Accepted Article

Title: Electrolyte engineering toward efficient water splitting at mild pH

Authors: Tatsuya Shinagawa, Marcus Tze-Kiat Ng, and Kazuhiro Takanabe

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201701266

Link to VoR: http://dx.doi.org/10.1002/cssc.201701266
Electrolyte engineering toward efficient water splitting at mild pH

Tatsuya Shinagawa,[a] Marcus Tze-Kiat Ng,[a] and Kazuhiro Takanabe*[a]

Abstract: The development of processes for the conversion of \( \text{H}_2\text{O}/\text{CO}_2 \) driven by electricity generated in renewable manners is essential to achieve sustainable energy and chemical cycles, in which the electrocatalytic oxygen evolution reaction (OER) is one of the bottlenecks. In this contribution, the influences of the electrolyte molarity and identity on OER at alkaline to neutral pH were investigated at an appreciable current density of \(~10\ \text{mA cm}^{-2}\), revealing (1) the clear boundary of reactant switching between \( \text{H}_2\text{O}/\text{OH}^- \) due to the diffusion limitation of \( \text{OH}^- \) and (2) the substantial contribution of the mass transport of the buffered species in buffered mild pH conditions. These findings propose a strategy of electrolyte engineering: tuning the electrolyte properties to maximize the mass-transport flux. The concept was successfully demonstrated for OER as well as overall water electrolysis in buffered mild pH conditions, shedding light on the development of practical solar fuel production systems.

Introduction

In recent decades, increasing attention has been given to the construction of a sustainable society. The realization of sustainability largely relies on the development of systems that enable the efficient conversion of chemicals in renewable manners. One of the core technologies in such a scheme is the electrocatalytic conversion of thermodynamic dead-end chemicals, i.e., \( \text{H}_2\text{O} \) and \( \text{CO}_2 \), using electricity generated from renewable energy sources.[1-4] Particularly, for targeting off-site and/or small-scale processes that are suitable for renewable-energy-driven systems, the development of electrocatalytic systems operating at near-neutral pH has emerged as a promising concept.[5-8] For both reactants, the oxygen evolution reaction (OER) is the anodic half-reaction in common, to which accordingly tremendous research efforts have been dedicated. Among cost-effective and earth-abundant materials, \( \text{CoO}_x \), \( \text{MnO}_x \), and \( \text{NiO} \), have been the most extensively studied,[9,7,8,10] which exhibited stable performances in non-extreme pH conditions.

For solar-driven fuel production, such as PV electrolysis,[11-13] photoelectrochemical water splitting,[14] and photocatalytic water splitting,[15-17] a solar-to-hydrogen conversion efficiency of 10% is considered a benchmarking value.[8,18,19] Based on the photon irradiation of Air Mass 1.5, this efficiency corresponds to an approximate current density of \( 8.2\ \text{mA cm}^{-2} \).[6] This value, or a rounded value of \( 10\ \text{mA cm}^{-2} \), has been considered as a figure of merit in evaluating practical solar hydrogen production systems. Nevertheless, in most literature, the studies on OER at near-neutral pH have been conducted in a range of electric current densities of only up to \( 2-3\ \text{mA cm}^{-2} \) at maximum, which is smaller than the aforementioned target benchmark. Therefore, at the current stage, an effective examination of the feasibility of electrocatalytic OER at non-extreme pH has been lacking. To address electrochemical performances in more relevant conditions to the practical applications, a comprehensive and detailed investigation of OER as well as overall water electrolysis at mild pH levels at current densities reaching \( 10\ \text{mA cm}^{-2} \) is thus of paramount importance.

