Towards Versatile and Sustainable Hydrogen Production through Electrocatalytic Water Splitting: Electrolyte Engineering

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Recent advances in power generation from renewable resources necessitate conversion of electricity to chemicals and fuels in an efficient manner. Electrocatalytic water splitting is one of the most powerful and widespread technologies. The development of highly efficient, inexpensive, flexible, and versatile water electrolysis devices is desired. This review discusses the significance and impact of the electrolyte on electrocatalytic performance. Depending on the circumstances under which the water splitting reaction is conducted, the required solution conditions, such as the identity and molarity of ions, may significantly differ. Quantitative understanding of such electrolyte properties on electrolysis performance is effective to facilitate the development of efficient electrocatalytic systems. The electrolyte can directly participate in reaction schemes (kinetics), affect electrode stability, and/or indirectly impact the performance by influencing the concentration overpotential (mass transport). This review aims to guide fine-tuning of the electrolyte properties, or electrolyte engineering, for (photo)electrochemical water splitting reactions.

1. Introduction

The global energy demand can potentially be met by renewable energy supplies: the estimated technical potential for renewable energy sources—geothermal, ocean, wind, biomass, and solar energy— is greater than the current world energy demand.[1] One of the main issues associated with the practical utilization of renewable energy sources is the gap between demand and supply.[2, 3] The intermittent generation of electricity from renewable energy sources requires technologies for storing and releasing energy for practical large-scale applications. One of the promising solutions towards this issue is the electrocatalytic conversion to produce energy carriers. In this context, hydrogen has attracted tremendous attention in this decade[4–7] owing to its extremely high energy density (H₂: 120 MJ kg⁻¹ and gasoline: 44 MJ kg⁻¹).[4, 5]

Hydrogen can be produced from ubiquitous and abundant water by using the electricity generated from renewable energy sources. Electrochemical water splitting has been intensively studied for more than 200 years.[8–13] In 1789, water electrolysis was first reported by van Troostwijk and Deiman.[14] More than a century later, in the 1920s and 1930s, a large number of large-scale electrolysis plants were built in Canada, Norway, and elsewhere.[15] More efficient electrolyzers were developed in the middle of the 20th century.[16–18] The cost breakdown for electrolyzers is available in the literature.[19–21] At the current stage of the process development for water electrolysis, three main objectives have been considered: (1) greater efficiency of large-scale water electrolyzers; (2) water electrolysis in conjunction with renewable energy sources; and (3) integrated photovoltaic (PV) electrolysis.[22] PV electrolysis[23–25] is further categorized into three: (a) photocatalytic water splitting,[26–28] (b) photoelectrochemical water splitting,[29, 30] and (c) PV + electrolyzer configurations.[31, 32]

**Figure 1.** Schematic illustration of (a) photocatalytic water splitting, (b) photovoltaic water splitting, and (c–e) PV + electrolyzer configurations: (c) wired, (d) partially wired, and (e) wireless configurations.

Photocatalytic (Figure 1 a) and photoelectrochemical (Figure 1 b) water splitting directly utilize semiconductor (photon absorber) surfaces for surface redox reactions (hydrogen and oxygen production from water through reduction/oxidation reactions). In these cases, light irradiation on a photon absorber initiates the overall reaction, in which an exciton is generated. After separation of the electron–hole pair, the electron and hole can diffuse to the interface between solid and liquid. Finally, the electron and hole can be transferred into the reduction and oxidation reaction sites, where hydrogen and oxygen evolve, respectively.[22, 23] In contrast, in the PV + electrolyzer configuration, the surface potential, or the Fermi level, of the semiconductor does not equilibrate with the potential of the surface redox reactions. This PV + electrolyzer configuration is
classified into three types: wired (Figure 1c), partially wired (Figure 1d), and wireless configurations (Figure 1e).

