TITLE:
Origin of the Electrochemical Stability of Aqueous Concentrated Electrolyte Solutions

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Aqueous solutions have attracted considerable attention for use in aqueous-based energy-conversion devices such as aqueous lithium-ion batteries. While aqueous solutions have some desirable properties as electrolyte solutions, one drawback is the narrow potential window of water due to the electrolysis reactions of water (oxygen/hydrogen evolution reaction, OER/HER). Recently, it has been reported that the potential windows were expanded in concentrated electrolyte solutions. In this study, we investigated the potential windows in aqueous concentrated electrolyte solutions with various salts at different concentrations. A neutral pH solution with the lowest water concentration showed the largest potential window, and the potential windows were not affected by the electrolyte salts. In addition, we observed an asymmetric expansion of potential windows: the upper potential limits were shifted more than the lower limits. This can be explained by the local pH change in the vicinity of electrodes caused by OER/HER and the decrease rate of OER due to the reduced water concentrations.

**Experimental**

**Materials.**—As electrolyte salts, NaClO4 (Strem Chemicals, Inc., 99%), NaNO3 (Nacalai Tesque Co., Ltd., 99.0%), disodium propane-1,3-disulfonate (PDSS; Tosoh Organic Chemical Co., Ltd.), LiNO3 (Nacalai Tesque Co., Ltd., 98.0%), lithium bis(trifluoromethanesulfonyl)amide (LiTFSA; Kishida Chemical Co., Ltd., 99.9%), H2SO4 (Nacalai Tesque Co., Ltd., 97.0%), HClO4 (Tama Chemicals Co., Ltd., 70.0%), H3PO4 (Nacalai Tesque Co., Ltd., 85.0%) and NaOH (Nacalai Tesque Co., Ltd., 97.0%) were used without further purification. Electrolyte solutions were prepared with deionized water. The concentrations of the electrolyte solutions are shown in Table I. Using a neutral pH salt, two solutions were prepared: 1 mol dm−3 (M) and nearly saturated. To standardize the concentration of cations, the concentrations of PDSS, H2SO4 and H3PO4 were set to 0.5, 0.5 and 0.33 M, respectively. In addition, 0.1 M Na2PO4 buffer solution (pH = 6.6; mixture of NaH2PO4 and Na2HPO4, purchased from Nacalai Tesque Co., Ltd., 99.0%) was also prepared in the same way as above to investigate the effect of the local pH on the potential window.

**Physicochemical properties of electrolyte solutions.**—The densities were evaluated with a 1 cm3 Ostwald pycnometer (Sansho Co., Ltd), and water concentrations were evaluated by densities. Specific ion conductivities were evaluated with a two-electrode cell with Pt plates by AC impedance spectroscopy (VSP-300, Bio-Logic Science Instruments). Viscosities were measured by an automated micro viscosimeter (Anton Paar GmbH). The pHs were measured with a pH meter (D-52, Horiba, Ltd.). A pulsed 1H NMR spectrometer (13 MHz, Acorn Area, Xigo Nanotools) was used to measure spin-spin relaxation times (T2) of water in electrolyte solutions. Neutral pH solutions were used, except for PDSS which has H atom in the solute itself. For T1 measurement, the Carr-Purcell-Meiboom-Gill (CPMG) method was used, which involves repeated 90°–180° pulse sequences, where t is the time interval between the two pulses. The
Table I. Properties of the prepared solutions.

