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J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.5b05295 • Publication Date (Web): 18 Aug 2015

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Electrocatalytic Hydrogen Evolution Under Densely Buffered Neutral pH Conditions

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Abstract

Under buffered neutral pH conditions, solute concentrations drastically influence the hydrogen evolution reaction (HER). The iR-free HER performance as a function of solute concentration was found to exhibit a volcano-shaped trend in sodium phosphate solution at pH 5, with the maximum occurring at 2 M. A detailed microkinetic model that includes calculated activity coefficients, solution resistance, and mass-transport parameters accurately describes the measured values, clarifying that the overall HER performance is predominantly governed by mass-transport of slow phosphate ions (weak acid). In the HER at the optimum concentration of approximately 2 M sodium phosphate at pH 5, our theoretical model predicts that the concentration overpotential accounts for more than half of the required overpotential. The substantial concentration overpotential would originate from the electrolyte property, suggesting that the proper electrolyte engineering will result in an improved apparent HER performances.

The significance of concentration overpotential shown in the study is critical in the advancement of electrocatalysis, biocatalysis, and photocatalysis.

Introduction

The generation of solar fuel has attracted tremendous attentions as a solution for meeting increasing future energy demands. There have been various promising methods proposed to produce fuels from sunlight,^{1,2} e.g., photovoltaic cells,^{3,4} photoelectrochemical water splitting⁵⁻⁹ and photocatalytic water splitting.⁸⁻¹³ Photovoltaic cells can be conjugated with electrolyzers^{1,2} to generate hydrogen from water.¹⁴⁻¹⁸ When electrochemically splitting water into hydrogen and oxygen, extremely acidic¹⁹⁻²⁶ or alkaline²²⁻²⁸ pH conditions are favored because higher electrocatalytic activities are generally obtained compared with those at neutral pH.²⁹⁻³¹ The fundamental issue regarding the hydrogen evolution reaction (HER) and oxygen evolution reaction under neutral pH conditions is reactant switching: hydronium and hydroxyl ions are the reactants at acidic and alkaline pH, respectively, whereas to attain substantial reaction rates at neutral pH, water molecule must act as the reactant.²⁹⁻³³ Some studies have been dedicated to achieving higher performances under neutral pH conditions using buffered solutions^{32,33} such as phosphate, borate and carbonate,³⁴⁻³⁷ in which onset potentials comparable to those at acidic and alkaline pH levels have been reported.^{32,33,37} Simply put, this result may originate from the maintained local pH near the electrode surfaces during reactions ongoing due to the buffering action. In the buffered electrolyte solution, the buffering action ($\text{HA} = \text{A}^- + \text{H}^+$) is rapid in both directions to reach equilibrium between HA and ($\text{H}^+ + \text{A}^-$), which functions to maintain a given pH level at least in the bulk of the solution. Alternatively, some claim that the weak acid itself

acts as the reactant under such conditions, although clear evidences of such “direct weak acid reduction” have not yet been documented.³⁷⁻⁴⁰ The authors of such claims have shown that electric currents increase with the solute concentration up to 0.5 mol L^{-1} . Although higher concentrations were not investigated,⁴⁰ the performances under such conditions are speculated to be much higher. Furthermore, an electrolyte, either NaCl ,³⁷ LiClO_4 ³⁸ or KCl ^{39,40} was added to the solution in their system to enhance the conductivity, which might hinder proper understanding of the electrochemistry in buffered solutions.