Herein, this contribution reports a comprehensive study on OER in various electrolytes at alkaline to near-neutral pH levels using \( \text{NiO} \) and \( \text{CoO}_x \) model electrodes, with a particular focus placed on electrocatalytic performances at \( 10\ \text{mA cm}^{-2} \). Our experimental as well as macroscopic theoretical studies clarify the reaction switching for OER between the oxidation of water molecules and hydroxide ions occurring at pH \(~11\) to reach the appreciable electric current density. At non-extreme pH levels, in which the oxidation of \( \text{H}_2\text{O} \) evidences OER, the presence of buffered species improved the apparent OER performances, as reported in the literature. Importantly, in such buffered mild pH conditions, our study on the molarity and identity of buffered electrolytes from the view point of specific ion effects revealed considerable impacts of mass transport of the buffered species on the apparent OER performances. In turn, tuning of the electrolyte properties to maximize the mass-transport flux, i.e., electrolyte engineering, was revealed as a promising concept to improve the performance of OER and thus the overall water electrolysis. In an optimal electrolyte, overall water electrolysis was examined, in which \( 10\ \text{mA cm}^{-2} \) was readily achieved at ca. 1.7 V with an onset voltage less than 1.6 V at a mild pH level. Presented here are fundamental yet critical aspects of electrocatalytic water splitting, which must be considered for the development of practical solar fuel production devices.

Results and Discussion

In this study, the influences of electrolyte molarity and identity on OER were investigated with a particular focus placed on the appreciable current density (~10 mA cm\(^{-2}\)). Figures 1 and 2 show cyclic voltammograms (CVs) using Ni and Co disk electrodes,
respectively, performed in 0.1 M KOH, 0.5 M K-sulfate (pH 10.8), and 0.1 M K-phosphate (pH 10.8 and 9.4) at varying disk-rotation speeds (400-3600 rpm) in a rotating-disk electrode (RDE) configuration to regulate the contribution of diffusion, i.e., diffusion layer thickness.

In 0.1 M KOH, monotonically increasing anodic current densities above 0.8 V vs. standard hydrogen electrode (SHE) were observed (Figures 1a and 2a), which were independent of the disk-rotation speed. In contrast, at pH 10.8 (Figures 1b, 1c, 2b and 2c), a two-step anodic event was observed, in which larger current densities were achieved at higher disk-rotation speeds (i.e., shorter diffusion layer thicknesses), indicating mass-transport limitation. At a lower pH level of 9.4, only monotonically increasing anodic currents were again observed, which depended on the disk-rotation speed.

**Figure 1.** CVs using a Ni RDE in (a) 0.1 M KOH (pH 12.8), (b) 0.5 M K-sulfate (pH 10.8), (c) 0.1 M K-phosphate (pH 10.8), and (d) 0.1 M K-phosphate (pH 9.4) at 298 K at various disk-rotation speeds (400-3600 rpm) and a scan rate of 10 mV s⁻¹. $E_{\text{eq}}$ indicates the standard potential for OER (1.23 V vs. RHE).

**Figure 2.** CVs using a Co RDE in (a) 0.1 M KOH (pH 12.8), (b) 0.5 M K-sulfate (pH 10.8), (c) 0.1 M K-phosphate (pH 10.8), and (d) 0.1 M K-phosphate (pH 9.4) at 298 K at various disk-rotation speeds (400-3600 rpm) and a scan rate of 10 mV s⁻¹. $E_{\text{eq}}$ indicates the standard potential for OER (1.23 V vs. RHE).
The equation for OER can be described in two ways depending on the reaction conditions: 

\[4\text{OH} \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \]  \hspace{1cm} (1)

and the oxidation of water molecules at acidic pH:

\[6\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}_2\text{O}^- + 4e^- \]  \hspace{1cm} (2)