| Water concentration/M | Specific conductivity/10⁻³ S cm⁻¹ | Viscosity/mPa s | pH | Spin-spin relaxation time (T₂)/s |
|------------------------|----------------------------------|----------------|----|---------------------------------|
| 1.0 M NaClO₄           | 54.0                             | 78             | 0.93 | 6.6                             | 2.5 |
| 9.0 M NaClO₄           | 32.9                             | 115            | 7.3  | 7.1                             | 1.5 |
| 0.50 M PDSS            | 53.4                             | 56             | 1.2  | 6.8                             | —   |
| 2.5 M PDSS             | 41.0                             | 65             | 6.3  | 6.8                             | —   |
| 1.0 M NaNO₃            | 54.7                             | 76             | 0.95 | 5.9                             | 2.5 |
| 7.6 M NaNO₃            | 42.0                             | 200            | 2.5  | 6.3                             | 2.2 |
| 1.0 M LiNO₃            | 54.3                             | 71             | 0.99 | 6.6                             | 2.6 |
| 7.8 M LiNO₃            | 43.0                             | 152            | 2.8  | 6.4                             | 1.9 |
| 1.0 M LiTFSA           | 48.7                             | 36             | 1.5  | 8.2                             | 2.1 |
| 5.2 M LiTFSA           | 14.4                             | 10             | 51   | 6.0                             | 0.47|
| 0.50 M H₂SO₄           | 54.4                             | 227            | 0.98 | —                               | —   |
| 1.0 M HClO₄            | 53.8                             | 342            | 0.86 | —                               | —   |
| 0.33 M H₃PO₄           | 55.5                             | 25             | 0.96 | —                               | —   |
| 1.0 M NaOH             | 56.6                             | 194            | 1.1  | —                               | —   |

Water vapor pressures were measured with an absolute pressure gauge (AVG-300C11, Okano Works, LTD.).

Electrochemical measurements.—To estimate the potential windows, cyclic voltammetry was performed with a three-electrode cell by an ALS/CHI Electrochemical Analyzer (Model 600A, BAS Inc.). The cell was composed of a Pt plate and Pt wire as working and counter electrodes, respectively. As a reference electrode, saturated Ag/AgCl was used for neutral pH electrolyte solutions, and a reversible hydrogen electrode (RHE) was used for acidic or alkaline electrolyte solutions. Prior to each cyclic voltammetry, electrolyte solutions were thoroughly deaerated with Ar gas for at least 30 min. The sweep rate in cyclic voltammetry was 1 mV s⁻¹. Each measurement was carried out at a constant temperature of 25°C. The current density was calculated by dividing the measured current by the geometrical area of the Pt surface.

Results

Physicochemical properties of the electrolyte solutions are listed in Table I. No clear correlation was observed between the specific ion conductivity or the viscosity and the water concentration. However, \( T₂ \) decreased with a decrease in the water concentration (Fig. 1). \( T₂ \) is sensitive to molecular motion and a decrease in \( T₂ \) means that there is an increase in solvated water, i.e., there is a decrease in free water.²² It should be noted here that \( T₂ \) is not directly related to the activity of water.

Cyclic voltammograms (CVs) of Pt in neutral pH solutions without buffer capacity are shown in Fig. 2. In these electrolyte solutions, the right-hand side of the potential window is determined by the OER, and the left-hand side is determined by the HER. When we compared two solutions with different concentrations (1 M and saturated) of the same salt, the potential windows of saturated solutions were broader than those of 1 M solutions. These windows were much wider than the thermodynamically expected value of 1.23 V. Notably, the upper limits were more expanded than the lower limits in all solutions, indicating that the OER was much more suppressed than the HER in saturated solutions.

Cyclic voltammetry was also performed in 0.50 M H₂SO₄, 1.0 M HClO₄, 0.33 M H₃PO₄, and 1.0 M NaOH. CVs are shown in Fig. 3 with a potential referenced to RHE. All solutions showed almost the same potential windows except for NaOH. In NaOH, the onset potential of the OER was lower than that in acid solutions. It is known that the oxidation potential of OH⁻ is more negative than that of solvent water due to the difference in the reactivities of OH⁻ and H₂O on Pt.²³ Therefore, NaOH solution showed the lowest onset potential for the OER. Comprehensively, from Figs. 2 and 3, it was clarified...
that the potential windows in neutral pH electrolyte solution, even in 
1 M solution, were wider than those in acidic or alkaline electrolyte 
solutions.

