A Perspective of ZnCl₂ Electrolytes: the Physical and Electrochemical Properties

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Abstract Molten ZnCl₂ hydrates are ionic liquids at room temperature, which exhibit intriguing physical and electrochemical properties. Continuous efforts have been devoted over several decades to understanding the properties of the molten ZnCl₂ hydrates that have recently been dubbed as water-in-salt electrolytes. The physical properties of molten ZnCl₂ hydrates can be described from the perspectives of ions in their speciation and water molecules regarding their chemical environments. Recently, attention has been given to molten ZnCl₂ hydrates as electrolytes for Zn metal batteries. It was revealed that the physical properties of such electrolytes have rich implications in their electrochemical properties. Therefore, it demands a holistic understanding of the physical and electrochemical properties of molten ZnCl₂ hydrates to design functional electrolytes to serve high-performing Zn metal batteries. This review attempts to review the works that described the properties of concentrated ZnCl₂ as an ionic liquid and as an emerging electrolyte. The author also provides a perspective to highlight the needs of future research to circumvent the limits of this electrolyte.

Keywords: Energy storage, battery, electrolyte, molten salt, ZnCl₂, water in salt

1. Introduction

The electrolyte defines the chemical environment for the reactions in batteries.[1] The properties of electrolytes demarcate the thermodynamic properties of electrodes to play out in batteries.[2] In 2019, the author described considerations for the design of storage batteries from a synthetic reaction’s point of view that include (1) viewing electrodes and the ion charge carriers as the reactants, (2) focusing on the chemical bonding between the ion charge carrier and the electrode that defines the energetics and kinetics of the reactions of electrodes, (3) selecting the electrolytes as the reaction medium, and (4) setting the battery operation principles according to the migration directions of charge carriers.[3] In electrochemical cells, the electrolyte not only mediates the mass and charge transfer by serving as a salt bridge but also contains ion charge carriers as a reactant by solvation and speciation.[4, 5] Furthermore, the electrolyte constitutes the venues for electrochemical reactions, which are at the interface with the electrodes, i.e., electrical double layers (EDL),[6] or inside the solid electrolyte interphase (SEI).[7] Therefore, the choice of electrolytes has been of centrality pertinent to the nature of a battery. The high ionic conductivity of the electrolyte that is a function of the viscosity of the liquid and diffusivity of the ions is often the premise for an electrochemical reaction to operate.[8] The redox reactivity of the electrolyte itself needs to be kept minimal, where the bottom-line is that the electrolyte should not be continuously consumed by side reactions over the cycling of the batteries. The electrolyte is inert mass in rocking-chair batteries (RCBs);[9] however, the electrolyte can serve as the sole source of ions, as a part of the active mass, often being the determinant for the energy
density of dual-ion batteries (DIBs)[10] or reverse dual-ion batteries (RDIBs).[11] The nuances of utilities of electrolytes were not reckoned until the non-aqueous electrolytes were widely employed for Li-ion batteries (LIBs),[12] where the formula of the electrolyte dictates the nature of the SEI and cathode electrolyte interphase (CEI).[13] Critically, on the graphite anode, the self-passivating reaction facilitates the kinetically stable (de)intercalation of Li-ions into the graphite intercalation compounds (GIC), which readied the commercialization of LIBs.[14, 15]

The concentration is a primary parameter of electrolytes, which directly affects the ionic conductivity of electrolytes. The conductivity of electrolytes receives the most attention because without an excellent conductivity, the batteries cannot deliver acceptable performance under the “so-called” lean electrolyte conditions.[16] In fact, nearly all commercial batteries must employ lean electrolyte conditions, where in RCBs the volume of the liquid electrolyte should be no more than what is needed to wet the voids of electrodes and the pores of the separator. For LIBs, the optimal concentration of aprotic electrolytes is conveniently around 1 M. Beyond 1 M, the conductivity of electrolytes declines. It is worth noting that in aqueous batteries, the optimal concentrations of electrolytes often deviate from the unity molarity. For example, Lead-Acid batteries usually employ 5 M H2SO4 as the electrolyte, and NiMH batteries and the Edison NiFe battery often use 6 M KOH as the electrolyte.

However, this trend of conductivity is not monotonous for polymers as a “solvent”, where Angell found that in polymer electrolytes, once the salt’s concentration goes beyond a critical value, the trend reverses, and a higher concentration leads to higher conductivity in the so-called “polymer in salt” regions.[17] Besides conductivity, the salt concentration in electrolytes is associated with other utilities. In 1984, McKinnon and Dahn reported that saturated LiAsF6 in propylene carbonate (PC) could inhibit the co-intercalation of PC into layered compounds.[18] Jeong et al. found that higher concentrations of lithium salts avail reversible intercalation of Li-ions in graphite in forming the stage-I graphite intercalation compound.[19] Abe et al. studied the solvation structures, in particular, the coordination number of Li-ions in DMSO electrolytes of different concentrations for the purpose of Li-ion intercalation in graphite. They found that a smaller coordination number of Li-ions in a more concentrated electrolyte suppresses the co-intercalation of DMSO.[20] The concept of superconcentration of salts in electrolytes has recently entered new areas of solvent-in-salt electrolytes first formulated by Hu et al. to address the polysulfide shuttle problem in Li-S batteries[21], water-in-salt electrolytes (WiSE) initially defined by Xu and Wang et al.[22], and molecular crowding electrolytes reported by Lu et al.[23] to widen the electrochemical stability window for aqueous Li-ion batteries.

The question is how high the solute concentration renders the electrolytes qualified as WiSE. Although there is no widely accepted standard to demarcate the WiSE from the dilute or relatively concentrated electrolytes, generally, one can use whether the cations of the solute have a sufficient number of aqua ligands to be fully hydrated as a factor to consider. If there is no second hydration shell or the first hydration shell of the cation is incomplete, such an electrolyte can be referred to as WiSE.