These descriptions clearly show that reactant switching (H\textsubscript{2}O/OH\textsuperscript{−}) for OER is expected to occur between acidic and alkaline pH levels. Although, in the case of the hydrogen evolution reaction (HER), which is the counterpart reaction to OER in water splitting, theoretical macroscopic calculations as well as experimental studies on reactant switching were reported, a detailed investigation on reactant switching for OER has not been reported to the best of our knowledge. In this context, a simple macroscopic calculation was performed to quantitatively elucidate the reactant switching event (H\textsubscript{2}O vs OH\textsuperscript{−}) for OER. In the RDE configuration, the limiting diffusion current density follows the Levich equation:

\[j_L = 0.62nF\omega^{1/2}D^{1/2}\delta a_i,\]  \hspace{1cm} (3)

where \(n\) is the number of electrons involved, \(F\) is the Faraday constant, \(\omega\) is the disk rotation speed, \(\delta\) is the thickness of the diffusion layer in a static condition, and \(a_i\) is the activity of species \(i\). Using this equation, theoretical limiting diffusion current densities were calculated with the following values: \(n = 4\), \(F = 96500 \text{ C mol}^{-1}\), \(D_{\text{OH}} = 5.24 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\), \(\delta = 8.93 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}\), \(a_{\text{OH}} = 10^{-7} - 10^{-4} \text{ M}\), and \(\omega = 400\) and 3600 rpm (≈ 41.9 and 377 rad s\(^{-1}\), respectively). The obtained values are compiled as a function of pH in Figure 3. The thickness of the diffusion layer in a static condition is known to increase to a micrometer scale in several seconds, \(^{24}\) and at steady-state the thickness is typically considered to be 0.5 mm. \(^{25,26}\) Using this value as the thickness of the diffusion layer, the limiting diffusion current densities \((j_L)\) in non-stirring conditions are also calculated and shown in the figure.

The calculation revealed that, at pH 12.8 (corresponding to 0.1 M KOH), the OH\textsuperscript{−}-diffusion-limited OER current density reached as high as 300 mA cm\(^{-2}\) at 400 rpm, and thus, experimentally, no apparent disk-rotation-speed-dependent currents are expected in the region of our interest, e.g., ~10 mA cm\(^{-2}\) that has been considered a benchmarking value for solar fuel production. \(^{28}\) As the pH decreased, the limiting diffusion current densities decreased on a logarithmic scale. At pH 10.8, the limiting diffusion current density at 400 rpm was theoretically 3.8 mA cm\(^{-2}\), which is quantitatively in good agreement with the observed potential-independent current densities in Figures 1b, 1c, 2b and 2c, clearly disclosing that the first step of the observed anodic events in both buffered and unbuffered electrolytes is ascribable to the oxidation of hydroxide ions (Equation 1). Notably, above the plateau region in such conditions, the anodic current densities increased when the electrode experienced more positive potentials. Because current densities higher than the OH\textsuperscript{−}-diffusion-limited OER current density cannot be achieved via the oxidation of hydroxide ions, the second anodic currents observed here were ascribable to the oxidation of water molecules (Equation 2), i.e., reactant switching from OH\textsuperscript{−} to H\textsubscript{2}O at ca. pH 9~11. The same reactant switching was observed for a Pt RDE (Figure S1). When the pH was further lowered to 9.4, a theoretical OH\textsuperscript{−}-diffusion-limited current density was as small as 0.12 mA cm\(^{-2}\) at 400 rpm; and accordingly, an apparent single-step anodic event is expected in the near-neutral pH region originating from the oxidation of water molecules, which is consistent with the experimental observations (Figures 1d and 2d). Interestingly, in the buffered solution at such a near-neutral pH (0.1 M K\textsubscript{2}HPO\textsubscript{4} at pH 9.4; Figures 1d and 2d), the observed anodic current densities depended on the disk-rotation speed. The observed disk-rotation-speed dependence cannot be assigned to the diffusion of hydroxide ions because the variation in the OH\textsuperscript{−}-diffusion-limited current densities with disk-rotation speed was only several hundreds of microamperes, which were considerably smaller than the observed changes in the current densities. In addition, the gas bubbles formed during the reaction would not perturb the diffusion in the RDE configuration as reported in the previous studies. \(^{27,28}\) Essentially because the current density should determine the rate of gas bubble formation, irrespective of the reaction conditions.