Next, we focused on the water concentration, since the potential 
windows are determined by the water electrolysis reactions (OER 
and HER). The potential windows are shown in Fig. 4 as a function 
of the water concentrations. In this study, the onset potential of the 
OER/HER was defined when the current density was ±0.1 mA cm⁻² 
in CVs at 1 mV s⁻¹. There are two clear tendencies in Fig. 4. First, 
the windows in neutral pH electrolyte solutions (closed symbols 
in Fig. 4) were obviously wider than those in acidic/alkaline electrolyte 
solutions (open symbols in Fig. 4), even at a dilute salt concentration 
(ca. 55 M water concentration). The same trends were observed in 
1 M LiNO₃ aqueous solution, as reported by Wessells et al. 20 Sec-
ond, the windows in neutral pH electrolyte solution (closed symbols 
in Fig. 4) were not affected by the kind of the electrolyte salt, but 
depended linearly on the water concentration. The windows were ex-

panded when the water concentration decreased, i.e., the electrolyte 
salt concentrations increased.

Discussion

Effect of a local pH change on the potential window.—First, we 
consider why the potential windows in dilute neutral pH electrolyte 
solutions were wider than those in acidic/alkaline electrolyte solu-
tions. The change in local pH in the vicinity of the electrodes can 
explain these wide potential windows in neutral pH electrolyte solu-
tions. When OER/HER occurs at pH = 7, protons/hydroxide ions are 
formed by the following reactions;

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \tag{1}
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \tag{2}
\]

In neutral pH solutions, the concentration of proton is low, ca. 10⁻⁷ M. 
Hence, in unbuffered neutral pH solutions, the local pH conditions in 
the vicinity of the electrodes change drastically to acid/alkaline as a 
result of OER/HER. According to the Nernst equation, the thermo-
dynamic reaction potentials of OER and HER shift with the pH as 
follows, assuming that the water activity and fugacity of H₂ and O₂ 
are equal to unity;

\[
E_{\text{OER}} = E'_{\text{H}_2\text{O}/\text{O}_2} - 2.303 \frac{RT}{F} \text{pH} \tag{3}
\]

\[
E_{\text{HER}} = E'_{\text{H}_2/\text{H}_2\text{O}} + 2.303 \frac{RT}{F} (14 - \text{pH}) \tag{4}
\]

where \(E_{\text{OER}}\) and \(E_{\text{HER}}\) are the reaction potentials of Eqs. 1 and 2, 
and \(E'_{\text{H}_2\text{O}/\text{O}_2}\) and \(E'_{\text{H}_2/\text{H}_2\text{O}}\) are standard reaction potentials of Eqs. 1 
and 2, respectively. \(R, T,\) and \(F\) are the gas constant, the absolute 
temperature, and the Faraday constant. According to Eqs. 3 and 4, 
\(E_{\text{OER}}\) and \(E_{\text{HER}}\) changed according to the pH value (Fig. 5). \(E_{\text{OER}}\) 
increases with decreasing pH, and \(E_{\text{HER}}\) decreases with increasing 
pH. Due to the changes in local pH, \(E_{\text{OER}}\) and \(E_{\text{HER}}\) were shifted as 
indicated by the blue arrows (Fig. 5). As a result, the potential window 
was expanded by the local pH change. (Fig. 5, red arrow).

The influence of a local pH change on the potential windows was 
investigated by cyclic voltammetry in neutral pH solutions with a 
buffer capacity. The 0.10 M Na₃PO₄ buffer solution (pH = 6.6) was 
used to compare the results with the 1.0 M NaClO₄ (pH = 6.6) solution.

Figure 3. CVs of Pt in 0.50 M H₂SO₄ (black line), 1.0 M HClO₄ (red line), 
0.33 M H₃PO₄ (blue line) and 1.0 M NaOH (green line). Measurements 
were performed with RHE reference electrode. Sweep rate was 1 mV s⁻¹.

Figure 4. Potential window width dependence on water concentration. On-
set potential of the OER/HER was defined when the current density was 
±0.1 mA cm⁻² in CVs. Closed symbols denote neutral pH aqueous electro-
lyte solution, and open symbols denote acid/alkaline aqueous solutions.

