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# Electrochemical behavior of protons and cupric ions in water in salt electrolytes with alkaline metal chloride



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# ABSTRACT

The proton reduction and copper deposition in water-in-salt electrolytes with LiCl were studied. Cyclic voltammetry on stationary electrode with various scan rates and linear sweep voltammetry on disk electrodes with different rotation rates were used to determine not only the diffusion coefficients but also the effective concentrations of protons and cupric cations. The suppression of hydrogen evolution limiting current observed in water-in-salt electrolyte was determined to result from the inhibition of proton diffusion. This diffusion inhibition was mainly related to the structural diffusion across hydrogen bond network and is not observed for cupric cations. The effects of alkaline metal cations on the acidity of electrolytes, the diffusivity of protons as well as the copper deposition rate were also studied using various super high concentrations of LiCl, NaCl and KCl.

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# 1. Introduction

Water-in-salt refers to an aqueous electrolyte with a super high concentration of salt, where the hydration of salt depletes free water molecules in electrolyte. It has been particularly of interest to electrochemical systems such as batteries, as it can potentially replace organic solvents used, which have been of safety concerns. As a matter of fact, since its first introduction into lithium ion battery[1], numerous battery systems have been reported using various type of water-in-salt [2–9]. A significantly widened electrochemical window has been observed due to not only the formation of a passivation layer on electrolytes[1,10].

This suppression in proton reduction has also shown benefits for electrochemical deposition applications. For example, hydrogen evolution is decreased in water-in-salt with high concentrations of LiCl, lowering hydrogen brittleness and film stresses, improving film morphology and eliminating cracks observed in the electrodeposited films[11,12]. While organic solvents [13–17] including ionic liquids [18–20] and deep eutectic systems [21–23] have been

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explored for the same purpose, such a new aqueous system can potentially provide the same benefits while maintaining the advantages of aqueous system such as high salt solubility, high conductivity, low viscosity, and better compatibility with current industrial plating processes.

It is well known that water molecules are more confined around the charged anions and cations upon the hydration of salts. A large body of studies and reports are available on the strength and hydration coordination of various type of salts. Readers are referred to the comprehensive reviewers by Ohtaki and Radnai[24], and by Marcus [25]. In our previous study with 5 M LiCl electrolyte[12], a simple estimation based on the water coordination number suggests a significantly different behavior from dilute solutions would be expected due to the consumption of 10 water molecules for each pair of Li<sup>+</sup> and Cl<sup>-</sup>. The decrease of proton reduction limiting current was therefore conveniently attributed to the depletion of free water molecules. However, it is unclear how such depletion of water molecule impacts the proton reduction. Theoretic simulation study has shown that ion paring is expected to occur and slow down the diffusion of the solute ions[26]. In a very recent study using organic solvent with a trace amount of water [27], an increase of acidity was indeed reported upon the addition of inorganic salt. An inner Helmholtz layer comprising solute cations adsorbed on the electrode surface was proposed to behave as a local Lewis acid,



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accepting electron pairs from the oxygen atoms in water molecules and increasing the acidity of water. Furthermore, such a Lewis acidity effect was found to be much less pronounced when Li<sup>+</sup> was replaced by a similar alkaline metal cation with large size, Na<sup>+</sup>.

This manuscript reports a systematic study on the electrochemical behaviors of protons and a metal cation, cupric ion, in water-in-salt electrolytes. Various alkaline metal chlorides at various concentrations are used to dissect the contributions from the cation and anion. The study aims to determine the mechanism why proton reduction is suppressed in such electrolytes and how the speciation and concentration of cations and anions impact such suppression as well as the metal reduction.

# 2. Experimental

# 2.1. Chemicals

Water-in-salt electrolytes with various low concentrations of  $H_2SO_4$  (from BDH chemicals),  $CuSO_4 \cdot 5H_2O$  (from BDH chemicals), and various super high concentrations of LiCl (from Alpha Aesar), NaCl (from RICCA chemical), and KCl (from BDH chemicals) were used for the studies. All chemicals were at least of ACS grade and were used as received. Deionized water with a resistivity of 18 Mohm were used for all studies. Water-in-salt electrolytes were prepared by dissolving desired amounts of LiCl, NaCl, or KCl, in minimal amount of water until fully dissolved, followed by adding water to the desired volume in volumetric flask.