To elucidate the origin of the observed disk-rotation-speed dependent OER in buffered mild pH conditions, the influences of molarity and identity of the buffered ions on the OER performances were further investigated in detail. Figures 4a and b display potentials reaching 10 mA on the reversible hydrogen electrode (RHE) scale in K\textsubscript{2}HPO\textsubscript{4} (pH ~9.4) and K-carbonate (KHCO\textsubscript{3}/K\textsubscript{2}CO\textsubscript{3} = 50/50; pH ~10.1), respectively, using NiO, and CoO\textsubscript{x} plates with a geometric surface area of 1×1 cm\(^2\) (see Figure S2 for the quantification of product gases and Figure S3b for Tafel slopes). The figures show that, for both the CoO\textsubscript{x} and NiO electrocatalysts, the overpotentials decreased with an increasing
solute concentration and that OER in K$_3$H$_2$CO$_3$ required a lower overpotential than that in K$_3$HPO$_4$. Figure S4 summarizes the OER performances in various electrolytes (phosphate, carbonate and borate) with respect to the solution pH, which revealed that the OER performances at similar pH for both electrodes were found to follow the order of: phosphate < borate < carbonate.

Figure 4. Potential reaching 10 mA using NiO$_x$ and CoO$_x$ plates (1×1 cm$^2$) and potential reaching ~10 mA cm$^{-2}$ using a Pt RDE at 3600 rpm in (a) K$_3$HPO$_4$ (pH 9.5) and (b) K$_3$-carbonate (pH 10.1) at 298 K; the figures are plotted as a function of the solute concentration. The data for Pt in K$_3$HPO$_4$ were adopted from reference.[29]

These data clearly disclosed the considerable influences of the identity and molarity of the buffered ions on the OER performance at the appreciable current density, independent of the identity of the electrode. One possibility accounting for the observed monotonic improvement in the apparent OER performance with increasing solute concentration (Figure 4) would be an interaction between the buffered ions and the electrode; i.e., the specific adsorption of buffered anions on the surface and/or the formation of complexes active toward OER.[8] However, this model cannot rationalize the observed diffusion limitation under steady-state conditions in Figures 1 and 2 and thus cannot be the primary factor determining the apparent OER performances. Another scenario is the participation of the buffered species in the surface reaction during OER. Recent studies on OER over CoO$_x$ and MnO$_x$ in buffered near-neutral pH conditions indicated that the surface deprotonation reaction is likely the limiting step, which is facilitated by chemical reactions between surface protons (generated via H$_2$O oxidation on the surface) and buffered species. Such chemical reactions involving buffered species were well represented by the pKa of the buffered species.[6,7] The pKa values of the electrolytes used in this study were (H$_2$PO$_4$/HPO$_4^{2-}$) = 7.2, (H$_2$CO$_3$/HCO$_3^-$) = 6.5, and (H$_3$BO$_3$/B(OH)$_4^-$) = 9.2,[29] while the OER performances in these electrolytes at similar pH levels followed the order of K-phosphate < K-borate < K-carbonate. Therefore, there was no clear correlation found between the OER performance and pKa for both NiO$_x$ and CoO$_x$, implying that the surface deprotonation kinetics were not the limiting step under the current conditions (i.e., high current densities such as ~10 mA cm$^{-2}$). In turn, it is suggested that the diffusion of buffered species participating in this step limited the overall performance at the appreciable current density, which has been overlooked in previously reported studies.