Figure 5. Oxygen/hydrogen evolution reaction potential change occurred by 
local pH change through Eqs. 3 and 4. The local pH near the electrode is 
decreased/increased by OER/HER, and by which reaction potential is in-
creased/decreased.

Figure 165. (14) A3299–A3303 (2018) A3301
without a buffer capacity. This buffer solution can suppress the local pH change in the vicinity of the electrodes via the following chemical reaction:

$$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$$  \hspace{1cm} \text{(5)}

Therefore, the onset potentials of OER/HER in buffered neutral pH solutions should be the same as those in acid or alkaline solutions. CV in 0.10 M Na-PO₄ buffered solution is shown in Fig. 6, compared with CVs in 1.0 M NaClO₄ and 0.33 M H₃PO₄. The inset in Fig. 6 is a magnified view of the OER potential region. Potentials in 0.1 M Na-PO₄ and 1.0 M NaClO₄ were converted to the RHE scale using their pH, although they were measured with Ag/AgCl as a reference electrode. The inset is a magnified view of the OER potential region.

**Water concentration-dependence of the potential windows.**—Next, when we focus on the water concentration-dependence of the potential windows, we consider that the reduced water concentration in concentrated electrolyte solutions alters the OER/HER potentials and decreases the rate of water electrolysis reactions. In the case of concentrated electrolyte solutions, the activity of water can no longer be approximated as being equal to unity. Thus, Eqs. 3 and 4 should be rewritten as follows:

$$E_{\text{OER}} = E^{\circ}_{\text{H}_2\text{O}/\text{O}_2} - 2.303 \frac{RT}{F} \cdot \text{pH} - \frac{RT}{4F} \ln(a_{\text{H}_2\text{O}})^2$$ \hspace{1cm} \text{(6)}

$$E_{\text{HER}} = E^{\circ}_{\text{H}_2\text{O}/\text{H}_2} - 2.303 \frac{RT}{F} \cdot \text{pH} - \frac{RT}{2F} \ln K$$ \hspace{1cm} \text{(7)}

where $a_{\text{H}_2\text{O}}$ is the activity of water, and $K$ is defined as the equilibrium constant of the reaction $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. When the water concentration decreases, the activity of water should also decrease, resulting in an increase in the reaction potential of OER. In addition to a shift in the reaction potential, the reaction rate will change with a decrease in the water concentration. Assuming that HER on Pt electrodes is reversible,25–27 and migration is ignored, the current density $i$ can be described via Fick’s first law:26

$$i = -F \left( D_H^+ \nabla c_H^+ - D_{\text{OH}^-} \nabla c_{\text{OH}^-} \right)$$ \hspace{1cm} \text{(8)}

where $D_j$ and $c_j$ are the diffusion coefficient and the concentration of component $j$, respectively. Eqs. 7 and 8 do not include a term for the water concentration. Thus, there is little correlation between water concentration and current density in the HER. On the other hand, OER is an irreversible reaction and the current density is usually represented by the Butler–Volmer equation. However, the OER mechanism cannot be simply described because of its complexity, and the rate-determining step is still unclear. Hence, while the kinetic equation cannot be described, the water concentration term must be incorporated in the Butler–Volmer equation as a kinetic factor. Therefore, the water concentration has an asymmetrical influence on HER and OER.