# 2.2. Electrochemical cell

All electrochemical studies were carried out in a homemade three-compartment cell. A platinum rotating disk electrode (from PINE research) with a diameter of 6 mm operated at various rotating rates was used as the working electrode. A platinum foil (99.9%, from Alpha Aesar) was used as the counter electrode in the anolyte compartment separated from the catholyte compartment with a glass frit. A saturated calomel electrode (SCE, from Radiometer Analytical) was used as the reference connected to the catholyte through a capillary placed close to the cathode. All voltages are referred to with respect to the SCE in this report.

An Autolab 302N electrochemical station with a frequency analyzer (from Metrohm) was used for all the electrochemical studies. Cyclic voltammetry and linear sweep voltammetry were carried out using various scan rates and RDE rotation rates. The electrolyte resistance was determined with electrochemical impedance spectrum (EIS) using a small cathodic DC bias and a 10 mV sinusoidal oscillation with frequencies up to 1 MHz. The resistance was used to correct the ohmic drop in voltages.

# 3. Results and discussion

# 3.1. Proton reduction in water-in-salt

The proton reduction reaction was first studied on Pt electrodes using water-in-salt electrolytes with various concentrations of LiCl. Cyclic voltammetry (CV) studies on stationary electrodes with different scan rates and linear sweep voltammetry (LSV) studies on rotating electrodes were carried out to determine the active concentrations and diffusion coefficients of protons in different electrolytes. Fig. 1 shows an example set of CVs on stationary Pt electrode in an electrolyte containing 5 M LiCl and 10 mM H<sub>2</sub>SO<sub>4</sub>. Due to the evolution and detachment of hydrogen bubbles, the reduction reaction of proton is not completely reversible, resulting in a much lower anodic current peak than the cathodic peak. The cathodic peak height is plotted in Fig. 1(b) against the square root of



**Fig. 1.** (a) Cyclic voltammograms with different sweep rates in an electrolyte with 10 mM  $H_2SO_4$  and 5 M LiCl on a stationary Pt electrode; and (b) the linear relationship between cathodic peak current density and the square root of potential scan rate.

each sweep rate. A perfectly linear relationship between the two was observed, with a slope of  $19.04 \times 10^{-3} \text{ A/cm}^2/(\text{V/sec})^{1/2}$  and a R<sup>2</sup> at 0.9998. Such a linear relationship can be described with the Randles-Sevsik equation shown as Eq. (1) [28].

$$i_p = 0.446 \cdot n \cdot F \cdot C_a \cdot \left(\frac{n \cdot F \cdot v \cdot D_H}{R \cdot T}\right)^{\frac{1}{2}}$$
 Eq. 1

where  $i_p$  is the cathodic current peak height, n is the number of charges transferred per each redox species, 1 in this case; F Faraday's constant, 96,485 C/mol;  $C_a$  the active concentration of the redox species in mol/mL, i.e., the active proton concentration in this case;  $D_H$  the diffusion coefficient of proton in cm<sup>2</sup>/sec; v the voltage sweep rate in V/sec; R the gas constant, 8.314 J/mol/K; and T the temperature, 298 K in this case. Therefore, the slope of the linear relationship between  $i_p$  and  $v^{\frac{1}{2}}$  can be described as a function of the active concentration and diffusion coefficient of proton, shown in Eq. (2).

$$\frac{i_p}{\nu^2} = 0.446 \cdot n^{\frac{3}{2}} \cdot F^{\frac{3}{2}} \cdot C_a \cdot \left(\frac{D_H}{R \cdot T}\right)^{\frac{1}{2}} = 2.686 \times 10^5 \cdot D_H^{\frac{1}{2}} \cdot \gamma_H \cdot C_{SA} \qquad \text{Eq. 2}$$

where  $C_{SA}$  is the sulfuric acid concentration in mol/mL and  $\gamma_H$  is a