The concentration of salts in the electrolytes is a chief knob to tune the proprieties of the electrolytes. In 1968, Braunstein classified aqueous solutions into five concentration regions according to the molar fraction of water: I. Debye-Huckel limiting law (1 – > 0.99), II. extended Debye-Huckel theory (0.99 –0.9), III. hydrate melts (0.9 –0.75), IV. incomplete hydration
sheaths \((0.75 - 0.01)\), and V. gas solubility \(<0.01\).[24] Here, water may be replaced by other solvents in non-aqueous electrolytes. The dilute electrolytes can be described by the model of Debye-Huckel (1923), where in this single-particle model, each cation or anion is surrounded by an atmosphere of negative charges and positive charges of dipoles, respectively.[25] Conventional electrolytes in batteries normally fall in the range of the extended Debye-Huckel theory; WiSE and aqueous deep eutectic solvent (DES) electrolytes are in the ranges of hydrate melts or incomplete hydration sheaths. Braunstein pointed out that when the hydration shells of the ions are incomplete, the ion-ion, water-water, and water-ion interactions must be considered. It is the ion-ion interaction, particularly the cation-anion pair and aggregates of ions, which differentiates the properties of concentrated electrolytes from the dilute ones. When the concentration gets higher, the cation-anion pairing becomes more prevalent, which is demonstrated in the recent reports of promoted anion-derived SEI formation on metal anodes.[26-28]

Concentrated electrolytes such as WiSE can significantly widen the electrochemical stability window of aqueous electrolytes, where WiSE push further apart the potentials of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[29] The first reported WiSE dissolves 21 \(m\) (mol/kg) lithium bis(trifluoromethanesulfonyl)imide (LiTFSI),[22] whereafter similar fluorinated salts continued to receive salient attention due to their appealing properties.[30] For example, such salts can avail the formation of SEI via the decomposition of TFSI- anions on electrodes, which helps further widen the electrochemical window of aqueous electrolytes.[31] However, the high cost of fluorinated electrolytes remains a challenge to their wide applications in storage batteries. Therefore, it is sensible to extend the studies to highly soluble salts composed of non-fluorinated anions such as potassium acetate[32, 33] and ZnCl2. As a digression, ZnCl2 can serve as a cathode in ZEBRA batteries in its molten state.[34] ZnCl2 has long been employed as an electrolyte for electrochemical devices, albeit until recently only dilute ZnCl2 electrolytes had been employed, e.g., mixed with NH4Cl for optimal conductivity properties.[35, 36]

ZnCl2 is one of the most soluble inorganic salt in water. At room temperature, saturated ZnCl2 solution reaches a concentration of 31 \(m\) with 64 mol% H2O. The concentrated ZnCl2 solutions can be considered as molten hydrates of ZnCl2·RH2O, where R is the molar ratio between equivalent water and the equivalent formula of ZnCl2. The high solubility of ZnCl2 in water has been known for over 150 years. In 1859, a patent was granted to Taylor for a process of turning paper translucent by a concentrated ZnCl2 solution.[37, 38] It is later known that molten hydrates, e.g., ZnCl2·4H2O, can dissolve cellulose because [ZnCl4]2- ions attack and break the hydrogen bonds of cellulose fibers.[39, 40] Such properties may facilitate molten ZnCl2 as an agent in the chemical activation of biomasses in preparation of activated carbon.[41, 42]

Recently, heed has been paid to Zn metal batteries for their potential of scalable grid storage,[43, 44] where primary challenges turn out to be HER on the anode and capacity fading of the cathode.[45, 46] The solutions to address such challenges will most likely come from the electrolytes that inhibit HER and OER simultaneously,[47] where aqueous ZnCl2-based solutions represent a promising group of electrolytes, as exemplified by recent studies.[48-50]. In this brief review, the author will highlight the current understanding of the physical properties of concentrated ZnCl2 electrolytes in conjunction with the advances of knowledge of their electrochemical performance in Zn metal batteries. As far as the author understands, this topic...
has not been reviewed before. Note that ZnCl$_2$ is an essential component of many DES that often contain choline chloride and urea as the hydrogen bond donor and acceptor, where the properties of such DES are beyond the scope of this review.[51] Interested readers are recommended to read reviews on DES.[52, 53]

2. **Physical Properties of Concentrated ZnCl$_2$**

![Figure 1](image)

**Figure 1.** A water:ZnCl$_2$ phase diagram for H$_2$O (blue) and D$_2$O (red) in the compositional region between R=3 (57 mol. % water) and pure water. Squares represent eutectic points, and circles represent melting points (liquidous curve).[54] Reproduced with permission from ref. 55. Copyright 2015, American Chemical Society.

The first phase diagram of ZnCl$_2$$\cdot$3H$_2$O was devised by Mylius and Dietz in 1905, which suggested five different phases of ZnCl$_2$ hydrates.[55] The contemporary phase diagram was constructed by Martin and coworkers (Fig 1).[54, 56, 57] The phase diagram displays that at room temperature all phases of ZnCl$_2$ hydrates are molten as a liquid. About the properties of these molten hydrates, there are two primary questions: (1) the speciation of cations and anions and (2) the chemical environment of water molecules. Continuous characterization efforts over several decades have provided tremendous insights into these questions.

Vibrational spectroscopic tools such as Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR) are valuable to reveal the speciation of ions in concentrated ZnCl$_2$ solutions. When R is above 3, there exist water molecules in the second hydration shell of the Zn$^{2+}$ ions. In dilute ZnCl$_2$ solutions, significant percentages of chloride ions are free ions. In such
solutions, most Zn$^{2+}$ ions are hydrated cations, i.e., [Zn(H$_2$O)$_6$]$^{2+}$, which correspond to a characteristic Raman peak at ~ 390 cm$^{-1}$.[58] Other possible cations, [ZnCl(H$_2$O)$_3$]$^+$ (or [ZnCl(H$_2$O)$_3$]$^+$) that contain a Zn-Cl ion-pair have been contemplated, where the insertion of such monovalent ions into electrodes can be energetically more favorable.[59] In dilute solutions, other Zn-Cl complex species may exist, which include [ZnCl$_2$], [ZnCl$_3$]$^-$, and primarily [ZnCl$_4$]$^{2-}$.[60] It is worth noting that for [ZnCl$_2$] and [ZnCl$_3$]$^-$, the real species should be [ZnCl$_2$(H$_2$O)$_2$] and [ZnCl$_3$(H$_2$O)]$^-$.[61] [ZnCl$_4$]$^{2-}$ is the primary anion whenever there is an excess of chloride ions, and its characteristic Raman peak is around 280-290 cm$^{-1}$.