Recently, a few papers have been published on the potential windows in concentrated electrolyte solutions. Suo et al. used a ‘water-in-salt’ solution (almost-saturated LiTFSI aqueous solution) and reported a wide potential window of ca. 3.0 V.29 They argued that the OER overpotential was probably a result of the reduced water activity at an inner Helmholtz layer that was increasingly populated by TFSA anions. In our study, a clear correlation between water concentration and potential window was observed (Fig. 4). However, in this study, we found that the water/cation ratio was not directly related to the potential windows, unlike such a solvated ionic liquid system. For example, 1 M LiTFSA (water concentration: 49 M) and 7.8 M LiNO₃ (water concentration: 43 M) had a similar potential window, though the water/cation ratios were significantly different: 49 in 1 M LiTFSA and 5.5 in 7.8 M LiNO₃. As already shown in Fig. 1, the number of water molecules that were solvated to ions varied inversely with the water concentration. Hence, in this study, we show that the water concentration is important as a universal feature that determines the potential windows of aqueous solutions. Furthermore, we performed cyclic voltammetry in sulfonic acid solutions with different water concentrations (0.50 and 10 M) to differentiate the effect of a local pH change from the effect of the water concentration. CVs of Pt are shown in Fig. 7. The onset potentials of HER were almost the same in the two solutions. However, the onset potential of OER in 10 M solution was higher than that in 0.50 M
solution, similar to the results in neutral pH solutions as shown in Fig. 2. Here, in acid solutions, we have to consider the reaction potentials and kinetics of HER and OER. If we assume that HER on the Pt electrode surface is reversible, the reaction occurs as follows:

$$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2 \quad [9]$$

When the fugacity of $\text{H}_2$ is assumed to be equal to unity, the reaction potential $E_{\text{HER}}$ is evaluated via the Nernst equation:

$$E_{\text{HER}} = E_{\text{H}_2/\text{H}^+} + \frac{RT}{2F} \ln (a_{\text{H}_2}) $$

where $E_{\text{H}_2/\text{H}^+}$ is the standard reaction potential of Eq. 9. If migration is ignored, the current density $i$ can be described by the same Eq. 8. Eqs. 8 and 10 do not include a term for the water concentration. Thus, the water concentration is not related to either the reaction potential or the current density of HER. Consequently, the onset potentials of HER were almost the same in solutions with different water concentrations. On the other hand, when the fugacity of $\text{O}_2$ is assumed to be equal to unity, but the activity of water cannot be set to unity, the reaction potential $E_{\text{OER}}$ is the same as in Eq. 6. In contrast to HER, there is a term for the activity of water. However, even if $a_{\text{H}_2\text{O}}$ changes by one order of magnitude, $E_{\text{OER}}$ changes by only ca. 30 mV at 25°C. In Fig. 7, the difference in OER potential was at least ca. 100 mV, and if the 100-mV shift is considered to be caused only by this reaction potential shift, $a_{\text{H}_2\text{O}}$ has to change by three orders of magnitude. Herein, we measured the vapor pressures of water for both 0.50 and 10 M $\text{H}_2\text{SO}_4$ solutions to estimate the change in the activity of water. The ratio of vapor pressures of water can be thought to be equal to the ratio of the activities of water. As a result, the ratio of vapor pressures of water changes by an order of magnitude as shown in Fig. 7. The difference in OER potential was at least ca. 100 mV, and if the 100-mV shift is considered to be caused only by this reaction potential shift, $a_{\text{H}_2\text{O}}$ has to change by three orders of magnitude. Herein, we measured the vapor pressures of water for both 0.50 and 10 M $\text{H}_2\text{SO}_4$ solutions to estimate the change in the activity of water. The ratio of vapor pressures of water can be thought to be equal to the ratio of the activities of water. As a result, the ratio of vapor pressures of water changes by an order of magnitude as shown in Fig. 7. The difference in OER potential was at least ca. 100 mV, and if the 100-mV shift is considered to be caused only by this reaction potential shift, $a_{\text{H}_2\text{O}}$ has to change by three orders of magnitude.

Conclusions

Potential windows of aqueous solutions were investigated systematically using various salts at different concentrations. Cyclic voltammetry measurements of Pt electrodes revealed two important points. First, the potential window in unbuffered neutral pH solution was broader than that in acidic/alkaline solutions. This expansion of potential windows can be explained by the shift in the reaction potential with local pH changes in the vicinity of the electrode. Second, the potential windows were not affected by electrolyte salts, but rather depended linearly on the water concentration. The difference for OER overpotentials was much larger than that for HER overpotentials. While HER overpotentials were derived from a local pH change, OER overpotentials were derived from both a reduced water concentration and local pH change. This study highlights the importance of these two main factors (water concentration and local pH change) in determining the potential windows of concentrated electrolyte solutions.

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