Herein we experimentally and theoretically investigated influences of electrolyte concentration on the HER under neutral-buffered conditions. A Pt disk electrode ($0.071 \text{ cm}_{\text{geo}}^2$) was employed as a model catalyst and sodium phosphate was used as electrolyte solutions ($0.2 - 4.2 \text{ mol L}^{-1}$ at pH 5). All of the current densities are expressed in terms of the geometric surface area and all of the potentials have been iR-corrected using measured impedance values unless specified. Experimentally it was revealed that HER activities dependence on the solute concentration was volcano-shaped: the HER performances were increased with the solute concentration below 2 mol L^{-1} , whereas further increasing the solute concentration led to decreased performances. Our microkinetic model conjugated with a mass-transport description showed excellent agreement with the experimental observation, implying that significant concentration overpotentials exist during the HER under buffered-neutral conditions. According to the simulation model, the concentration overpotential exceeds 46 % even at 0.5 mol L^{-1} whereas kinetic overpotential remains the smallest ($\sim 10 \%$) in the entire concentration range among the considered overpotentials (kinetic and concentration overpotential, and ohmic potential drop) due to the slow mass-transport. The mass-transport phenomenon is governed by the diffusion coefficient, which is in function of effective ionic sizes and electrolyte viscosity, and the activity coefficient.

Tuning these three parameters is speculated to result in enhanced overall HER performances. This aspect shown in the study regarding electrochemical processes under neutral conditions would lead to the further advancement of electrocatalysis, biocatalysis and photocatalysis.

Experimental methods

All of the electrochemical activity tests were conducted using a rotating disk electrode (RDE) system. A poly-crystalline Pt disk electrode with a 3.0 mm diameter (0.071 cm^2 geometric surface area) was purchased from BAS, Inc. For all of the measurements, various concentrations ($0.2 - 4.2 \text{ mol L}^{-1}$) of sodium phosphate electrolyte solutions were used. The pH of the sodium phosphate solutions was adjusted to pH 5 by adding H_3PO_4 to Na_2HPO_4 . The total concentration (initial Na_2HPO_4 + added H_3PO_4) ranged from 0.2 to 4.2 mol L^{-1} . All of the chemicals were purchased from Sigma-Aldrich in the following purities: HClO_4 (99.999 %), Na_2HPO_4 (99.5 %), H_3PO_4 (99.9 %) and KOH (99.99 %). Cyclic and linear-sweep voltammogram measurements were performed at a scan rate of 50 mV s^{-1} using a 16-channel, research-grade potentiostat system (VMP3) purchased from BioLogic Science Instruments. A three-electrode system was employed, in which a KCl-saturated Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. Before and during all of the measurements, Ar (99.999 %) or H_2 (produced using a NMH_2 300 Hydrogen Generator, D. B. S. Strumenti Scientifici S.p.A.) was continuously supplied. The disk rotation speed was maintained at 1600–4900 rpm. Before all the measurements, the Pt disk-electrode was polished first with $1 \mu\text{m}$ diamond and then with $0.05 \mu\text{m}$ alumina (both purchased from BAS, Inc.). All of the current densities described in this report are expressed in terms of the geometric electrode surface area, and all of the current-potential

relationships have been iR-corrected using measured impedance values (100 kHz, amplitude 10 mV and 298 K) unless otherwise specified. Typical cyclic voltammograms using a polycrystalline Pt disk electrode in various concentration sodium phosphate solutions at pH 5 under bubbling Ar are shown in Figure S1.

Results and discussion

In Figure 1a, linear sweep voltammograms (LSVs) obtained in various concentrations of sodium phosphate solutions at pH 5 are depicted. In all cases, the cathodic currents increased monotonically with overpotential below 0 V vs. RHE, although the current-potential relationship varied with the solute concentration. Figure 1c compiles the current densities in sodium phosphate solution as a function of solute concentration at -50 mV vs. RHE (solid symbols). The HER performances increased with the solute concentration, reaching a maximum at approximately 2 mol L⁻¹, and then decreased at higher concentrations.