When R is 3, the formula of ZnCl$_2$·3H$_2$O can be misleading because the primary ionic species in this molten salt are [Zn(H$_2$O)$_6$]$^{2+}$ and [ZnCl$_4$]$^{2-}$, respectively, where both ions are nonpolar, making this liquid an interestingly nonpolar ionic liquid. The ionic liquid nature of the molten ZnCl$_2$·RH$_2$O is supported by the remarkable decrease of water’s activity coefficient around R of 3, reported by Maki et al.[62] It is reasonable to consider that water molecules in ZnCl$_2$ solutions with R no higher than 3 are rather the aqua ligands of ions. The ZnCl$_2$ solution reaches its saturation molality of 31 m with an R of 1.79 at room temperature. When R is below 3, [ZnCl$_4$]$^{2-}$ ions oligomerize to form aggregates by sharing chloride corners of tetrahedral complex ions. The aggregation of [ZnCl$_4$]$^{2-}$ releases spared chloride ions that will seize Zn$^{2+}$ from its hydrated ions, thus freeing up water molecules as water “monomers”. Such monomers do not seem to serve as the ligands for Zn$^{2+}$. This postulation may be viable due to the strong electrostatic interactions between such water molecules and highly negatively charged [ZnCl$_4$]$^{2-}$ and its oligomers. Deki et al. reported that the vapor pressure of ZnCl$_2$ is higher than that of Zn(NO$_3$)$_2$ and Mn(NO$_3$)$_2$ aqueous solutions with the same concentration.[63] This observation can be rationalized by the polymerization of Zn-Cl complex ions.

### 2.1 The Ion Speciation

It is generally accepted that above a certain concentration, the local ordering of the molten salt resembles that of its solid crystals. Losey determined that in the liquid of ZnCl$_2$·3H$_2$O, the ions [Zn(H$_2$O)$_6$]$^{2+}$ and [ZnCl$_4$]$^{2-}$ are packed, resembling the local order of CsCl.[57] Yamaguchi collected XRD and Raman results suggesting that there exist aggregates of tetrahedral species that are linked by chloride ions.[64]

Raman spectroscopy provides rich information about the speciation of ions in concentrated ZnCl$_2$. By using Gauss-Lorentzian curve forms, Maeda et al. fit their Raman spectra of solutions that comprise different ratios of Zn$^{2+}$ and Cl$^-$. They assigned 277, 283, and 300 cm$^{-1}$ to [ZnCl$_4$]$^{2-}$, [ZnCl$_3$]$^-$, and ([ZnCl$_2$] + [ZnCl]$^+$). Such assignments to species are aligned with the different Zn-Cl bond lengths,[65] where the Zn-Cl bond is shorter in lower complex ions than in higher ones. Recent Raman studies of dilute ZnCl$_2$ and relatively concentrated ZnCl$_2$ solutions by Pei and Chen et al. also reported the Raman signals assigned to ([ZnCl$_2$] + [ZnCl]$^+$).[59]

The Raman studies on different concentrations of ZnCl$_2$ by Fang and Ji et al. showed that [ZnCl$_4$]$^{2-}$ dominates at concentrations of 5 m, 10 m, and 20 m (Figure 2).[48] The existence of lower complex ions/molecule of [ZnCl$_3$], [ZnCl$_2$], and [ZnCl]$^+$ should not be ruled out; however, their presence is rather minor. Notably, at 30 m, a new peak appears at 243 cm$^{-1}$, which is assigned to oligomerized [ZnCl$_4$]$^{2-}$. When the concentration increases, the peak at around 290 cm$^{-1}$ that is assigned to [ZnCl$_4$]$^{2-}$ is blue-shifted. The blue shifted peak indicates a shorter Zn-Cl
bond length, which can be attributed to the progressively stronger electrostatic repulsion between the increasingly crowded \([\text{ZnCl}_2]^2-\).

Note that the peak at \(~390\ \text{cm}^{-1}\) originally assigned to \([\text{Zn(H}_2\text{O})_6]^2+\) persists upon increasing the concentration. At the concentrations of 20 \(m\) and 30 \(m\), \(R\) is 2.78 and 1.85, respectively, and if all chloride ions are consumed to form \([\text{ZnCl}_4]^2-\), the hydrated \(\text{Zn}^{2+}\) should be \([\text{Zn(H}_2\text{O})_{5.6}]^{2+}\) and \([\text{Zn(H}_2\text{O})_{3.7}]^{2+}\), respectively, where the latter is a substantially incomplete hydration shell. It is observed that from 20 to 30 \(m\), this peak at \(~390\ \text{cm}^{-1}\) shifts to a higher wavenumber, albeit the peak intensity decreases. Understandably, the interaction between \(\text{Zn}^{2+}\) and aqua ligands in an incomplete hydration shell should be stronger than that of a complete hydration shell, thus resulting in shorter \(\text{Zn-O}\) bonds.