coefficient defined as the ratio between active proton concentration and the sulfuric acid concentration. The latter is unknown because the scarcity of free water molecules in water-in-salt electrolytes is expected to impact the dissociation of proton from acid molecules. Therefore, such CV studies were repeated with different sulfuric acid concentrations at 5, 10, and 15 mM. While a high concentration of acid itself might further depletes water and competes with LiCl for water molecules, resulting in non-linear behavior of  $C_a$ , such complication is believed to be minimum at the extremely low acid concentrations used here. As the LiCl concentrations are at least several hundreds of times higher than the acid,  $\gamma_H$  is believed to be a constant dependent only on the fixed concentration of LiCl. In other words, the slope in equation Eq. (2) can be rewritten as a linear function of  $C_{SA}$ . As shown in Eq. (3), the slope of this linear function only depends on two unknowns, the diffusion coefficient  $D_H$  and the proton-acid concentration ratio  $\gamma_H$ .

$$\frac{i_p}{\left(\nu^{\frac{1}{2}} \cdot C_{SA}\right)} = 2.686 \times 10^5 \cdot D_H^{\frac{1}{2}} \cdot \gamma_H$$
 Eq. 3

Fig. 2(a) shows the LSV studies carried out on RDE in the same water-in-salt electrolytes shown in Fig. 1. Various rotation rates from 200 rpm to 1600 rpm were used for the study. A linear extrapolation between the limiting current densities and the square roots of rotational angular velocities is shown in Fig. 2(b), consistent with the Levich equation shown as Eq. (4) [28,29].

$$i_{I} = 0.62 \cdot n \cdot F \cdot D_{H^{\frac{2}{3}}} \cdot \omega^{\frac{1}{2}} \cdot \nu^{-\frac{1}{6}} \cdot C_{a}$$
 Eq. 4

where *n*, *F*,  $D_H$ , and  $C_a$  are the same as defined in Eq. (1);  $\omega$  the angular velocity of rotation in rad/sec, and  $\nu$  the kinematic viscosity of electrolyte in cm<sup>2</sup>/sec. Due to the hydrogen bubbles blocking the electrode surface at low rotation speeds, only the limiting current densities at rotations above 400 rpm were used. A R<sup>2</sup> coefficient of 0.977 was obtained. The slope of the extrapolated line can be described as

$$\frac{i_L}{\frac{1}{2}} = 5.982 \times 10^4 \cdot D_H^{\frac{2}{3}} \cdot \nu^{-\frac{1}{6}} \cdot \gamma_H \cdot C_{SA}$$
 Eq. 5

The viscosity of electrolyte is dependent on the temperature and the concentration of electrolyte. Because the acid concentrations are much lower than LiCl solute in water-in-salt solutions for all cases, the contribution of acid on the viscosity is believed to be negligible. A constant viscosity can be obtained from literature and used for studies at each LiCl concentration[30–32]. The same approximation is taken for  $\gamma_H$  and  $D_H$  as well. Studies were carried out with various acid concentrations with each water-in-salt electrolyte, and the Levich slopes linearly depend on the acid concentration as described in Eq. (6).

$$\frac{i_L}{\left(\omega^{\frac{1}{2}}\cdot C_{SA}\right)} = \left(5.982 \times 10^4 \cdot \nu^{-\frac{1}{6}}\right) \cdot D_H^{\frac{2}{3}} \cdot \gamma_H \qquad \text{Eq. 6}$$

Fig. 3 shows the summary of the CV and LSV studies with 5, 10 and 15 mM H<sub>2</sub>SO<sub>4</sub> in 5 M LiCl water-in-salt electrolytes. Nearly perfect linear relations were observed ( $R^2 > 0.99$ ) for both the slope between peak currents and square roots of scan rate in CVs and the slope between limiting currents and square roots of angular velocity in LSVs. It is worth noting here that each data point represents a series of experiments with different scan rates or rotation rates. For example, the results obtained in Figs. 1(b) and Figure 2(b) are represented by the CV  $i_p$  slope and the LSV  $i_L$  slope, respectively, at an acid concentration of  $5.0 \times 10^{-6}$  mol/ml, or 5 mM. The nearly



**Fig. 2.** (a) Linear sweep voltammograms in an electrolyte with 10 mM  $H_2SO_4$  and 5 M LiCl on a Pt RDE at different rotation rates; and (b) the linear relationship between the proton reduction limiting current density and the square root of angular velocity of RDE.