Regardless of the type of electrolyzer, the electrochemical reaction performance is one of the most significant components that determines the energy efficiency of the overall system. The water splitting reaction is composed of two half-reactions, namely, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Conventionally, it is well known that the extreme pH of the highly acidic/alkaline conditions can maximize the efficiency. Accordingly, most of the fundamental understanding of water splitting has been established at extreme pH levels. However, when the electrochemical water splitting process is considered with respect to the use of renewable energy sources, factors other than the electrochemical reaction performance have to be considered. In solar fuel production technologies (such as photovoltaic cells conjugated with electrolyzers[33–39], and photoelectrochemical[40, 41] and photocatalytic water splitting[42, 43]), the performance and stability of the photon absorber as well as the overall system performance have to be optimized, which is achieved in less harsh conditions in many cases. Additionally, in the localized energy system that has been proposed as a future method for energy management[42, 43], safety concerns might be overcome under milder conditions, which also contribute to the reduction of the capital cost. Therefore, at the current stage, understanding and improving the water electrolysis performance under milder conditions, for example, at near-neutral pH, is of great importance in the construction of a future sustainable society.

In this review, we discuss electrocatalytic water splitting, with particular focus placed on the “electrolyte”. First, the theoretical aspects of water electrolysis are addressed, in which thermodynamics, kinetics, mass transport, and associated parameters are detailed. Based on the theoretical descriptions, the proposed impact of supporting ions on the reaction is discussed. Then, we separately review the HER and OER; both sections are composed of the following viewpoints: (a) the conventional understanding at extreme pH, (b) the influence of ions at extreme pH, (c) the influence of pH, and (d) the influence of ions at near-neutral pH. In the final section, one example of the utilization of ionic properties is introduced, by which selective hydrogen production in the presence of oxygen is demonstrated.

2. Theoretical Aspects of Water Electrolysis

This section aims to present the fundamentals of water electrolysis, which is essential for interpreting and rationalizing the effects of ions on the water splitting reaction reported in the literature. The theoretical aspects, namely, thermodynamics, kinetics, mass transport, and associated parameters, are detailed. The effects of ions on the reaction, which are speculated based on the theoretical description, are also briefly addressed, which can bridge the theory described in this section and the experimental observations in the following sections.

2.1. Thermodynamics

Overall water splitting is described by Equation (1):

$$2 \text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$$  \hspace{1cm} (1)

The Gibbs free energy and enthalpy of the water splitting reaction under the standard conditions (ambient pressure and temperature) are $\Delta G^0 = 237 \text{ kJ mol}^{-1}$ and $\Delta H^0 = 286 \text{ kJ mol}^{-1}$, respectively.[44] The energy is converted into the standard cell voltage with the following relation [Eq. (2)].[45]

$$\Delta G^0 = nFE^0$$  \hspace{1cm} (2)

in which $n$ is the number of electrons, $F$ is Faraday’s constant, and $E^0$ is the standard cell voltage. With Equation (2), the thermodynamically required voltage to split the water molecule into hydrogen and oxygen is calculated as 1.23 V, which is called the reversible voltage. In particular, in the water electrolysis, the efficiency is typically described in terms of the reaction enthalpy. The enthalpy-based voltage is easily calculated by replacing $\Delta G^0$ with $\Delta H^0$ in Equation (2), which gives us a voltage of 1.48 V, which is referred to as the thermoneutral voltage. As such, efficiencies higher than 100% are attainable if water electrolysis is evaluated between 1.23 and 1.48 V. An efficiency higher than 100% indicates that the heat generated during the reaction is utilized for the water splitting. The effi-
ciency calculated based on the reversible and thermoneutral voltage corresponds to the low and high heating value, respectively.

Water splitting is described by two half-reactions: the HER as the reduction reaction, and the OER as the oxidation reaction. The thermodynamics for the typical half-reaction, for example, Equation (3)

$$\text{O} + n\text{e}^- \rightleftharpoons R$$

(3)

is rationalized by the Nernst equation [Eq. (4)]:

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \left( \frac{a_i}{a_j} \right)$$

(4)

in which $E_{eq}$ is the equilibrium potential, $R$ is the universal gas constant, $T$ is the temperature, and $a_i$ is the activity of species $i$. When Equation (4) is applied to the HER and OER, the following equilibrium potentials ($E_{eq}$) are obtained on the standard hydrogen electrode (SHE) scale under the standard conditions given by Equations (5) and (6):

**HER:** $E_{eq} = -0.059 \times \text{pH}$

(5)

**OER:** $E_{eq} = -0.059 \times \text{pH} + 1.23$

(6)