![Figure 2. Raman spectra of ZnCl2 aqueous solutions of different molality concentrations.[48] Reproduced with permission from ref. 48. Copy right 2018, The Royal Society of Chemistry.](image)

2.2 Water’s Chemical Environment

Concentrated \(\text{ZnCl}_2\) electrolytes are intriguing because such solutions constitute a peculiar chemical environment for not only the ions but also water molecules, in which the properties of water are yet to be well understood. There exist a trio of tools that can help describe the chemical environment of water molecules in these electrolytes. In 1955, Shoolery and Alder reported deshielding effect to the nuclei of hydrogen atoms in \(^1\text{H}\) nuclear magnetic resonance (NMR) of concentrated \(\text{ZnCl}_2\), where the chemical shift, \(\delta\), of \(^1\text{H}\) compared to that of pure water in NMR increases from 4.3 to 9.6, which suggests the broken hydrogen-bonded network and stronger interaction between water and ions.[66] \(^1\text{H}\)-NMR can help understand the dynamic properties of water in molten \(\text{ZnCl}_2\) hydrates, \(i.e.,\) the motions of water molecules. Nakamura calculated the relaxation times for the translation motion \((\tau_{\text{inter}})\) and the rotational motion \((\tau_{\text{intro}})\) of water molecules in \(\text{ZnCl}_2\) solutions of different \(R\) values.[67] They found that ratio of \(\tau_{\text{inter}}/\tau_{\text{intro}}\)
rises gradually when R decreases but increases precipitously when R is below 6. The results suggest that the translational motion of water is hindered in ZnCl₂ WiSE, which pertains to the coordination of water to Zn²⁺ as ligands and also relates to the oligomerization of the Zn-Cl complex ions.

Studies of synchrotron X-ray total scattering and neutron total scattering can offer much information about liquid structures.[68] In particular, the scattering intensity underneath the Bragg peaks of these two techniques can generate pair distribution function (PDF) of the electrolytes.[69] PDF profiles do not identify elements but measure the local distances between neighboring atoms. Note that X-ray interacts with the electrons of atoms, and even high-energy X-rays cannot “see” light atoms of hydrogen or deuterium. Therefore, the PDF derived from X-rays cannot reveal the pair correlations involving hydrogen atoms. On the other hand, neutron interacts with the nuclei, where neutrons can detect light atoms, particularly deuterium of heavy water. Thus, for neutron studies, samples are usually deuterated. For concentrated ZnCl₂, an important question is whether there are hydrogen-bonded water molecules that are not aqua ligands, where PDF can shed light on this question. As Figure 3 shows, in the electrolyte of 30 m ZnCl₂ and its mixtures with 5 m LiCl and 10 m LiCl, there lacks a peak at 1.8 Å, which is the characteristic pair correlation for hydrogen bonding between water molecules. Herein, the results, thus, show that in these WiSE, few water molecules form hydrogen bonding.

Figure 3. PDF profiles associated with neutron total scattering of different WiSE: 30 m ZnCl₂ (30ZC), 30 m ZnCl₂ + 5 m LiCl (30ZC5LC), and 30 m ZnCl₂ + 10 m LiCl (30ZC10LC), where the D₂O is used as the solvent, and O-D, Zn-O, Li-O, Zn-Cl, O-O, Cl-Cl denote the pair correlations between neighboring atoms.[49] Reproduced with permission from ref. 49. Copyright 2021, Wiley-VCH.

Raman spectroscopy is sensitive to the changes in water’s chemical environment as well. Of the gas phase of water, there are three modes—the H-O-H bending (A₁), the symmetric O-H stretch
(A₁), and the asymmetric O-H stretch (B₂). For liquid water, there are two peaks for the O-H stretching. One O-H stretching peak at a lower wavenumber below 3200 cm⁻¹ corresponds to the fully hydrogen-bonded water molecules with a DDAA environment, i.e., the same degree of hydrogen bonding as in ice Ih,[70] which is red-shifted from asymmetric and symmetric stretches at 3652 and 3756 cm⁻¹ in the gas phase of water at room temperature. Regarding the hydrogen bonding of water, DDAA means that one water molecule simultaneously donates two hydrogen atoms and accept two hydrogen atoms with its two lone pairs of electrons. The other stretching peak at a higher wavenumber above 3400 cm⁻¹, less red-shifted, is assigned to water molecules that are not fully hydrogen-bonded, e.g., with DA and DDA environments (Figure 4a).[71, 72] Hydrogen bonding weakens and elongates the covalent O-H bonds of water, thus lowering the vibration frequencies of the stretching modes. By increasing the concentration of ZnCl₂ to nearly saturated 30 m, the clusters of water molecules disintegrate, which eliminates the DDAA environment. Therefore, the peak below 3200 cm⁻¹ is significantly dampened, which corroborates the above PDF results on the lack of pair distribution characteristic of the hydrogen bond of water molecules. This is also in line with the incomplete hydration shell of Zn²⁺, where the shortage of aqua ligands would not allow water molecules to “nucleate” into clusters. Spectroscopic studies on other concentrated aqueous electrolytes such as LiNO₃[73] and LiTFSI[74] also reported the disappearance of the peak at the lower wavenumber around 3200 cm⁻¹.