It is reasonable to consider that the buffering action ($\text{HA} = \text{A}^- + \text{H}^+$) is rapid in both directions, which maintained the bulk solution pH at 5, irrespective of the solute concentration. Additionally, the phosphate concentration is sufficiently higher than the hydronium ion activity ($0.5 \text{ mol L}^{-1} \gg 10^{-5} \text{ mol L}^{-1}$ (pH 5)) under our reaction condition. The buffering action in the bulk of the solution is described as follows:

$$a_{\text{A}^-} = K \frac{a_{\text{HA}} a_{\text{H}_2\text{O}}}{a_{\text{H}_3\text{O}^+}} = K' a_{\text{HA}} \quad (1)$$

where a_i is the activity of i , K denotes the equilibrium constant of the buffering action. In unbuffered solutions at pH 5, the Levich limiting current density of 0.10 mA cm² from

hydronium ion reduction is expected.³¹ Lack of this limiting current behavior in Fig. 1a indicates either successful buffering action of phosphate ions to release hydronium ions at close proximity of the surface or occurrence of direct reduction of weak acid, as previously proposed.³⁷⁻⁴⁰ Taking various rate determining steps with different reactants, the hydrogen evolution reaction (HER) kinetics can be either zero-order or first-order in weak acid activities (the details of discussion are described in the supporting information). Due to the rapid buffering action and rapid kinetics of HER on Pt, we failed to experimentally differentiate the true reactant (hydronium ion vs. weak acid) on the Pt surfaces. In any cases, the fact that the HER performances decrease with increasing the solute concentration beyond a certain concentration ($\sim 2 \text{ mol L}^{-1}$ for sodium phosphate at pH 5) cannot be explained by this kinetic description.

We thus introduce a contribution of mass-transport of the weak acid. Effects of the mass-transport on the overall performances were evident from different attainable current at various disk-rotation speeds as shown in Figure S2. In the following, the Fick's law is considered in conjunction with the Nernst-type diffusion for the mass-transport of HA and A^- :

$$J = D_i \frac{\partial a_i}{\partial x_i} = \frac{D_i}{\delta_i} (a_{i,b} - a_{i,s}) , \quad (2)$$

where D_i is the diffusion coefficient of i and δ_i represents the diffusion layer thickness. The indices b and s refer to the bulk and surface, respectively. In the overall picture, the weak acid (HA: H_2PO_4^-) is consumed and produced via the HER and hydrogen oxidation reactions (HOR), respectively, and is transported from the bulk to the surface (or from the surface to the bulk, depending on the direction of the concentration gradient), which is described by the following continuity equation:

$$\frac{\partial a_{\text{HA},s}}{\partial t} = \frac{D_{\text{HA}}}{\delta_{\text{HA}}} (a_{\text{HA},b} - a_{\text{HA},s}) + (-I_{\text{HER}} + I_{\text{HOR}}). \quad (3)$$

where I_{HER} and I_{HOR} are the kinetic reaction rates for the HER and HOR, respectively (see supporting information for the detailed discussion on I_{HER} and I_{HOR} and effects of HER in H_2 gas present; Figure S3). The same argument is applicable to the counter anion (A^- : HPO_4^{2-}), which gives the following relationship under the steady-state approximation:

$$\frac{D_{\text{A}^-}}{\delta_{\text{A}^-}} (a_{\text{A}^-,s} - a_{\text{A}^-,b}) = \frac{D_{\text{HA}}}{\delta_{\text{HA}}} (a_{\text{HA},b} - a_{\text{HA},s}). \quad (4)$$

Combining Equations 1 and 4 leads to the following description of the A^- activity at the surface of the electrode:

$$a_{\text{A}^-,s} = \left(\frac{D_{\text{HA}} \delta_{\text{A}^-}}{D_{\text{A}^-} \delta_{\text{HA}}} + K_8' \right) a_{\text{HA},b} - \frac{D_{\text{HA}} \delta_{\text{A}^-}}{D_{\text{A}^-} \delta_{\text{HA}}} a_{\text{HA},s}. \quad (5)$$