Importantly, the equilibrium potentials for these reactions shift with the pH on the SHE scale. In contrast, the equilibrium potentials for HER and OER on the reversible hydrogen electrode (RHE) scale become 0 and 1.23 V, respectively, at any pH level because of the scale of the potential shift associated with hydronium ion activity (59 mV per pH shift). The relationship between the pH and reaction performance in the experimental results has to be checked with a great care; for example, the pH-independent performance on the RHE scale is pH-dependent on the SHE scale. Notably, the supporting ions cannot directly affect the thermodynamics, as such ions are neither the reactant nor the product in the water splitting reaction. Nevertheless, the activity of the reactant/product can be altered by the supporting ions in dense electrolyte solutions, as will be described later; this can indirectly alter the thermodynamic potentials. However, the extent of its alteration is usually relatively small and thus negligible (for example, a decrease in the activity or fugacity by 0.1 shifts the potential by only 2.7 mV).

### 2.2. Reaction mechanism and kinetics

Even if the potential of the electrocatalyst is sufficiently shifted beyond the thermodynamic point, the reaction may not always proceed. Appreciable electric currents are attainable only when kinetic overpotential is overcome. This section describes the kinetic aspects of water electrolysis.

In principle, there are two ways to describe the HER in equations: hydronium ion reduction [Eq. (7)] and water molecule reduction [Eq. (8)], depending on the reaction conditions.

$$2\text{H}_2\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{H}_2\text{O}$$

(7)

$$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$$

(8)

The same applies to the OER, which is described by water molecule oxidation [Eq. (9)]:

$$6\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}_2\text{O}^+ + 4\text{e}^-$$

(9)

and by hydroxide ion oxidation [Eq. (10)]:

$$4\text{OH}^- \rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$$

(10)

Both reactions involve proton and charge transfer, and accordingly, two major classifications have been considered to describe the elementary steps of the reaction: the decoupled proton/electron transfer mechanism and the concerted pathway. For the former, proton transfer [PT; Eq. (11)] and electron transfer [ET; Eq. (12)] can be the sole elementary step:

**PT:** $M + \text{H}^+ \rightleftharpoons M\text{--H}^+$

(11)

**ET:** $M + \text{e}^- \rightleftharpoons M^-$

(12)

in which $M$ is the active site. The concerted path, that is, proton-coupled electron transfer (PCET), is simply described by the following step [Eq. (13)]:

$$M + \text{H}^+ + \text{e}^- \rightleftharpoons M\text{--H}$$

(13)

These reaction schemes are presented in Figure 2.

![Figure 2](image)

**Figure 2.** The square scheme for proton-coupled electron transfer. ET = electron transfer, PT = proton transfer, and PCET = concerted proton-electron transfer. Reproduced from Reference [48] with permission from the Royal Society of Chemistry.

The decoupled pathway is more likely the case for the molecular and oxide catalysts than the metallic catalysts as they can hold local positive/negative charge by altering the oxidation state of the metal (center). The proton affinity of the electrode surface is another important factor, which describes the extent to which the ion can approach the surface. For example, when the isoelectric point is higher than the effective surface pH, the surface can be positively charged, which attracts the negatively charged ion to the surface or vice versa.

Inorganic heterogeneous electrodes have been well investigated for both reactions. The HER over metal inorganic electrodes is considered to proceed through the PCET scheme be-
cause a typical metal sustains its metallic state in the cathodic environment (i.e., the HER condition). In the PCET scheme, the following elementary steps are considered for the HER [Eqs. (14)–(16)]:

\[
\begin{align*}
M + H_3O^+ + e^- & \rightarrow M - H + H_2O \\
M - H + H_2O^+ + e^- & \rightarrow H_2 + H_2O + M \\
2M - H & \rightarrow H_2 + 2M
\end{align*}
\] (14) (15) (16)

On the other hand, the decoupled pathway can be considered for molecular catalysts. Figure 3a summarizes the possible pathways and intermediates for the HER by both the decoupled and concerted pathways.