**Fig. 3.** The two different linear dependence of the slopes (blue) between CV peak current densities and square roots of voltage scan rate and (orange) between LSV limiting current densities and square roots of rotation angular velocity on the acid concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

perfect linear correlation in Fig. 3 demonstrates a proportional change of the peak current densities or limiting current densities with the acid concentration. This also validates the assumption that the diffusion coefficient,  $D_H$ , and the concentration coefficient,  $\gamma_H$ , are nearly constants at a fixed concentration of LiCl, albeit a small increase of acid concentration. With a mass density of 1.103 g/ml from experiment and dynamic viscosity of 2.044 cP[32], the kinematic viscosity is calculated as 0.01853 cm<sup>2</sup>/s for 5 M LiCl electrolytes. Therefore, the two slopes in Eq. (3) and Eq. (6) evolve into two coupled non-linear algebraic equations as below.

$$2.686 \times 10^5 \cdot D_H^{\frac{1}{2}} \cdot \gamma_H = 1925.6$$
 Eq. 7

$$\left(5.982 \times 10^4 \times 0.1854^{-\frac{1}{6}}\right) \cdot D_H^{\frac{2}{3}} \cdot \gamma_H = 127.99$$
 Eq. 8

The proton diffusion coefficient  $D_H$  and effective proton concentration coefficient  $\gamma_H$  can be solved simultaneously as  $1.31 \times 10^{-5}$  cm<sup>2</sup>/sec and 1.981, respectively, in 5 M LiCl water-in-salt electrolytes. Such studies were repeated for different concentrations of LiCl from 1 to 8 M, and the results are summarized in Table 1. First, at a low concentration of 1 M LiCl, the proton diffusion coefficient was determined as  $6.30 \times 10^{-5}$  cm<sup>2</sup>/sec, close to the ideal case of dilute solution[32]. This diffusion coefficient continuously decreases as the LiCl concentration increases, reaching a value of  $5.08 \times 10^{-6}$  cm<sup>2</sup>/sec at 8 M LiCl, which is more than 10 times lower than in conventional dilute electrolytes.

While the protons in water can form various complexed structures upon hydration, such as  $H_9O_4^+$  and  $H_5O_2^+$ [33,34], a simplified view typically includes the simplest hydronium ions, H<sub>3</sub>O<sup>+</sup>. The diffusion mechanism of proton not only includes the physical movement or vehicle diffusion of protons under a concentration gradient, but also a proton "hopping" mechanism, or so-called structural diffusion or the Grotthuss mechanism [35], where hydrogen bonds are constantly broken and formed between proton and water molecules. Fig. 4(a) shows a simplified 2-dimensional representation of the tetrahedral network of hydrogen bond in bulk water. As shown in Fig. 4(b), this continuous network allows a proton to form hydrogen bond with a water molecule in one place and another proton to break off from a hydronium ion at another place, resulting in an extremely fast diffusion coefficient. However, as illustrated by the diagram in Fig. 4(c) using Li<sup>+</sup> as the example, the hydration of ions requires the reorganization of water molecules, thus perturbating the perfect tetrahedral coordination in bulk water. As more and more LiCl is added into the electrolyte, the hydration of Li<sup>+</sup> and Cl<sup>-</sup> confines the water molecules and disrupts the intrinsic hydrogen bond network present among free water. This disruption impedes or even disables the proton hopping between adjacent water molecules, resulting in a significant decrease of proton diffusion coefficient.

On the other hand, the proton-acid concentration coefficient,  $\gamma_{H}$ , gradually increases as the LiCl concentration increases. While the activity coefficients of ionic species in non-ideal highly

#### Table 1

Dynamic viscosities, proton diffusion coefficients, and effective concentration coefficients of proton from  $H_2SO_4$  in water-in-salt electrolytes with different concentrations of LiCl.

