



Impact of solute concentration on the electrocatalytic conversion of dissolved gases in buffered solutions



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HIGHLIGHTS

- Impact of electrolyte concentration on electrochemical performance was investigated.
- Increasing the solute concentration logarithmically decreases the limiting currents.
- The solute concentration alters gas solubility, diffusion and kinematic viscosity.
- Electrolyte properties altered by the concentration describe the observed currents.

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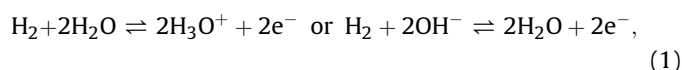
ABSTRACT

To maintain local pH levels near the electrode during electrochemical reactions, the use of buffer solutions is effective. Nevertheless, the critical effects of the buffer concentration on electrocatalytic performances have not been discussed in detail. In this study, two fundamental electrochemical reactions, oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR), on a platinum rotating disk electrode are chosen as model gas-related aqueous electrochemical reactions at various phosphate concentrations. Our detailed investigations revealed that the kinetic and limiting diffusion current densities for both the ORR and HOR logarithmically decrease with increasing solute concentration ($\log|j_{\text{ORR}}| = -0.39c + 0.92$, $\log|j_{\text{HOR}}| = -0.35c + 0.73$). To clarify the physical aspects of this phenomenon, the electrolyte characteristics are addressed: with increasing phosphate concentration, the gas solubility decrease, the kinematic viscosity of the solution increase and the diffusion coefficient of the dissolved gases decrease. The simulated limiting diffusion currents using the aforementioned parameters match the measured ones very well ($\log|j_{\text{ORR}}| = -0.43c + 0.99$, $\log|j_{\text{HOR}}| = -0.40c + 0.54$), accurately describing the consequences of the electrolyte concentration. These alterations of the electrolyte properties associated with the solute concentration are universally applicable to other aqueous gas-related electrochemical reactions because the currents are purely determined by mass transfer of the dissolved gases.

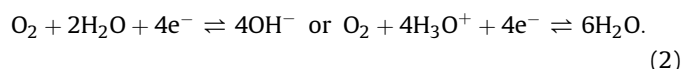
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1. Introduction

To achieve a sustainable energy system, efficient methods for the conversion of chemical energy into electricity are desired. Fuel cells are one of the most promising technologies for efficient energy conversion and have been extensively investigated in the past decades. In the fuel cell system, hydrogen is oxidized as follows (hydrogen oxidation reaction: HOR):



and oxygen is reduced at the anode as follows (oxygen reduction reaction: ORR):



For these reactions to exhibit higher activities, extreme pH conditions are generally applied. Typically, the electrolyte solutions are KOH [1–5], NaOH [4], and HClO₄ [3–5] for the HOR and NaOH

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[6], KOH [7,8], HClO₄ [8–10,12,13], and H₂SO₄ [8,10–13] for the ORR. Under unbuffered, near-neutral pH conditions, more overpotential is required to obtain substantial electric currents [3,14–19] where reactants switch from hydronium or hydroxyl ions to water molecules, which are not kinetically favored [3,14]. Under neutral condition of pH 5–9, to maintain local pH levels (hydronium and hydroxyl ion activities) at the electrode–electrolyte interface while the reaction is ongoing, buffered solutions such as phosphate, carbonate, or borate are used [20], resulting in comparable performances to those under acidic and alkaline conditions. In some cases, it has been proposed that the counter anions (e.g., phosphate ions) are involved in the reaction mechanism [21,22]. From this viewpoint, the buffer concentrations should be expected to have a great impact on electrocatalytic performance. For the hydrogen evolution reaction (HER), it has been reported that increasing the buffer concentration improves the HER performance [21,22]. Although this finding should also be very relevant to other aqueous electrochemical reactions, there is no fundamental study reported regarding the effects of the electrolyte concentration on the ORR/HOR.