Contrary to the HER, there are four surface states involved in the OER in the PCET scheme: M, MOH, MO, and MOOH.\[46, 49\]

The OER in the PCET scheme is accordingly represented by the following elementary steps [Eqs. (17)–(20)]:\[49\]

\[
\begin{align*}
M + OH^- & \rightarrow M - OH + e^- \\
M - OH + OH^- & \rightarrow M - O + H_2O + e^- \\
M - O + OH^- & \rightarrow M - OOH + e^- \\
M - OOH + OH^- & \rightarrow M + O_2 + H_2O + e^-
\end{align*}
\] (17) (18) (19) (20)

The situation is complicated for the OER because ET or PT can be the sole rate-determining step on the inorganic oxide surface.\[46\] An overall picture of possible pathways is presented in Figure 3b. For detailed descriptions of the rate expression using Tafel analysis, the reader is referred to another article.\[49\]

For both the HER and the OER, there are at least three ways for supporting ions to influence the kinetics:

1) Participation of ions in the reaction scheme: Ions can participate in the surface protonation/deprotonation reaction (PT and/or PCET) because the protonation/deprotonation involves a pure chemical reaction, and a significant influence of the ions is expected, particularly in the decoupled scheme, as reported by Koper.\[46\] The participation of ions in the elementary steps indicate an alteration of the transition state by the ion. In this scenario, the anion that can be protonated/deprotonated impacts the reaction, for example, buffered species such as phosphate and carbonate.

In addition, under some reaction conditions, the water molecule has to be the reactant, irrespective of if the reaction follows a concerted or decoupled pathway, in which the cation can impact the hydrolysis of the water molecule.\[46\] The hydrolysis step, that is, the dissociation of O–H bonding of the water molecule, is facilitated by cations such as alkali metal ions. The charge density of a hydrated cation cluster is a significant factor that influences the cation-assisted hydrolysis step.

2) Alteration of the local pH: Hydronium and hydroxide ions are the direct reactants of the water splitting reaction. Importantly, during the reaction, the local pH near the electrode surface can be completely different from the pH level in the bulk of the solution as a result of consumption/production of these ions. In such cases, the buffering action helps to maintain the local pH, which influences the reaction kinetics. The buffering capacity is a key parameter for maintaining the local pH, which is a function of the nature of the buffered species (pK_a) and the molarity of the ion. The common buffered species are phosphate, carbonate, and borate anions. In addition, the hydrolysis of the water molecule aided by the hydrated cation near the negatively charged electrode surface can theoretically help to maintain the local pH, the extent of which is deter-
mined by the charge density of the hydrated cation cluster (associated with pH) and its molarity.\(^\text{[1]}\)

3) Surface blockage: Generally, the reaction rate is represented, in principle, by the nature and number of active sites; when the ions block the surface through adsorption or noncovalent interactions, the kinetics are altered owing to the change in the number of active sites. Anions are known to adsorb on the surface (specific adsorption) in some conditions, and cations can also block the surface through noncovalent interactions.\(^\text{[52–54]}\)

### 2.3. Mass transport

The catalytic reaction is composed of the surface reaction and mass transport. When the mass transport flux is much faster than the surface reaction rate, the surface kinetics can be accurately addressed; otherwise, the system performance largely depends on the mass transport in the system. The mass transport phenomenon in electrochemistry is classified into three modes:

1) Diffusion: as a result of the gradient of the chemical potential;

2) Migration: as a result of the gradient of the electrical potential;

3) Convection: owing to the imbalance of the forces in the solution.

It is theoretically described by the Nernst–Planck equation (for species \(i\) in the \(x\)-direction [Eq. (21)]):

\[
J_i(x) = -D_i \frac{\partial \phi_i(x)}{\partial x} - z_i F \frac{\partial \phi_i(x)}{\partial x} - a_i \nu(x)
\]

in which \(J\) is the flux, \(D\) is the diffusion coefficient, \(z\) is the charge number, and \(\nu\) is the velocity of the forces in the solution.\(^\text{[55]}\) The first, second, and third terms on the right-hand side of the equation represent the diffusion, migration, and convection, respectively.

The diffusion term in Equation (21), that is, Fick’s law, is generally applicable in combination with the Nernst-type diffusion model, by which the diffusion flux is expressed as Equation (22):

\[
J_{\text{diffusion}} = -D_i \frac{\partial \phi_i(x)}{\partial x} - D_i (a_i - a_s)
\]

in which \(\delta\) is the diffusion layer thickness, and the indices \(b\) and \(s\) refer to the bulk and surface, respectively. The migration term is derived from the drift of the charged species, that is, the second term of Equation (21) is determined from the following relationships [Eqs. (23) and (24)].\(^\text{[56]}\)

\[
J_{\text{migration}} = u \frac{\partial \phi_i}{\partial x}
\]

(23)

(24)

in which \(u\) is the ion mobility. Most importantly, both the diffusion and migration terms are predominantly determined by the diffusion coefficient, as observed in these equations.