The diffusion coefficient is obtained using the Stokes-Einstein equation:⁴³

$$D = \frac{kT}{6\pi a \mu}, \quad (6)$$

where k is the Boltzmann constant, a represents the ion radius and μ is the solution viscosity. The viscosity of sodium phosphate is experimentally measured (see our previous study, ref 44). The diffusion layer thickness is derived using the Levich equation,

$$j_L = 0.62 n F \omega^{1/2} \nu^{-1/6} D^{2/3} \delta C, \quad (7)$$

and Fick's law (Equation 2), which is expressed as

$$\delta x = 1.62 D^{1/3} \nu^{1/6} \omega^{-1/2}, \quad (8)$$

where j_L is the Levich current density, ω denotes the disk rotation speed (3600 rpm $\approx$ 377 rad s⁻¹), ν is the kinematic viscosity and δC represents the difference in the reactant concentrations between the surface and bulk (see Figure S4 for the calculated values).⁴⁵ The activity is defined as the concentration multiplied by the mean activity coefficient, which is described by the extended Debye-Hückel theory (~ 0.1 mol L⁻¹):^{43,46,47}

$$RT \ln \gamma_{\pm}^s = - \frac{N_A (ze)^2}{8\pi\epsilon_0\epsilon b} \frac{1}{1+a/b}. \quad (9)$$

Taking hydration into consideration, Equation 9 can be expanded further into:⁴⁶

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^s - \ln \frac{p+q+S-h}{p+q+S} - \frac{h}{p+q} \ln \gamma_w, \quad (10)$$

which is applicable in a wide solute concentration range (≈ 4 mol L⁻¹). In the above, z is the charge number, e represents the elementary charge, ϵ and ϵ_0 denote the permittivity in the solution and vacuum, respectively, b is the Debye length, N is the Avogadro's number, p , q , S and h define the number of cations, anions, water molecules and water molecules used for the hydration, and γ_w represents the activity coefficient of water. Using these equations, the mean activity coefficients of HA and A⁻ were calculated (see Figure S5 for the calculated values).

Finally, the results of the theoretical model are displayed in Figure 1b (see Figure S6 for the schematic illustration and Figure S7 for direct comparison of experimental and theoretical linear-sweep voltammograms). From the figure, the current densities at -50 mV vs. RHE were taken and summarized as a function of the solute concentration in Figure 1c. This simulation showed

that the HER current densities increased with the solute concentration below 2 mol L⁻¹ and further increasing the solute concentration lowered the HER currents, which is in excellent agreement with our experimental observation. To solve this continuity equation, we must pick up a kinetic description, where we tentatively chose the weak acid reduction via the Heyrovsky step being rate determining step, as recently reported (details are described in supporting information).³⁷⁻⁴¹ Essentially, the contribution of kinetic component to overall current remains very small regardless of the chosen rate determining step. The larger mismatch between the theoretical and experimental currents at lower concentration region is likely originating from stronger influence by the choice of rate determining step and standard rate constants arbitrarily chosen. It can be concluded that the HER in buffered solution is predominantly governed by the mass-transport.

Based on the theoretical model, we now turn the discussion to cell efficiency. The kinetic current is described by the application of Equations S18 and S20 (green line in Figure 2a), while the overall overpotential is calculated using Equations 3 and S28 (orange line in Figure 2a). The solution resistance is theoretically described as:

$$R = K_{cell} \frac{6\pi\mu a}{z^2 ecF}, \quad (11)$$

where K_{cell} is the cell constant (see also Figure S8),^{43,44} from which the overpotentials induced by solution resistance were simulated (black line in Figure 2a). These theoretical overpotentials for the system composed of NaH₂PO₄ at pH 5 are compiled as a function of solute concentration in Figure 2b. Notably, in this simulation the viscosity values were obtained from a database,⁴² which enabled us to carry out the simulation over a wide concentration range. As shown in the figure, the overall overpotential decreased with increasing solute concentration and reached a