Possibly there are two types of diffusion of the buffered species; either the diffusion of (1) the deprotonated buffered species from the bulk of the electrolyte to the surface of the electrode that takes a proton from the surface, e.g., HPO$_4^{2-}$, or (2) the protonated buffered species from the electrode surface to the bulk of the electrolyte, e.g., H$_2$PO$_4^-$. Notably, the influences of the identity and molarity of the electrolyte were previously reported for HER using a Pt RDE under the identical conditions of K$_3$HPO$_4$ electrolytes (reproduced in Figure 4a; also see Figure S3c for HER using a Ni RDE,[80] in which the apparent HER performance was found to improve with an increasing solute concentration below a certain concentration (~1.5 M), while in denser electrolyte solutions, larger overpotentials were required. Such a volcano-shaped relationship for HER between the performance and the solute concentration in buffered near-neutral pH conditions was well accounted for by the diffusion of the proton source (e.g., HPO$_4^{2-}$ in K$_3$HPO$_4$, independent of the identity of the electrode.[30] A similar experiment using the Pt RDE was performed here in K-carbonate electrolyte at pH 10.1, which also exhibited a volcano-shaped relationship between the HER overpotential and the solute concentration (Figure 4b). These results show that, when the apparent performance is impacted by the diffusion of the deprotonated species, the performance-concentration relationship is volcano-shaped; in turn, the observed monotonically improving OER performance with an increasing solute concentration indicates that the diffusion of the protonated species (after the reaction with generated proton) most probably impacted OER.

Figure 5. Calculated diffusion coefficients and activities of the buffered species in K$_3$HPO$_4$ (pH 9.5) and KHCO$_3$ (pH 8.6) at 298 K.

This article is protected by copyright. All rights reserved.
Importantly, these mass-transport phenomena are solely determined by the properties of the electrolyte that are independent of the identity of the electrode, and thus can be separately studied. In general, mass transport is known to be a function of the molarity, the mean activity coefficient, the size of the species, and the viscosity.\cite{10} By separately evaluating the associated parameters (see Figure S5 for the viscosity, Figure S6 for the relative fraction of the buffered species, and Figure S7 for the mean activity coefficient) from the viewpoint of so-called specific ion effects,\cite{31,32} the diffusion coefficients and activities of the deprotonated buffered species in KHPO$_4$ and KHCO$_3$ (i.e., HPO$_4^{2−}$ and HCO$_3^{−}$) were identified and are presented in Figure 5. It should be noted that only primitive electrolytes can be vigorously dealt with for this purpose (e.g., KHCO$_3$: not a mixture of KHCO$_3$/$K_2$CO$_3$), and thus, the properties of borate at mild pH levels (a mixture of H$_2$BO$_3$ and B(OH)$_2^{−}$) cannot be unambiguously elucidated (see the discussion in the Supplementary Information).

In both electrolytes, smaller diffusion coefficients were observed with an increasing solute concentration due to an increase in the viscosity. In contrast, the activity of the buffered species, which is obtained by multiplying the concentration by the mean activity coefficient, was found to increase with solute concentration. Such a trade-off relationship between the diffusion coefficient and the activity of the deprotonated buffered species (e.g., HPO$_4^{2−}$ and HCO$_3^{−}$) indicates the existence of an optimal solute concentration, in which the mass-transport flux is maximized. In the condition in which the flux is maximized, the apparently lowest HER overpotential would be observed when influenced by mass transport, consistent with experimental observations (Figure 4). In contrast, the electrolyte properties of the protonated buffered species (e.g., H$_3$PO$_4^{−}$) that are most likely responsible for the diffusion event during OER are technically challenging to quantitatively determine, as the local activity of the protonated species generated via surface reactions varies with reaction conditions. Nonetheless, because (1) the concentration of the protonated species in the bulk of the electrolyte is considerably small (see the relative fraction shown in Figure S6) and (2) thus the local concentration of the protonated species is predominantly determined by the generation of protons via the surface reaction and its reaction with the buffered species, the local concentration is anticipated to be quite small (e.g., the generation rate at 10 mA corresponds to 26 nmol $s^{-1}$). Such circumstances can be considered as a “diluted electrolyte”, meaning that the mean activity coefficient can be assumed unity independently of the electrolyte molarity and identity. This rationale suggests that the other parameter, i.e., the diffusion coefficient, is predominantly responsible for the diffusion event during OER, which is a function of the size of the species of interest and the viscosity of the solution. Because the variation in the size of the protonated species used in this study is quite small (see the Supporting Information), the viscosity predominantly determines the diffusion coefficient. The viscosity was lower in KHCO$_3$ than KHPO$_4$ (Figure S5), which is expected to provide faster diffusion and an apparently smaller overpotential for OER in KHCO$_3$ than in KHPO$_4$, in excellent agreement with the experimental observations (Figures 4 and S3). The discussion here supports our rationale that OER in buffered mild pH conditions is limited by the mass transport of the protonated buffered species after the reaction with generated proton.