In the framework of the Stokes–Einstein model, the diffusion coefficient is described by Equation (25):

\[
D = \frac{kT}{3\pi \eta d_i}
\]

(25)

in which \(k\) is the Boltzmann constant, \(d\) is the effective diameter of the ion in the hydrated form (Stokes diameter), and \(\eta\) is the viscosity of the solution.\(^\text{[55]}\) Of note, with Equations (23), (24), and (25), the solution resistance is derived as Equation (26):

\[
R = \frac{K_{\text{cell}} 3\pi \mu d_i}{2\eta \epsilon a_i}
\]

(26)

in which \(K_{\text{cell}}\) is the cell constant and \(\epsilon\) is the elementary charge.\(^\text{[55, 56]}\) The cell constant is a system-specific value that depends on the electrode geometry and the gap between the electrodes.\(^\text{[33]}\) Overall, the following parameters can thus be considered to govern the mass transport flux:

1) effective size of the species;

2) viscosity of the solution;

3) activity (or fugacity for gases) of the species.

These values are dependent on the electrolyte properties; and thus, the supporting ions drastically impact the mass transport during the reaction. The details of these parameters are discussed in the next section.

**Rotating disk electrode (RDE) configuration:** A well-developed configuration for the study of the mass transport in electrochemical systems is the RDE configuration. In the RDE configuration, the diffusion and convection flux is theoretically deduced from the following Levich equation [Eq. (27)].\(^\text{[45]}\)

\[
j_i = 0.62nF\omega^{1/2} \nu^{-1/6} D^{2/3} \delta a_i
\]

(27)

in which \(j_i\) is the limiting diffusion current (the Levich current), \(\omega\) is the rotation speed of the disk electrode, \(\nu\) is the kinematic viscosity of the solution, and \(\delta a_i\) represents the activity difference between the surface and bulk. From Equations (22) and (27), Equation (28) is obtained for the diffusion layer thickness:

\[
\delta = 1.62D^{1/3} \nu^{1/6} \omega^{-1/2}
\]

(28)

Basically, in the RDE configuration, the mass transport is well defined by accurately controlling the diffusion layer thickness, as observed in Equation (28). Notably, the diffusion layer thickness in the absence of any hydrodynamic motion in the system is 0.1–0.5 mm, which is orders of magnitude greater than that in the RDE configuration.
2.4. Molarity, activity, and fugacity

The activity and fugacity of the species are directly involved in the thermodynamics, kinetics, and mass transport. This section briefly outlines how the activity and fugacity of the species can be addressed theoretically and practically.

The activity of the ions in the electrolyte solution is represented by the product of the concentration and the mean activity coefficient. The mean activity coefficients of some aqueous electrolytes are summarized in Table 1.[44, 57]

The mean activity coefficient can theoretically be obtained by the Debye–Hückel theory at infinite dilution for a simple electrolyte [Eq. (29)].

$$\ln \gamma_i = -\frac{z_i^2 e^2}{2 kT \varepsilon_0 b}$$  

(29)

By considering the effective ion size, the theory can be extended, which is applicable up to approximately 0.1 mol L\(^{-1}\) [Eq. (30)].

$$RT \ln \gamma_i^* = -\frac{N_A z_i^2 e^2}{8 \pi \varepsilon_0 b} \left[\frac{1}{\varepsilon_0}\right]$$  

(30)

In denser solutions, hydration needs to be considered, and the following further extended form was proposed [Equation (31)].

$$\ln \gamma_i = \ln \gamma_i^* - \ln \frac{p + q + 5 - h}{p + q + 5} - \frac{h}{p + q} \ln \gamma'_w$$  

(31)

In Equations (29)–(31), \(\varepsilon_0\) denotes the permittivity in the solution and vacuum, respectively, \(b\) is the Debye length, \(N_A\) is Avogadro’s number, \(p, q, S,\) and \(h\) define the number of cations, anions, water molecules, and water molecules used for hydration, and \(\gamma'_w\) represents the activity coefficient of water.