LiCl/M	$\nu/(cm^2/sec)$	D <sub>H</sub> /(cm <sup>2</sup> /sec)	γн
1	0.01128	$6.30\ \times\ 10^{-5}$	1.412
3	0.01422	$3.70~\times~10^{-5}$	1.457
5	0.01853	$1.31~\times~10^{-5}$	1.981
8	0.03030	$5.08~\times~10^{-6}$	2.254



**Fig. 4.** Simplified 2D diagram of (a) tetrahedral hydrogen bond network in bulk water; (b) the fast hydrogen diffusion by Grotthuss or proton hopping mechanism; and (c) disruption of the perfect tetrahedral hydrogen bond network upon the hydration Li<sup>+</sup>.

concentrated electrolytes are typically higher than the infinitely diluted ideal solutions due to the crowdedness of ions, the concentration coefficient here is mainly related to the acid dissociation or the total amount of proton in electrolyte. In an extremely dilute ideal H<sub>2</sub>SO<sub>4</sub> solution, a  $\gamma_H$  of 1.57 can be calculated with the first and second  $pK_a$ 's at -6.4 and 2.0, respectively. This is similar to the values obtained for 1 M and 3 M LiCl electrolytes. In other words, these mediocre concentrations of LiCl does not significantly deplete the water and does not change the dissociation of H<sub>2</sub>SO<sub>4</sub>. Every H<sub>2</sub>SO<sub>4</sub> molecule will approximately result in 1.5 protons in these solutions. However, 2 protons will be resulted from each acid molecule as the LiCl concentration reached 5 M. This trend continues and even more than 2 protons can be observed at 8 M LiCl. Li<sup>+</sup> is a small cation with a high charge density, which can be viewed as a strong Lewis acid. The interaction between Li<sup>+</sup> and oxygen atoms in the water molecules increases the acidity of water and, therefore, increases the total amount of protons apparently available in electrolyte. While this effect is negligible at low LiCl concentrations, a significant increase of  $\gamma_H$  is resulted when the water molecules are forced in the close vicinity of Li<sup>+</sup> at high LiCl concentrations

Previous studies have shown that the limiting current of proton reduction decreases in various water-in-salt electrolytes and it was attributed to the depletion of free water molecules[1,11]. The studies here clearly demonstrate that the dominant effect is indeed due to the decrease of proton diffusion coefficient upon the disruption of hydrogen bond network. For example, this limiting current in a same 0.1 M sulfuric acid solution with 5 M and 8 M LiCl decreased 30% and 54% from the value with 3 M LiCl[12]. It is understood from Eq. (5) that the limiting current is proportional to  $D_{H^{\frac{2}{3}}} \gamma_{H}$ . Therefore, the expected decrease in limiting current calculated from Table 1 would be 32% and 59% for 5 and 8 M LiCl, respectively, very consistent from the experimental observations. This not only confirms the calculated diffusion coefficients and proton-concentration coefficients at different LiCl concentrations, but also agrees with the assumption that the electrolyte chemistry behavior is dominated by the high concentration of LiCl and the effect of the low concentration of acid is negligible.

#### 3.2. Copper deposition in water-in-salt

Cyclic voltammetry studies were first carried out with CuSO<sub>4</sub> solutions with different concentrations of LiCl. Fig. 5(a) shows a comparison between two cases, 1 M and 8 M LiCl. Two cathodicanodic peak pairs are observed in the potential range of study. The first pair is located at between 0.2 and 0.3 V with 1 M LiCl, and the second pair at between -0.1 and -0.3 V. Cu deposition in acidic electrolyte undergoes two single-electron transfer steps, the reduction of cupric and cuprous cations, respectively. While the intermediate cuprous ions are typically short lived, it can be stabilized in the form of [CuCl<sub>2</sub>]<sup>-</sup> anions in the presence of abundant chloride in the solution [36], resulting in the two well-resolved pairs of redox peaks. Since the concentration of chloride in this study is at least 100 times higher than total concentration of Cu, all cuprous ions are assumed to be complexed into [CuCl<sub>2</sub>]<sup>-</sup> and the two reactions are listed as Eq. (9) and Eq. (10) below. The increase of LiCl concentration to 8 M further stabilizes the [CuCl<sub>2</sub>]<sup>-</sup> complex, facilitating the reduction of cupric cations and hindering the reduction of (complexed) cuprous cations. Therefore, the two pairs are further separated.