The question is what chemical environment corresponds to the peak above 3400 cm⁻¹ in the Raman spectra. Similar Raman results were reported in 2003 by Zhang and Chan on supersaturated NaClO₄, LiClO₄, and Mg(ClO₄)₂, where the authors attributed the observed O-H stretching peak to water “monomers” whose presence is facilitated by the structure breaking effect of superconcentrated ClO₄⁻.[75] In concentrated ZnCl₂, it should be [ZnCl₄]²⁻ that breaks water into such non-bonded molecules via its electrostatic field, a field most likely stronger than that of ClO₄⁻. The electrostatic interaction between [ZnCl₄]²⁻ and water molecules seems to strengthen the O-H bond of water. It was observed that upon adding LiCl into 30 m ZnCl₂ with the increasing concentration from 3 m to 5 m and to 10 m, the Raman peak above 3400 cm⁻¹ blue-shifts monotonously (Figure 4b).[49] The function of added LiCl is to offer additional chloride ions to bind with Zn⁵⁺ to form [ZnCl₄]²⁻, which increases the concentration of [ZnCl₄]²⁻, thus enhancing the electrostatic interaction between [ZnCl₄]²⁻ and water. In addition, the minor peak at 3650 cm⁻¹ of pure water that is assigned to free O-H is completely vanished in ZnCl₂ based WiSE.
Figure 4. Raman spectra of water regarding the stretching modes. a. The Raman O-H stretching band of water deconvolution using five Gaussian functions centered at 3005 cm\(^{-1}\) (DAA-OH, single donor–double acceptor), 3226 cm\(^{-1}\) (DDAA-OH, double donor–double acceptor), 3434 cm\(^{-1}\) (DA-OH, single donor–single acceptor), 3573 cm\(^{-1}\) (DDA-OH, double donor–single acceptor) and 3640 cm\(^{-1}\) (free-OH).[71] Reproduced with permission from ref. 71. Copyright 2016, The Royal Society of Chemistry. b. Femtosecond stimulated Raman spectra (FSRS) in the high-frequency region for water O-H stretching, 30 \text{ m} \text{ ZnCl}_2 (30ZC), 30 \text{ m} \text{ ZnCl}_2 + 3 \text{ m} \text{ LiCl}
The acidity of hydrated metal salts comes from the binding between the metal cations and the oxygen atoms of water molecules. The inductive effect caused by this M-O bond weakens the O-H bonds of aqua ligands, which stabilizes the conjugate base of \([\text{M(OH}_2]^+\) for a divalent metal ion. The acidic properties of molten hydrates are strengthened when most water molecules are in the primary hydration shell, particularly when this shell is incomplete. In other words, the acidity of the aqueous solution is high when water’s activity is low. ZnCl\(_2\) hydrate is known as acidic due to the strong polarizing capability of Zn\(^{2+}\). Recently, Aurbach et al. reported the pH values of the ZnCl\(_2\) aqueous solutions of different concentrations. When the concentration enters the realms of WiSE, the measured pH values are comparable to strong acids.\(^{[76]}\) It is worth noting that the acidity of concentrated acids and salts cannot be most accurately described by electrometric pH values. In 1932, Hammett and Deyrup described the measurements of Hammett Acidity, which is defined by the following equation: 

\[
H_0 = -\log \frac{a_{H^+}f_B}{f_{BH^+}},
\]

where \(a_{H^+}\) is the activity of protons, and \(f_B\) and \(f_{BH^+}\) are activity coefficients of the indicator base and the conjugate acid, respectively.\(^{[77]}\) However, it is difficult to estimate the activity coefficients precisely. On the other hand, the Hammett acidity, \(H_0\), can be calculated with the following equation as a working definition:

\[
H_0 = pK_{BH^+} + \log \left( \frac{[B]}{[BH^+]} \right)
\]

where \(K_{BH^+}\) is the acid dissociation constant of the conjugate acids of BH\(^+\). The ratio of concentrations of \(\frac{[B]}{[BH^+]})\) can be measured by spectrophotometric methods.\(^{[78]}\)

In 1978, Duffy and Ingram reported that the Hammett acidity, \(H_0\), of concentrated ZnCl\(_2\) is on par with strong acids, where \(H_0\) of ZnCl\(_2\)-4.43H\(_2\)O is at the level of -2, evaluated with different indicators, whereas \(H_0\) of ZnCl\(_2\)-11.16H\(_2\)O ranges from -0.55 to -0.11.\(^{[79]}\) However, in 1979, McDaniel pointed out that the above-reported acidity does not consider the lowered activity of water, which could overestimate the acidity of concentrated ZnCl\(_2\).\(^{[80]}\) The author are also concerned here about whether the Hammet acidity can be compared between strong acids and concentrated ZnCl\(_2\) directly. Indeed, Zn metal cannot survive in strong acids but can be reversibly plated/stripped in ZnCl\(_2\) WiSE. The acidity of ZnCl\(_2\) WiSE as the electrolyte is expected to negatively impact the metal anode's stability. Therefore, it is of interest to lower the acidity of ZnCl\(_2\)-based WiSE. In 1980, Crane and Easteal measured the Hammet acidity of concentrated ZnCl\(_2\) and its mixture with LiCl. They found that when the molar ratio between ZnCl\(_2\)-RH\(_2\)O and LiCl-RH\(_2\)O reaches 1:2, the acidity is minimized among the mixture solutions.\(^{[79]}\)

Temperature affects the formation constants of complex ions, e.g., [Zn(H\(_2\)O)_6], in the electrolytes, where at a higher temperature the complex ions will shift to a greater extent of dissociation, resulting in more free water molecules. Thus, at a lower temperature, the CE of Zn
should be enhanced due to the fewer free water molecules and thermodynamically more inert water molecules.

3. \textbf{ZnCl}_2 \textit{Solutions as Electrolytes for Zn Metal Batteries}

![Figure 5. Electrochemical stability window of ZnCl$_2$ electrolytes with different concentrations.\cite{48} Reproduced with permission from ref. 48. Copy right 2018, The Royal Society of Chemistry.]

Dilute ZnCl$_2$ electrolytes can exhibit interesting results compared to other dilute Zn electrolytes. Pei, Meng, and Chen \textit{et al.} reported that 2 m ZnCl$_2$ is the optimal electrolyte for the aqueous Zn$^{2+}$ based electrical double layer capacitors (EDLCs).\cite{59} The authors compared the properties of the electrolytes of some common salts, including ZnCl$_2$, ZnSO$_4$, Zn(CF$_3$SO$_3$)$_2$, Zn(Ac)$_2$, and Zn(NO$_3$)$_2$, and found that ZnCl$_2$ exhibits a higher capacitance and better charge transfer properties. In particular, the density functional theory (DFT) studies here suggest that the desolvation energy is much lower for [ZnCl]$^+$ than Zn$^{2+}$ from the electrolytes, which is unique for ZnCl$_2$. The notion of [ZnCl]$^+$ as the cation charge carrier is interesting, which begs the answer for the question: whether Zn$^{2+}$ or [ZnCl]$^+$ is the \textit{de facto} charge carrier for the operation of cathode materials in aqueous batteries that employ ZnCl$_2$, including its WiSE as the electrolyte. Further investigations on this question are warranted.