Although the Debye–Hückel theory and its extension have been identified as promising tools to quantitatively analyze the coefficient, the electrostatic interaction is overemphasized, and other parameters, such as water affinity and volumetric changes, are overlooked. Particularly, a quantitative theoretical discussion of the mean activity coefficient for different ions is under debate, and is thus not practical. Nevertheless, on the basis of the “like sees like” and “matching water affinity” concepts, a qualitative discussion can be attempted.

The dissolution of gases depends on the identity and molarity of ions, which indicates that there are interactions among the solute, solvent, and gas. As such, a further rationalization of the solubility of the gases is clearly more complicated, and it falls outside of our scope here. For details of such “specific ion effects”, the readers are referred to other articles.

### Table 1. Mean activity coefficient of various solutions. Data taken from References [44] and [57].

| Molarity [mol kg\(^{-1}\)] | HClO\(_4\) | KOH | KCl | KH\(_2\)PO\(_4\) |
|---------------------------|---------|-----|-----|----------------|
| 0.1                       | 0.803   | 0.798 | 0.770 | 0.731         |
| 0.3                       | 0.768   | 0.742 | 0.688 | 0.602         |
| 0.5                       | 0.769   | 0.732 | 0.649 | 0.529         |
| 1.0                       | 0.823   | 0.756 | 0.604 | 0.421         |
| 2.0                       | 1.055   | 0.888 | 0.573 | -             |

Figure 4 summarizes the “matching water affinity” concept.[61] The concept correlates the ion size with the mean activity coefficient based on a consideration of the hydration sphere. The ions can be categorized into two types:

1) Kosmotropes: with strongly hydrated and large hydration spheres;
2) Chaotropes: with weakly hydrated and small hydration spheres.

The ions associate with other ions in the same group, and the associated hydrated ion pairs reduce the mean activity coefficient.

The fugacity of a gas can be estimated as the gas solubility. The solubility of various gases in a variety of electrolytes has been experimentally investigated, and Equation (32), known as the Sechenov equation, has been proposed:

$$\log \left( \frac{C_{e,0}}{C_e} \right) = KC_s$$  

(32)

in which \(C_{e,0}\) represents the gas solubility in pure water, \(C_e\) denotes the gas solubility in the electrolyte solution, \(K\) is the molar salt concentration, and \(S\) is the Sechenov constant, which depends on the salt, gas, and temperature. This equation was later extended to Equation (33):

$$\log \left( \frac{C_{e,0}}{C_e} \right) = \sum (h_i + h_o) C_s$$  

(33)

in which \(h_i\) and \(h_o\) are constants that depend on the ion and gas, respectively. For the system with larger values of these constants, the solubility becomes exponentially smaller as the solute concentration increases. Some examples of these constants are listed in Table 2.

The dissolution of gases depends on the identity and molarity of ions, which indicates that there are interactions among the solute, solvent, and gas. As such, a further rationalization of the solubility of the gases is clearly more complicated, and it falls outside of our scope here. For details of such “specific ion effects”, the readers are referred to other articles.
### 3. Hydrogen Evolution Reaction (HER)

Electrochemical water splitting involves two half-reactions, namely, HER and OER. This section describes the HER in various electrolytes, and the OER will be discussed in the next section. The extreme pH conditions (highly acidic/alkaline pH) will be focused on first, followed by the discussion of the influences of supporting ions under these conditions. Later, the discussion is further extended to the influences of pH on the HER, and then, we describe the impacts of ions (particularly, buffered species) at near-neutral pH.

#### 3.1. HER at extreme pH: general aspects and introduction to the influence of ions

The industrialized water electrolyzers operate under extreme pH conditions, for example, pH = 0 in membrane electrode assembly form or 6.0–8.0 mol L\(^{-1}\) KOH, \(^{[8,72]}\) which minimizes the ohmic loss in the system (maximizes the migration of ions). Accordingly, most studies dedicated to the HER have been conducted in highly acidic \(^{[73-80]}\) and 0.1–1.0 mol L\(^{-1}\) alkaline \(^{[76-83]}\) electrolyte solutions. This section aims to present the general aspects of the HER under the extreme pH conditions, based on which the significance of the ionic effects will be introduced.