$$Cu^{2+} + 2 Cl^{-} + e \rightarrow [CuCl_2]^{-}$$
 Eq. 9

$$[CuCl_2]^- + e \rightarrow Cu + 2 Cl^-$$
Eq. 10





**Fig. 5.** (a) Cyclic voltammograms on stationary Pt electrode in electrolytes with (a blue) 1 M LiCl and 5 mM CuSO<sub>4</sub>; (a pink) 8 M LiCL and 10 mM CuSO<sub>4</sub>; (b) zoomed in cyclic voltammograms for cupric/cuprous pair in electrolytes with 10 mM CuSO<sub>4</sub> and various concentrations of LiCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Among the two redox pairs, the second pair involves the solid phase and the anodic stripping peak position highly depends on the amount of deposited metal. On the other hand, the first pair only involves redox species in solution. It is worth noting that the CuSO<sub>4</sub> concentration was 5 and 10 mM in the two cases with 1 M and 8 M LiCl, respectively. However, the peak heights of this  $Cu^{2+}/Cu^+$  pair appear approximately similar between the two cases, suggesting the overall availability or supply rate of cupric cation toward the electrode are similar despite of the different overall concentration.

Fig. 5(b) shows a detailed comparison of CVs around this Cu<sup>2+</sup>/ Cu<sup>+</sup> redox pair for different water-in-salt electrolytes with a constant sweep rate of 80 mV/s. A constant CuSO<sub>4</sub> concentration of 10 mM was used with various LiCl concentrations from 1 to 8 M. The difference between the anodic and cathodic peak potentials ( $\Delta E_p = E_{pa} - E_{pc}$ ) are experimentally determined as 75, 75, 71, and 75 mV for 1, 3, 5, and 8 M LiCl respectively. An ideally reversible redox reaction would have resulted in a  $\Delta E_p$  of 57 mV. The small difference between this ideal value and experimental observation is probably due to a non-ideal slower charge transfer kinetics and is believed insignificant. In addition, the height ratio between cathodic and anodic peaks are 1.09, 0.98, 1.06, and 1.01 for the four LiCl concentrations. These ratios are very close to 1, further confirming that the Cu<sup>2+</sup>/Cu<sup>+</sup> redox reaction in the excess of LiCl is approximately ideally reversible.

The same CV and LSV investigations carried in Figs. 1 and 2 were also carried out with 5, 10, 15 mM CuSO<sub>4</sub> in presence of 1, 3, 5, and 8 M LiCl. An example CV with the summary of cathodic peak current densities and an example LSV with the summary of limiting current densities, in the same way as Figs. 1 and 2, are presented as Figs. S1 and S2, respectively, in Supplemental Materials. The diffusion coefficients,  $D_{Cu}$ , and concentration coefficients,  $\gamma_{Cu}$ , of copper at these different LiCl concentrations are summarized in Table 2. Contrary to proton, the diffusion coefficient remained approximately unchanged across the LiCl concentrations. This further confirms that the significant decrease in proton diffusion coefficient is mainly due to the suppression of the structural diffusion while the physical diffusion remained the same. On the other hand, the concentration coefficient of cupric cation decreases from 0.653 to 0.477, a 28% decrease in the active concentration. While the complexation between chloride anion and cupric cation is extremely weak[36], CuSO<sub>4</sub> has a finite stability constant of 2.24 [37]. This ionic stability typically results in a concentration coefficient significantly lower than 1 as the salt concentration increase. For example, a  $\gamma_{Cu}$  value of 0.66 can be estimated for a simple electrolyte with 5 mM CuSO<sub>4</sub> in water. The addition of LiCl gradually depletes free water molecules and hinders the hydration of cupric cation. This may be responsible for the small decrease of the  $\gamma_{C\mu}$  observed at high concentrations of LiCl.

The ratio between the diffusion coefficients of proton and cupric ion is also listed in Table 2. At a dilute 1 M of LiCl, the diffusion of proton is 9 times faster than copper, consistent with the literature values of diffusion coefficients in dilute electrolytes[32]. However, as the LiCl concentration increases, this ratio significantly decreases as a result of slowdown of proton diffusion and a relatively unchanged diffusion rate of cupric ions. At a concentration of 8 M LiCl, this ratio decreases to below 1, in which the diffusion of proton is even slower than cupric ion. Given the fact that protons are much smaller and of a higher charge density than cupric cations, this slower diffusion of proton is believed to relate to a stronger ionic interaction between proton and water molecules, which hinders the physical movement of proton.