Herein, we present a detailed study on the effects of the electrolyte concentration on the ORR/HOR performances using a Pt disk electrode. For all the measurements, sodium phosphate was used as a buffered electrolyte and its pH was adjusted to 5. In an unbuffered solution at pH 5, activity of hydronium ion is limited and thus water molecules, instead of hydronium ions, start to get involved as a reactant in, e.g., ORR catalysis, requiring high overpotential. On the other hand, when a buffered electrolyte is present, sufficient amount of hydronium ions are provided due to a buffering action depending on the electrolyte concentration. As a result, cathodic *j*-*V* profiles for the ORR are drastically improved in the presence of a buffered electrolyte at pH 5 [14]. In addition, we have chosen to study at pH 5 because the solubility of phosphate species is much higher than those at more alkaline pH, providing a wide range of solute concentration to evaluate its effects on the ORR/HOR electrochemical performances [23]. Our controlled electrochemical study revealed that current densities for both the ORR and HOR logarithmically decreased with increased electrolyte concentration. The changes in the characteristics of the electrolyte accurately accounted for the measurements: the gas solubility decreased, the kinematic viscosity of the solution increased and the diffusion coefficient of the dissolved gases decreased with increasing solute concentration. The limiting diffusion currents simulated using these separate parameters were in good agreement with the measured currents, suggesting that the mass transfer parameters associated with the electrolyte property solely determines the overall electrochemical performance. To the best of our knowledge, this is the first report clarifying the significant influences of the electrolyte concentration on the gas-related aqueous electrochemical reaction performance.

2. Experimental

Cyclic voltammetry was performed using a rotating disk electrode (RDE) system. A Pt disk electrode with 3.0 mm diameter (0.071 cm² geometric surface area) was purchased from BAS Inc. Various concentrations of phosphate (>99.5% Na₂HPO₄ or 99.0% NaH₂PO₄) was used as an electrolyte, the pH of which was adjusted with H₃PO₄ (HPLC grade, 85–90 %) or NaOH (99.99%). All of the chemicals were purchased from Sigma–Aldrich. A three-electrode system was employed, using a KCl-saturated Ag/AgCl electrode and a platinum wire as reference and counter electrodes, respectively. Linear-sweep and cyclic voltammograms measurements were conducted using a 16-channel, research-grade potentiostat system (VMP3) from BioLogic Science Instruments. Before and

during all of the experiments, oxygen or hydrogen was continuously supplied into the cell. The disk rotation speed was controlled at 1600–4900 rpm. All of the current densities described in this report were expressed in terms of the geometric electrode surface area. To exclude the influence of the electrolyte resistance, the ohmic resistance was measured by electrochemical impedance spectroscopy, and all of the current–potential relationships described in this report were iR-corrected. The cell constant was evaluated using a standard solution of One-Shot conductivity calibration standards (00652–66, 1002 Ω cm, purchased from Fisher Scientific Inc.). The kinematic viscosity of the solution was measured using VISCO-SYSTEM AVS-370 (SI Analytics GmbH, Mainz) with the capillary 532 03 (instrument constant: 0.003138 mm² s⁻²) or 532 10 (instrument constant: 0.009567 mm² s⁻²).

3. Results and discussion

3.1. Electrochemical investigation in electrolyte solutions of various concentrations

Linear sweep voltammograms (LSVs) using a polycrystalline Pt disk electrode at 3600 rpm in electrolyte solutions with various phosphate concentrations (0.2, 1.0, 1.8, 2.7, 3.2 and 4.2 M) at pH 5 under oxygen bubbling are depicted in Fig. 1a. In all of the cases, cathodic currents were observed below 900 mV on the RHE scale. Increasing the concentration of phosphate resulted in smaller reduction currents, reaching an almost negligible current of approximately -0.15 mA cm⁻² in the 4.2 M solution. LSVs under hydrogen bubbling were also carried out and are compiled in Fig. 1b. In all of the solutions, anodic currents were measured above 0 V vs. RHE, showing clear limiting diffusion currents. Similar to the ORR, the oxidation currents in the less dense electrolyte solutions were smaller (approximately 0.26 mA cm⁻² in 4.2 M). These results clearly suggested that the electrolyte concentration has significant influences on the electrochemical performance. In Fig. 1c, the current densities taken from Fig. 1a and b at 400 mV vs. RHE are plotted as a function of the electrolyte concentration, showing that the limiting diffusion current densities decreased in a logarithmic scale with increasing phosphate concentration. The approximation curves were calculated as:

$$\log|j_{\text{ORR}}| = -0.39c + 0.92, \quad (3)$$

and

$$\log|j_{\text{HOR}}| = -0.35c + 0.73. \quad (4)$$

The limiting diffusion currents can be described by the Levich equation:

$$j_L = 0.62nF\omega^{1/2}\nu^{-1/6}D^{2/3}\delta C, \quad (5)$$

and the Koutecky–Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L}, \quad (6)$$

where *j*, *j_k* and *j_L* are the overall current density, the kinetic current density and the Levich currents density, respectively; *F* is the Faraday's constant; *ω* denotes the disk rotation speed; *ν* is the kinematic viscosity and *δC* represents the difference in the reactant concentrations between the surface and the bulk. To evaluate the dependence of the ORR limiting diffusion current density on the disk rotation speed, the inverse of current density at 400 mV vs. RHE was plotted as a function of square root of disk-rotation speed

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