When the concentration of ZnCl$_2$ is further increased, the viscosity of the electrolytes increases, which lowers the ionic conductivity. However, the benefits of higher concentrations may potentially outweigh the disadvantages of the decreased conductivity by conjuring intriguing properties. I will briefly introduce the advantages in several aspects: a low melting point, a wider
electrochemical window, mitigated solubility of the electrodes, and new speciation of ions in the electrolytes.

Aqueous ZnCl$_2$ solutions start to exhibit more unique properties when the concentration goes beyond the realm of being “diluted”. Chen et al. found that the 7.5 m ZnCl$_2$ electrolyte (R value of 7.4 or water occupies 88 mol.% of the solution) does not freeze above a temperature of -114 °C in experiments.[81] The authors demonstrated the cycling performance of full cell chemistry with Zn metal anode at -90 °C. The trend of depressed freezing temperatures as a function of the stoichiometry of ZnCl$_2$·RH$_2$O is aligned with the phase diagram although the experimentally determined lowest freezing temperature is significantly lower than that suggested by the Martin group.[54, 57] The low melting points, albeit not fully understood, may relate to the interrupted hydrogen bonding between water molecules and the low lattice energy of this particular hydrate of ZnCl$_2$·7.4H$_2$O, where the second hydration shell may play a critical role.

Because the comprised water molecules are more redox-inert, ZnCl$_2$ WiSE is promising to simultaneously suppress the OER on the cathode and the HER on the Zn metal anode. First, the onset potential of OER is raised by 0.5 V in 30 m ZnCl$_2$ compared to 5 m ZnCl$_2$, as shown in Figure 5. This means that an aqueous battery with this 30 m ZnCl$_2$ can employ a more oxidizing cathode to increase the voltage of the battery. At least two factors may be responsible for the raised onset potential of OER: (1) the lowered activity of water and (2) the lowered energy of the highest occupied molecular orbital (HOMO) of water. In light of the blue-shifted peaks assigned to the O-H stretching of water in the Raman spectra of ZnCl$_2$ based WiSE, the average bond length of O-H covalent bonds in water should be shorter, which indicates a stronger O-H covalent bonding and a wider HOMO-LUMO gap. Thus, with the energy level of LUMO raised for water molecules, it becomes more difficult to reduce water molecules, which suppresses HER of water on the Zn metal anode.

In our initial results, the average CE of Zn metal anode rises from 73.2% to 95.4% at a current density of 1 mA/cm$^2$ when the concentration of ZnCl$_2$ is increased from 5 to 30 m.[48] The average CE is measured with the following equation:[82, 83]

$$CE = \frac{100 \times Q_c + Q_s}{100 \times Q_c + Q_T}$$

where a capacity ($Q_T$) of 4 mAh/cm$^2$ was deposited onto the current collector first. In the following cycles, a capacity of 0.4 mAh/cm$^2$ ($Q_c$) was stripped and plated for 100 cycles, and $Q_s$ is the capacity from the last stripping. Later results from our group showed that by using a purer ZnCl$_2$, the CE of Zn metal anode in 30 m ZnCl$_2$ can be improved to 98.4% at 1 mA/cm$^2$, comparable to the CE value of the 23.8 m ZnCl$_2$ electrolyte reported by Xu et al.[50] To date, the highest CE from the ZnCl$_2$ based electrolyte, i.e., 30 m ZnCl$_2$ + 5 m LiCl at 1 mA/cm$^2$ approaches 100%; however, the measured CE goes down to 99.3% at a current density of 0.6 mA/cm$^2$ and to below 94% at 0.1 mA/cm$^2$.[49]

As aforementioned, ZnCl$_2$ WiSE exhibits a higher acidity but can better inhibit HER compared to a dilute ZnCl$_2$ electrolyte of a lower acidity, which is an intriguing phenomenon. We can understand this phenomenon from three aspects. First, in WiSE the concentration of Zn(H$_2$O)$_2$ is high, which raises the Zn plating/stripping potential in ZnCl$_2$ WiSE according to the Nernst
equation. Thus, Zn metal anode is anodically more stable in ZnCl\(_2\) WiSE. Second, thermodynamically, Zn metal can be oxidized by both protons and water. Albeit the concentration of protons in ZnCl\(_2\) WiSE rises, the concentration of water molecules in WiSE is much lower than dilute electrolytes, where the reaction rate between Zn metal and water molecules is mitigated. Third, the O-H bond of water is strengthened in WiSE, water is thermodynamically more stable, which mitigates the HER as well.

It is reported that in the ZnSO\(_4\)-based electrolyte, precipitation such as Zn\(_4\)SO\(_4\)(OH)\(_6\)\(_3\)H\(_2\)O can be formed due to the HER on Zn metal surface. [84, 85] However, in ZnCl\(_2\), this compound is not formed, which can be attributed to the lack of constituting ions and the higher acidity of the electrolyte.

In ZnCl\(_2\) based WiSE, Zn\(^{2+}\) (and/or [ZnCl]\(^+\)) and [ZnCl\(_4\)]\(^{2-}\) can serve as the cation and anion charge carriers, respectively. The Zn-cation hosting cathode materials share the same challenge of capacity fading as the storage of multi-valent cation charge carriers, which is often attributed to the large charge density of such highly polarizing cations and the oft-maligned dissolution of the electrodes. [86, 87] Note that the high acidity of ZnCl\(_2\) WiSE may have a destructive impact on the structures of cathode. Nevertheless, the dissolution of electrodes in aqueous electrolytes requires the availability of water molecules as a solvent. In ZnCl\(_2\) based WiSE, the vast majority of water molecules are occupied as aqua ligands for Zn\(^{2+}\). Indeed, our results show that the cycling stability of V\(_2\)O\(_5\)[88] and Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)O\(_1.6\)F\(_1.4\)[89] as the cathode materials of Zn-ion storage is enhanced by using ZnCl\(_2\) based WiSE. Another Zn-ion cathode material that usually fades fast in aqueous electrolytes is VOPO\(_4\). Sun et al. employed a mixture electrolyte of 13 m ZnCl\(_2\) + 0.8 m H\(_3\)PO\(_4\), where the common ion effect by having H\(_3\)PO\(_4\) in the electrolyte and the high concentration of ZnCl\(_2\) collectively inhibit the dissolution of VOPO\(_4\)·xH\(_2\)O as the cathode, thus mitigating its capacity fading. [90]