# 3.3. Effects of alkaline metal cation

Water-in-salt electrolytes with NaCl and KCl were also studied for the proton reduction and copper deposition. The room temperature solubilities of these two in water are both significantly lower than LiCl, 5.3 M for NaCl and 3.4 M for KCl. Therefore, three solutions – 3 M NaCl, 5 M NaCl and 3 M KCl – were used for comparisons with the LiCl cases. Fig. 6(a) shows three LSV curves at 1600 rpm for electrolytes with 10 mM H<sub>2</sub>SO<sub>4</sub> and 3 M LiCl, NaCl, or KCl, respectively. The limiting current of proton reduction increases from 26 mA/cm<sup>2</sup> for LiCl to 31 mA/cm<sup>2</sup> for NaCl, and to 37 mA/cm<sup>2</sup> for KCl. The proton diffusion coefficients and concentration

#### Table 2

Diffusion coefficients of  $Cu^{2+}$ , effective concentration coefficients of  $Cu^{2+}$  from  $CuSO_4$ , and the ratio between diffusion coefficients of proton and  $Cu^{2+}$  in water-insalt electrolytes with different concentrations of LiCl.

LiCl/M	D <sub>Cu</sub> /(cm <sup>2</sup> /sec)	γCu	$D_H/D_{Cu}$
1	$6.93 \times 10^{-6}$	0.635	9.09
3	$8.21\ \times\ 10^{-6}$	0.537	4.51
5	$6.38\ \times\ 10^{-6}$	0.542	2.05
8	$5.47 \times 10^{-6}$	0.477	0.93

coefficients were again determined with the combinatory studies of LSV with CV and are summarized in Table 3. While the concentration coefficients of proton slightly decrease from Li to K, the diffusion coefficients significantly increase. Again, the main mechanism for the less suppression of proton reduction by larger alkaline metal cation chloride salt is due to the less effective suppression on the proton diffusion. Furthermore, the limiting current density in presence of 3 M KCl is even higher than that of 1 M LiCl electrolyte. In other words, the additional 2 M chloride anions has little impact on the suppression of proton diffusion. This confirms that such suppression in diffusion or the interruption of hydrogen bond network in water is mainly due to the alkaline metal cations. This is consistent with the fact that the alkaline metal cations are of a much smaller size than the chloride anion and therefore a much higher charge density and a stronger ionic interaction with water molecules.

The stronger interaction with smaller cations not only results in stronger suppression of proton diffusion, but also increases the acidity of the electrolyte at same acid concentration. This is particularly pronounced at 5 M concentration. While the effective proton concentration of 10 mM  $H_2SO_4$  solution is about 20 mM in presence of 5 M LiCl, it is only about 13 mM in presence of 5 M NaCl.





**Fig. 6.** (a) Full and (b) zoomed in linear sweep voltammograms on Pt RDE at 1600 rpm in electrolytes containing 10 mM  $H_2SO_4$  and (solid line) 3 M or (dashed line) 5 M of (blue) LiCl, (red) NaCl, and (green) KCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

 Table 3

 Proton diffusion coefficients, and effective concentration coefficients of proton from H2SO4 in water-in-salt electrolytes with different concentrations of LiCl, NaCl, or KCl.

Salt	D <sub>H</sub> /(cm <sup>2</sup> /sec)	γн
3 M LiCl	$3.70 \times 10^{-5}$	1.457
3 M NaCl	$4.43~\times~10^{-5}$	1.485
3 M KCl	$6.42 \times 10^{-5}$	1.303
5 M LiCl	$1.31 \times 10^{-5}$	1.981
5 M NaCl	$3.31~\times~10^{-5}$	1.325

This difference can also be seen in the LSV curves. As shown in Fig. 6(b), the proton reduction starts at a less negative potential when LiCl is present than NaCl, and KCl. Further increasing the concentration of LiCl or NaCl also results in a shift of the curves to less negative potentials. A recent paper reported a study of the effects of salt on water reduction using organic solvent with a trace amount of salt water[27]. A similar shift of the water reduction potential was also reported between different alkaline metal salts. In that study perchlorate salts were used to avoid any electrochemical effect from anions. In our study, such shift was also observed in a water-in-salt electrolyte (instead of organic solvent) despite of the presence of chloride anions.

