiently addressed the reviewer's comments. It can be recommended for acceptance.

Reply: We sincerely thank you for your kind affirmation.

Reviewer #3:

The authors revealed that the unique cation-water structure, in the aqueous battery system with Zn-Al alloy anode, contributes to the low-temperature performance and cycling longevity.

This work is of interests to the fundamental understanding of solvation structures in aqueous electrolytes with multiple salt species. The methodologies integrate advanced characterization and simulation techniques, which bring multiple perspectives to the complex aqueous electrolyte phenomena.

Although little attention was paid to the cathode's role and the explicit interphase structure near anode, the authors elaborated several important questions in the multi-cation electrochemistry.

Reply: We sincerely appreciate your positive evaluation of this work. In consideration of your concerns regarding the cathode, we further clarified the rationale for selecting PANI as the positive electrode material: “**polyaniline (PANI) was selected as the positive electrode material since its charge storage is dominated by surface redox reactions rather than bulk Zn^{2+} intercalation. This feature makes the electrochemical behavior relatively less dependent on ion diffusion, thereby reducing temperature sensitivity compared with conventional inorganic positive electrodes.**” We have added this information in the revised manuscript in page 16, line 24-26; page 17, line 1-2.