Thus far, the current study on OER disclosed reactant switching driven by pH as well as the considerable contribution of mass transport of the protonated buffered species in the buffered mild pH conditions, which are schematically illustrated in Figure 6. At alkaline pH, OER proceeds via the oxidation of hydroxide ions, while at near-neutral pH levels (lower than pH ~11 in practice) the oxidation of the water molecules dictates OER due to the insufficiency of the hydroxide ion activity to reach substantial reaction rates. Under near-neutral pH conditions, protons are generated via the surface reaction, which must be removed from the surface to avoid poisoning the surface or corroding the electrode due to the local pH shift.\cite{10} When the buffered species is present in such conditions, the removal of protons from the surface can be facilitated by the chemical reaction between the buffered species and the surface protons, as reported in the literature,\cite{33,34} leading to a higher reaction rate compared to that in unbuffered conditions. In addition, as has been discussed in this study, the diffusion of buffered species greatly impacted the OER performance in the buffered mild pH conditions at appreciable current densities such as 10 mA cm$^{-2}$. This study thus points out the importance of electrolyte engineering, i.e., tuning the electrolyte properties to maximize the mass-transport flux of buffered species in mild pH conditions, which would lead to drastically improved apparent performances of overall water splitting.

To demonstrate the concept and significance of electrolyte engineering, overall water electrolysis was performed in a two-electrode configuration. As model electrodes, NiMoO$_3$\cite{35,36} and CoO$_x$\cite{37} were electrochemically deposited on Ni foam (NF) and used as a cathode and an anode, respectively. Figure 7a shows the current-voltage relationships in 0.1 and 1.5 M K-carbonate (pH 10.1), as well as in 0.5 M KOH as a reference. In 0.1 M K-carbonate electrolyte, which is the typical concentration of the
electrolyte for the electrochemical study, voltages higher than 1.9 V were required to reach 10 mA. As has been discussed in this article, the proper tuning of the electrolyte properties (electrolyte engineering) for both OER and HER can realize apparently improved performances by maximizing the mass-transport flux, which more reflects the intrinsic catalytic activity. Figure 7b summarizes the iR-free voltages required to reach 10 mA for water electrolysis in K-carbonate (pH ~10.1) at various concentrations. The figure reveals that there was a volcano-shaped trend in the voltage-concentration relationship with a minimum overvoltage observed at 1.5 M, the shape of which is most probably accounted for by the diffusion of the buffered species responsible for HER, as previously discussed in this study (Figure 4). It should also be noted that the electrolyte that maximizes the diffusion of ions naturally maximizes its migration (i.e., lowest solution resistance; see Figure S8).[30] Taken together, when water electrolysis was evaluated in the optimal electrolyte of 1.5 M K-carbonate, 10 mA cm$^{-2}$ was readily reached at approximately 1.7 V with excellent stability (>20 h, approximately 15 mV loss in total, Figure 7c). It is fair to note that the performance in 1.5 M K-carbonate electrolyte was still inferior to that in 0.5 M KOH, as shown in Figure 7a. Figure 7d clarifies the voltage distribution in 1.5 M K-carbonate at pH 10.1 obtained based on half-cell studies, which clearly shows that the voltage loss was most considerable for OER. Therefore, further studies on OER electrocatalysts to improve the overall performance are essential. Nevertheless, it should be strongly emphasized that the realization of overall water splitting at appreciable current densities below 1.75 V with an onset voltage of <1.6 V in non-extreme pH conditions simply by electrolyte engineering is a great stride toward sustainable solar fuel production, as three series-connected silicon solar cells can readily generate sufficient photovoltage to drive this device (operational photovoltage of 0.5–0.6 V × 3).