The electrodeposition of copper in presence of different alkaline metal chlorides was studied with cyclic voltammetry. The partial current density of copper deposition was determine using the anodic stripping charge. Fig. 7 shows two CVs on RDE at 1600 rpm in two electrolytes, both containing 10 mM H<sub>2</sub>SO<sub>4</sub> and 15 mM CuSO<sub>4</sub>. One comprises 5 M NaCl and the other 5 M LiCl. Similar to the CVs in Fig. 5, the reduction reactions of cupric and cuprous ions are well separated. The proton reduction not only starts at a more negative potential but also becomes much more sluggish in this case on the electrodeposited copper surface as compared to the platinum electrode in Fig. 2. Furthermore, the small shift to less negative potential for proton reduction is also observed from NaCl to LiCl. A more pronounced shift in the same direction was also observed for water reduction. The ohmic drop due to electrolyte resistance has been corrected in the potentials for direct comparison between two electrolytes because a non-zero finite current is present before the hydrogen evolution starts. This shift of water reduction potential toward a less negative potential in presence of



**Fig. 7.** (Solid lines) Cylic voltammograms and (symbols) copper deposition partial current densities in electrolytes containing 10 mM H<sub>2</sub>SO<sub>4</sub>, 25 mM CuSO<sub>4</sub>, and 5 M (blue) LiCl or (red) NaCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

5 M LiCl is also consistent with the recent study on trace water in organic solvent[27].

As shown in the partial current density curves, copper deposition starts at about -0.3 V. As expected, it quickly reaches a limiting current density and this current plateau remains the same after the proton reduction starts. However, the deposition rate slightly decreases as the potential decreases after the proton reduction reaches its limiting current. It quickly drops to zero, namely the copper deposition completely stops, once the reduction of water commences. While the surface proton concentration is similar to the bulk electrolyte in the kinetic region of proton reduction, the proton gets depleted and pH increases when the proton reduction reaches the limiting current. The surface pH rapidly increases once the water reduction starts. Therefore, it is believed that the decrease of the copper deposition rate observed here are related to the surface pH increase. It has been reported that Li<sup>+</sup> suppresses cathodic charge transfer at very negative potentials due to the surface blockage by LiOH precipitates<sup>[27]</sup>. The same suppression does not occur with Na<sup>+</sup> and the reason was attributed to a higher solubility of NaOH than LiOH. However, no difference is observed here between NaCl and LiCl in terms of the copper deposition rate suppression at highly negative potentials. The decrease of deposition rate observed here is believed due to the surface blockage by hydroxide species at high surface pH. In addition to copper hydroxide, NaOH and LiOH can both possibly block the surface at the extremely high concentrations of Na<sup>+</sup> and Li<sup>+</sup> in this study.

# 4. Conclusion

The proton reduction reaction in water-in-salt electrolytes with alkaline metal chloride solutes have been systematically studied. The proton diffusion coefficient decreases for more than 10 times upon the increase of LiCl concentration from 1 to 8 M, resulting in a significant suppression in proton reduction limiting current. This decrease in diffusion rate results from the disruption of hydrogen bond network and a suppression of proton hopping in water. At the same time, a mediocre increase of proton concentration is observed, due to the Lewis acid nature of Li<sup>+</sup>. Such impacts are also observed for NaCl and KCl, to a less pronounced degree due to a larger ionic size and lower charge density. The diffusion of cupric cations is almost unchanged by the LiCl concentration. On the other hand, the dissociation of CuSO<sub>4</sub> into cupric cations is suppressed as the free water molecules become depleted upon the increase of LiCl concentration. Copper deposition rate in water-in-salt electrolytes decreases at highly negative potential due to the increase of surface pH.

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# Author contribution

QH conceived the experimental idea; SD, JW, TB, and QH conducted electrochemistry experimental plan; CP and AK conducted viscosity characterization; SD and QH prepared and revised the manuscript.

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# Appendix A. Supplementary data

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