By increasing the concentration of the solute, the activities of cations and anions are greatly improved. The average activity coefficient of both cations and anions is a function of the molarity with the following relationship: \(\log \gamma_\pm = AZ \pm Z_\pm \sqrt{C}\), where \(\gamma_\pm\) is the average coefficient, \(A\) is a constant as a function of temperatures, \(Z_+\) and \(Z_-\) are the charge numbers of the ions, and \(C\) is the molarity of the solution. Based on the above equation, it is evident that the activity of ions that is the product of activity efficient and the concentration should increase dramatically by orders of magnitude, and the order is the square root of how many times the concentration increases by, i.e., \(C_2/C_1\). The increase of activity will, thus, cause the conspicuous shift of redox potentials proportional to 59\(\sqrt{C_2/C_1}\) mV. For the insertion of cations, the potential goes up; for the insertion of anions, the potential goes down, according to the Nernst equation. As Figure 6a shows, the two peaks for Zn\(^{2+}\) storage in a bilayered V\(_2\)O\(_5\) shift to higher potentials along with increasing the concentration of ZnCl\(_2\). A similar shift occurs for Zn plating/stripping, where the operation potential of Zn metal anode is higher by 0.35 V in 30 m ZnCl\(_2\) compared to in 1 M ZnCl\(_2\) (Figure 6b). The consequence is that Zn is more corrosion resistant in concentrated ZnCl\(_2\) than in dilute electrolytes.[89] For the anion storage, the potential shifts lower. For example, the storage of [ZnCl\(_4\)]\(^{2-}\) in the electrode of a ferrocene/carbon composite decreases by 0.2 V when increasing the concentration from 5 to 30 m ZnCl\(_2\) (Figure 6c).[48]
Figure 6. a. Shift of potentials according to the Nernstian relationship. CV curves of Ca$_{0.20}$V$_2$O$_5$·0.80H$_2$O from the 5th cycle with a scan rate of 0.5 mV s$^{-1}$, where in three-electrode cells zinc foil and Ag/AgCl serve as the counter electrode and reference electrode, respectively. Reproduced with permission from ref. 86. Copyright 2019, Wiley-VCH. b. The plating/stripping potential profiles in electrolytes of different concentrations of ZnCl$_2$. [89] c. CV curves of a composite electrode with ferrocene infiltrated in activated carbon in 5, 10, and 30 m ZnCl$_2$. 

[Image of graphs and diagrams]
electrolytes at a scan rate of 1 mV s⁻¹.[11] Reproduced with permission from ref. 11. Copyright 2019, American Chemical Society.

Chloride is a stronger Lewis base than water, and Zn²⁺ is a strong Lewis acid; therefore, in the presence of abundant chloride, hydrated Zn²⁺ would be transformed to [ZnCl₄]²⁻.[91] As an important fact, the primary anion of the concentrated ZnCl₂ is [ZnCl₄]²⁻ instead of chloride, and the concentration of chloride is low and can be estimated by the formation constant of the [ZnCl₄]²⁻ complex. A high concentration of [ZnCl₄]²⁻ in the ZnCl₂ WiSE may be an advantage for anion storage in DIBs.[92, 93] In DIBs, the electrolyte is a part of active mass as the sole source of ion charge carriers for both electrodes; therefore, a high electrolyte concentration lowers the needed volume of the electrolyte, thus improving the energy density. However, it is worth noting that a high concentration of anions can significantly lower the operation potential of the anion-hosting electrode because the activity of anions can be orders of magnitude larger.

[ZnCl₄]²⁻ has a radius around 0.335 nm,[94] which is a typical size of complex anions but is much larger than metal cations. To host [ZnCl₄]²⁻ as a charge carrier, the electrode materials ought to possess relatively large interstitials or voids. In this vein, porous carbon, MOF, and molecular solids are suitable hosting electrode materials. We reported reversible anion-storage properties of a composite with ferrocene infiltrated in activated carbon in the 30 m ZnCl₂ WiSE.[11] Later, we studied a few-layered nanoporous carbon to host anions from ZnCl₂ WiSE. This electrode operates in an integrated mechanism of EDLC and anion-insertion between graphenic layers.[95] Leung et al. reported a mixed electrolyte of NaCl, ZnSO₄·7H₂O, sodium alginate, and water with the mass ratio of 1:1:0.3:0.8, which was referred to as water-in-gel electrolyte. The authors assigned [ZnCl₄]²⁻ as the charge carrier for the operation of the Prussian blue analog cathode.[96]

Compared to chloride, iodide is a weaker Lewis base. Therefore, it is interesting to see if Zn-I complex ions with just iodo ligands or complex ions with mixed chloro and iodo ligands will be formed after KI is added to the ZnCl₂ WiSE. We added 5 m KI to 15 m ZnCl₂, and our results suggest that there exists a low concentration of free iodide ions in this electrolyte because most iodide ions are captured by Zn²⁺ to form complex ions.[97] The Raman results reveal that the complex ions with mixed chloro and iodo ligands are not formed; it is the iodo-zinc complex ions, [ZnIₓ(OH₂)₄-x]²⁻, which serve as the reservoirs of iodide ions, where x ranges from 1 to 4.