Figure 7. (a) Current-voltage relationships in 0.5 M KOH and 0.1 and 1.5 M K-carbonate (pH 10.1); (b) iR-free voltage at 10 mA in K-carbonate (pH ~10.1) at various concentrations; (c) long-term CP profile at 10 mA in 1.5 M K-carbonate (pH 10.1); (d) voltage distribution in 1.5 M K-carbonate (pH 10.1); performed using a CoO$_x$/NF anode and a NiMo/NF cathode (1×1 cm$^2$) with Ar bubbling at 298 K.
Conclusions

We presented a study on the influences of the identity and molarity of the electrolyte on OER as well as overall water electrolysis using NiO$_x$ and CoO$_x$ electrodes. Our experimental as well as theoretical macroscopic studies on OER in the RDE configuration clearly revealed reactant switching between OH$^{-}$/H$_2$O occurring at approximately pH 10–11. Below this threshold pH, the oxidation of H$_2$O prevails rather than that of OH$^{-}$ due to the insufficient hydroxide ion activity to reach an appreciable current density, e.g., 10 mA cm$^{-2}$ that approximately corresponds to 10% solar-to-hydrogen efficiency in the solar fuel production systems. For OER via H$_2$O oxidation at near-neutral pH, the presence of buffered species improved the reaction rate most likely by facilitating the removal of generated protons on the electrode surface. In such buffered mild pH conditions, the sensitivity analysis of the OER rate to the identity and molarity of the buffered species, as well as the separately performed study on the properties of the electrolyte from the view point of specific ion effects, indicated that slow mass transport of buffered species largely determined the apparent OER performance, which has been overlooked in the literature. As such, tuning of the electrolyte properties to maximize the flux of buffered species, or electrolyte engineering, was proposed as a powerful concept to realize a highly efficient water splitting device. As a proof of concept, water electrolysis was examined in a two-electrode configuration using a NiMo/NF cathode and a CoO$_x$/NF anode in the optimal electrolyte of 1.5 M K$_2$CO$_3$ at pH 10.1, in which 10 mA cm$^{-2}$ was readily achieved at approximately 1.70 V with an onset voltage less than 1.6 V as well as excellent stability (>20 h). The present interdisciplinary study based on electrochemistry, catalysis, engineering, and specific ion effects sheds light on the strategy of electrolyte engineering for improving the performance of water splitting and, in turn, solar fuel production under more practical conditions, which can be regarded as a great step toward the realization of sustainable material and energy circulation in our society.

Experimental Section

All chemicals were purchased with the following purities from Sigma-Aldrich unless otherwise specified: KOH (99.999%), NaOH (99.99%), K$_2$HPO$_4$ (≥98%), K$_3$PO$_4$ (≥99%), KHCO$_3$ (>99.99%), K$_2$CO$_3$ (99.995%: Aldrich), K$_2$C$_2$O$_4$ (≥99.9%, Aldrich), K$_2$SO$_4$ (99.999%: Aldrich), Na$_2$SO$_4$ (<99.99%: Aldrich), H$_2$PO$_4$ (85 wt% in H$_2$O, 99.999%), H$_3$BO$_3$ (≥99%), citric acid (assay ≥ 100.7%, Fisher Chemicals), H$_2$SO$_4$ (99.999%, Aldrich), Na$_2$MoO$_4$•2H$_2$O (99.99%, NiCO$_3$•6H$_2$O (99.999%: Aldrich), and Co(NO$_3$)$_2$•6H$_2$O (99.999%: Aldrich).