In acidic environments, hydronium ion reduction [Eq. (7)] occurs, \(^{[84]}\) in which lower pH levels (higher hydronium ion activity) are kinetically favored because no bond dissociation is involved. In alkaline electrolytes, a hydroxide ion activity of approximately 0.1 mol L\(^{-1}\) maximizes the HER performance by water molecule reduction over a Pt electrode. \(^{[84,85]}\) The reason for the performance maxima in alkaline media has not been clarified; however, some hypotheses have been proposed, including an influence of hydroxide ions on the surface-adsorbed hydrogen bond strength, a decrease in the solubility of hydrogen in strongly alkaline media, \(^{[84]}\) or simply, a decrease in the water activity with increasing hydroxide ion activity.

In both pH scenarios, the reaction intermediate of the HER is H adsorbed on the surface (M–H, where M represents the surface site). The strength of the binding between the intermediate and the surface is highly correlated with the reaction performance. When the HER performance (the mass activity or exchange current density) for a variety of materials is summarized with respect to the M–H binding energy, a volcano-shaped trend is obtained in both acidic \(^{[86-88]}\) and alkaline \(^{[88,89]}\) conditions, which is a typical example of the Sabatier principle. \(^{[90,91]}\) Noble metals, such as Pt, Pd, and Rh, which are scarce and expensive elements, are located at the top of the volcano plot. \(^{[92]}\) A classic approach to developing an active electrode with earth-abundant elements on the basis of the Sabatier principle is by mixing elements with lower and higher intermediate binding energies. A consistent example is Ni–Cu, which shows a greater HER performance than Ni and Cu in alkaline conditions. \(^{[93–97]}\) Another promising material is Ni–Mo, \(^{[98–101]}\) however, there have been issues associated with its low dispersion of the active surface. A breakthrough study in this context was reported in 2013, in which highly dispersed Ni–Mo nanopowders were successfully prepared and utilized. \(^{[102]}\) Indeed, these non-noble metal-based materials are promising candidates under alkaline conditions for the HER, but they readily dissolve in acidic solutions. As discussed later, these bimetallic systems may not simply depend on a single M–H binding energy as an activity descriptor if the dual sites are used for hydrogen evolution.

In 2005, inspired by hydrogen-producing enzymes, a density functional theory (DFT) calculation predicted that the edge sites of MoS\(_2\) would be active for the HER, which could be an alternative to the Pt group in acidic conditions. \(^{[92]}\) In 2007, it was experimentally confirmed that the edge sites of MoS\(_2\) are clearly the active sites for the HER, which can reach \(-10\) mA cm\(^{-2}\) at an overpotential of 200 mV. \(^{[104,105]}\) This finding has opened up new classes of electrode material for the HER: transition metal sulfides, carbides, nitrides, phosphides, and phosphosulfides. \(^{[106–111]}\)

The use of the volcano relationship to improve the HER performance with cost-effective materials has been successful in many cases; however, it has recently been emphasized that there is an inconsistency in the element order in the volcano behavior when the current density versus M–H bond strength is plotted for acidic and alkaline solutions. \(^{[88]}\) At alkaline pH, the water molecule is the reactant and proton source. \(^{[112]}\) Therefore, the HER sequence must involve an O–H bond dissociation step of the H\(_2\)O reactant, which is kinetically sluggish, as easily understood from the thermodynamic expectation to activate highly stable water molecules. In contrast, in acidic environments, the proton is used directly as a reactant. \(^{[113]}\) These rational suggest that not only the conventional M–H binding energy but also other factors associated with the processes that occur at the interface (for example, the kinetics of O–H bond dissociation) have to be accurately considered to account for the observed HER performance. \(^{[114]}\) As will be observed in the subsequent sections, not only the difference in the reactant (hydronium ion or water molecule) but also the supporting ions have a critical impact on the electrochemical reaction performance.