4. Perspectives of Zn Batteries with ZnCl₂ WiSE as the Electrolyte

One challenge for the ZnCl₂ based electrolytes comes the conundrum of current collectors. Aqueous solutions are well known for their corrosiveness toward metals, including aluminum, copper[98] and steel/iron.[99, 100] Chlorides are particularly corrosive for metals. Copper cannot be employed as the cathode current collector in chloride-based electrolytes because copper can be oxidized to cuprous chloride complex ions, starting from [CuCl₂]⁻ ; where the formation constant of [CuCl₂]⁻ is at the order of 10⁵ mol⁻²L².[98, 101] In a neutral or alkaline environment, [CuCl₂]⁻ can readily precipitate as Cu₂O. Furthermore, the diffusivity coefficient of [CuCl₂]⁻ is impressive at the level of 10⁻⁵ cm²s⁻¹, on par with proton’s conduction in acids.[102, 103] The fast diffusion of [CuCl₂]⁻ and its solubility in aqueous electrolytes warrant the corrosion
of copper in chloride electrolytes under anodic conditions or in the presence of oxygen. Iron corrodes in chloride solutions via a similar mechanism by forming chloro-complexes on the surface.[104] To my knowledge, concentrated ZnCl₂ electrolytes are also corrosive to nickel. The choice of current collectors can also have a large impact on the measured CE values of Zn metal anode. In light of the knowledge of corrosion, titanium is probably the only affordable choice of metallic current collector for the positive (and negative) electrode of aqueous Zn metal batteries. Titanium is innately stable in chloride solution due to the robust, native TiO₂ passivation layer on the surface of titanium foil.[105]

To date, many groups used titanium foil as the current collectors for both the cathode and anode of aqueous Zn batteries; however, the cost of titanium may be a showstopper for large-scale commercialization of Zn metal batteries. Therefore, it is necessary to investigate alternative current collectors, where the carbon-based materials, e.g., films, cloths, and paper, will go a long way for the commercialization of aqueous Zn metal batteries. When these current collectors are employed, one must consider the tabs of the batteries, where welding of carbon current collectors will be another challenge, and the conductivity of carbon-based materials will certainly be lower than the metallic ones.

The choice of current collectors also pertains to the configurations of batteries. To date, there are three primary configurations of battery cells: the cylindrical cells, like 18650 batteries Tesla has used, pouch cells that CATL has perfected, and box cells that Lead-Acid batteries use. For cylindrical cells, the performance of the battery is closely related to mechanical compression, which demands the high mechanical strength of the current collector. Some commercial NiMH batteries employ cylindrical cells. For pouch cells, electrodes are coated onto current collectors, where the pressure applied on the electrodes comes from one direction, which involves less rigorous requirements than the cylindrical cells. Pouch cells are widely used to demonstrate the viability of new battery technologies, which is originally designed for LIBs and later used for Na-ion batteries. However, the question is not settled about what cell configurations are most suitable to demonstrate and eventually scale up new aqueous batteries. The fact that ZnCl₂ WiSE is corrosive further complicates the design of such prototype cells. Can new aqueous battery technologies adopt the design of Lead-Acid batteries? The electrodes in Lead Acid batteries are extremely thick compared to the conventional electrodes in LIBs, which may not be suitable for new aqueous batteries, including Zn metal batteries. New design of battery configurations that are of low cost and are conducive to excellent electrochemical properties become indispensable for new aqueous batteries to be deployed successfully for the market.

Another challenge of ZnCl₂ is its incompatibility with many separators available in the market. One primary challenge is the wettability of the separators by the electrolytes. A battery will not deliver any performance if the electrolyte fails to wet the separator. It may be a challenge for ZnCl₂ to wet the polymer-based separators such as the polypropylene (PP)-based ones. Cellulose-based and glass-fiber-based separators will be wettable by this electrolyte. However, this electrolyte is not friendly with cellulose-based separators as ZnCl₂ dissolves cellulose. It means that thin cellulose membranes would be dissolved or disintegrated in the electrolyte over a period of cycling. Thus, the choice of separator narrows down to glass-fiber separators. Nevertheless, glass-fiber separators have been manufactured for Lead-Acid batteries. Different from the PP separators for LIBs that can be thin, e.g., with a thickness of 20 µm, glass-fiber separators available in the market are usually thicker than 100 µm. When the separator is thick, it
will soak up a large volume of electrolyte to be completely wetted, which increases the mass percentage of the electrolyte and dwarfs the electrode’s mass that is usually 10 to 20 mg/cm² formed by coating a slurry onto a metal foil current collector. The lack of a thin glass-fiber separator in the market will limit the development of new aqueous batteries, where it would be difficult to demonstrate a prototype with a practically meaningful energy density.

A fundamental challenge of ZnCl₂ electrolytes is their acidity. Albeit HER of Zn metal anode in ZnCl₂ WiSE is suppressed, it is clear that the full potential of ZnCl₂-based WiSE has yet not been fully reached. There exist many opportunities to lower the acidity of the ZnCl₂, where the author envisions that remarkable progress will be made. Along with the line of reducing the acidity of ZnCl₂ WiSE, adding another solvent to the WiSE will be a profitable route. Yet, if a nonaqueous solvent is added, the maximum addition of such solvent should be regulated by the flammability of the electrolyte. The core advantage of aqueous electrolytes is their non-flammability, where this key characteristic should not be compromised at all.

The last issue is the purity of the electrolytes, which pertains to the purity of the electrolytes and water. Based on our experience, we did observe that ZnCl₂ purchased from different vendors and of different purities could exhibit varying electrochemical performance. Indeed, studies in the industry style on the impacts of the impurity from various vendors will be highly informative for the community.

This article aims to share the understanding that is still being formed in this exciting area with the community. ZnCl₂ is a low-cost and abundant salt, being a competitive electrolyte of storage batteries. Its high solubility and unique properties of forming [ZnCl₄]²⁻, a superchalcogenide belonging to a parallel genre of complex ions compared to superhalides, will avail ZnCl₂-based concentrated electrolytes a remarkable potential for the design of new electrolytes and new battery chemistries.

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