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3 minimum at approximately 2 mol L^{-1} . Further increasing the solute concentration resulted in an
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5 increased overpotential. In Figure 2c, the relative fractions of the overpotentials are depicted (see
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7 Figure S9 for other conditions). Under these conditions using Pt as a catalyst, the kinetic
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9 overpotential was the smallest ($< 10 \%$) among the overpotentials considered regardless of rate
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11 determining steps. The concentration overpotential was as high as 48% in 0.5 mol L^{-1} and
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13 exceeded 50% in denser solutions. This study clearly envisages the importance of mass-
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15 transport properties of the dense-buffer solution. This consideration on the electrolyte properties
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17 under neutral-buffered condition is also applicable to biocatalysis and photocatalysis, where
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19 electrocatalysis plays a crucial role. Further studies on the HER in densely buffered solutions are
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21 ongoing in our laboratory.
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31 Conclusions

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34 The hydrogen evolution reaction (HER) under buffered-neutral conditions was experimentally
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36 and theoretically investigated using a Pt disk electrode, especially focused on solute
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38 concentration influences on HER performances at pH 5 in sodium phosphate solution ($0.2 - 4.2$
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40 mol L^{-1}). Overall HER performances dependence on the solute concentration were revealed as
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42 volcano-shaped: the HER performances increased with the solute concentration below around 2
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44 mol L^{-1} and further increasing the solute concentration led to decreased HER performances. Our
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46 theoretical model composed of microkinetic and mass-transport showed excellent agreement
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48 with the experimental observation, suggesting that the HER in neutral-buffered solutions is
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50 predominantly governed by the mass-transport of phosphate species (weak acid). Our simulation
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52 model for NaH_2PO_4 solution at pH 5 revealed that the overall overpotential (solution resistance,
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concentration overpotential and kinetic overpotential) can be minimized at around 2.0 mol L⁻¹ where yet the contribution of concentration overpotential was quite huge (>50 %). This study points out the substantial concentration overpotential present during the HER under neutral-buffered conditions, which has been overlooked in many studies. The mass-transport is described by the diffusion coefficient and the activity coefficient, and the former is a function of the effective ion size and viscosity of the electrolyte solution. Tuning these parameters, i.e., proper electrolyte engineering, will result in a drastic improvement of the HER performance under neutral conditions, irrespective of the identity of the electrocatalyst.

ASSOCIATED CONTENT

Supporting Information. CVs with Ar bubbling, consideration on the HER reactant and resultant kinetic description, LSVs at various disk-rotation speeds, calculated physical parameters (activity coefficient, diffusion layer thickness and solution resistance), and calculated half-cell efficiencies under various conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

The research reported in this work was supported by the King Abdullah University of Science and Technology.

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Figure 1. (a) LSVs using a polycrystalline Pt disk electrode in sodium phosphate solutions of various concentrations (1.0, 1.8, 3.2 or 4.2 mol L⁻¹) at pH 5 with bubbling H₂ (conditions: -50 mV s⁻¹, 3600 rpm, 298 K). For reference, those obtained in 0.1 mol L⁻¹ HClO₄ and KOH are presented in the figure as solid lines. (b) Theoretically derived polarization curves in sodium phosphate solutions of various concentration (0.2, 1.0, 1.8, 2.7, 3.2, and 4.2 mol L⁻¹) at pH 5. (c) Comparison between experimental (solid symbols) and theoretical (open symbols) HER current density. The current densities at -50 mV vs. RHE are compiled as a function of concentration.

Figure 2. (a) Simulated polarization curves with and without concentration overpotential and solution resistance in 1.0 mol L⁻¹ NaH₂PO₄ electrolyte solution. (b) Simulated kinetic, concentration and solution resistance overpotentials at -10 mA cm⁻² and (c) their relative fraction as a function of NaH₂PO₄ concentration. The solution resistance is calculated considering an electrode geometric surface area of 0.1 cm².

Insert Table of Contents Graphic and Synopsis Here

During the electrocatalytic hydrogen evolution reaction in buffered-neutral conditions, significant concentration overpotential is prevalent as high as 50 % originating from the properties of electrolyte solutions.

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