A Ni plate (0.3 mm thickness; 99%+) and Co plate (0.25 thickness; 99.9%) were purchased from Nilaco Corporation. Before each measurement, the plate was washed in 0.1 M HCl, Milli-Q water (18.2 MΩ cm) and ethanol sequentially for 5 min each. Ni and Pt rotating-disk electrodes (RDEs) were purchased from BAS Inc. (0.071 cm$^2$ geometric surface area). Co was deposited on a glassy carbon RDE (0.13 cm$^2$ geometric surface area) by direct current (DC) magnetron sputtering using a Co target (99.95% purity) under an Argon plasma. The Ar flow was held constant at 20 SCCM, the total pressure was 1.33 Pa, and the DC power density was set to 4.94 W cm$^{-2}$ (a power of 100 W applied to a target with a 2-inch diameter). All the RDEs were polished first with 1 μm diamond and then with 0.05 μm alumina (both purchased from BAS, Inc.) prior to each measurement. Ni foam (NF; thickness 1.6 mm, pore size 0.5 mm, 48–52 cells inch$^{-1}$, 7500 m$^2$ m$^{-3}$) was purchased from Nilaco Corporation. NiMo supported on NF electrode was prepared by an electrochemical deposition method.$^{[25,36]}$ NF with a geometric size of 1×1 cm$^2$ was immersed in a bath containing 0.02 M sodium molybdate, 0.04 M nickel chloride and 0.89 M sodium bicarbonate. An electric current of ~77.5 mA was applied to the NF for 30 min. The obtained NiMo electrode was kept in a 0.5 M KOH solution for >15 h. The CoO$_x$/NF electrode was prepared by electrochemical deposition.$^{[33]}$ NF with a geometric size of 1×1 cm$^2$ was immersed in a 0.1 M Co nitrate aqueous solution, and an electric current of ~10 mA was applied for 1 h.

Three- and two-electrode systems were employed for the half-cell and gas quantification studies, respectively. In all the half-cell measurements, a Pt wire and a KCl-saturated Ag/AgCl electrode (ALS Co., Ltd.) were used as a counter electrode and a reference electrode, respectively. Before and during all the measurements, Ar (99.9999%) or O$_2$ (99.9995%) gas was continuously supplied to the cell. Cyclic voltammetry (CV), chronoamperometry (CA), chronopotentiometry (CP) and potentiostatic electrochemical impedance spectroscopy measurements were performed at room temperature (298 K) using a 16-channel, research-grade potentiostat system (VMP3; BioLogic Science Instruments). All the current–potential relationships described in this study were iR-corrected using measured impedance values (≥100 kHz, amplitude 10 mV) unless otherwise specified. For quantification of the gases, a flow-type electrochemical cell was used while running CP at 10 mA. A constant gas flow of Ar (20 SCCM) was supplied as a carrier gas to the gas-tight electrochemical cell, which took generated O$_2$ and injected it into a gas chromatograph (GC) using a sampling loop. The GC (GC-8A; Shimadzu Co., Ltd.) was equipped with a TCD detector and a Molecular Sieve 8A column using Ar as a carrier gas. The Faradaic efficiency was calculated based on the measured O$_2$ generation rate in mol from the GC quantification with respect to the current in mol divided by 4 (O$_2$ evolution is a 4-electron reaction).

Acknowledgements

The research reported in this publication was supported by King Abdullah University of Science and Technology (KAUST). Dr. Ahmed Ziani and Lida Stegenburga are acknowledged for the preparation of the CoO$_x$, RDE, and the NiMo/NF and Co/NF electrodes, respectively. The authors appreciate the kind assistance of Prof. Nikos Hadjichristidis and Keisuke Obata for the viscosity measurements.

Keywords: electrocatalysis • energy conversion • heterogeneous catalysis • oxygen evolution

References


The electrocatalytic oxygen evolution reaction is studied in the conditions relevant to practical solar fuel production (~10 mA cm$^{-2}$) with focuses placed on the identity and molarity of electrolytes, disclosing the significance of mass transport on overall performance in buffered mild-pH conditions.