#### 3.2. The influence of ions on the HER at extreme pH

For the electrochemical reaction, not only the electrode material but also the reaction conditions have a critical impact on the performance. Some studies reported the influence of ions on the reaction performance on the microscale in addition to typical adsorption phenomena, which will be reviewed in this section.

| Cation | \(h^+\) | Anion | \(h^-\) | Gas | \(h_0\) |
|--------|---------|-------|-------|-----|--------|
| H\(^+\) | 0.0000  | OH\(^-\) | 0.0918 | H\(_2\) | -0.0176 |
| Li\(^+\) | 0.0687  | Cl\(^-\) | 0.0381 | O\(_2\) | 0.0000 |
| Na\(^+\) | 0.1079  | Cl\(_2\)\(^-\) | 0.0549 | Ar | -0.0026 |
| K\(^+\) | 0.0929  | H\(_2\)PO\(_4\)\(^-\) | 0.1009 | CO\(_2\) | -0.0183 |
| Cs\(^+\) | 0.0582  | HPO\(_4\)\(^2-\) | 0.1559 | N\(_2\) | -0.0002 |

Table 2. Ion-specific parameters \(h\) and gas-specific parameters \(h_0\) at 298 K [m\(^2\)kmol\(^{-1}\)]. Taken from Reference \([70]\).
The HER proceeds through water molecule reduction at alkaline pH,[49] where the dissociation of the O–H bond in the water molecule (or the Volmer step for water molecule reduction) is kinetically sluggish.[98,112] When the Pt metal electrode was decorated with Ni(OH)₃ islands, a drastic improvement in the HER performance was observed, plausibly because the water dissociation was facilitated at the interface around the Ni(OH)₃ islands.[50,112] This finding suggests the significance of switching the reactant, which is associated with the reaction pH. Interestingly, when a small amount of LiOH (1 mmol L⁻¹) was added to the 0.1 mol L⁻¹ KOH electrolyte, the HER performance over the Ni(OH)₂–Pt electrode was further improved by a factor of approximately two. The improvement was ascribed to the presence of a complex, Ni(OH)₂–Li⁺−OH−–H₂O, which presumably enhanced the probability of the water dissociation (Figure 5).[50] A similar improvement in the HER performance was reported over Ir and Ru.[113] In the order of supporting cations, K⁺ < Li⁺ < Ba²⁺ in 0.1 mol L⁻¹ KOH electrolyte. For more details on this subject, the readers are referred to the recent review published by the group.[114] These observations indicate that the local hydrolysis phenomenon (O–H bond dissociation) on the negatively charged surface is facilitated by a hydrated cation cluster, which is a function of the charge density of the ion cluster. Interestingly, under similar acidic conditions, cations were shown to influence the HER performance in 0.05 mol L⁻¹ H₂SO₄ + 0.05 mol L⁻¹ M₂SO₄, M = Li⁺ ≈ Na⁺ > K⁺ > Rb⁺ ≈ Cs⁺,[115] although protons are believed to be the direct reactants. As such, local hydrolysis cannot be used to explain this observation. A scientific explanation for the observation has not been identified, and thus, further studies are required.

There are a couple of examples that demonstrate the significant influence of the supporting ions that coexist in the electrolyte on the reaction performance. Importantly, the effect of these ions on the overall performance depends on the reaction conditions, for example, the order and extent of the ion effects differ at different pH, even on the same electrode. A quantitative description of the complex ion effect will certainly lead to the development of an efficient system for electrochemical energy conversion.

### 3.3. The influence of pH on the HER

The difference in the reactant (hydronium ion vs. water molecule) induces huge differences in the reaction performance, and switching the reactant is predominantly associated with the reaction pH. This section systematically discusses influences of pH on the HER performance. Conventionally, near-neutral pH conditions have been considered as unfavorable for the electrochemical water splitting reaction, and, until recently, little attention has been paid to these conditions.[116–118] We thus lack a clear fundamental understanding of the reaction under these conditions.

A systematic study on the influence of pH on the HER was reported by Markovic and co-workers in 2013.[118] In their study, 0.1 mol L⁻¹ KClO₄ (unbuffered) was used as a supporting electrolyte across the entire pH range (pH 1–13), and a single-crystal Pt (111) electrode was employed as a model electrode. The linear sweep voltammograms (LSVs) are depicted in Figure 6a.

*Figure 5. Schematic representation of water dissociation, formation of M–H₂O intermediates, the subsequent recombination of two H₂O atoms to form H₂ (magenta arrow), and OH⁻ desorption from the Ni(OH)₃ domains (red arrows) followed by the adsorption of another water molecule on the same site (blue arrows). Water adsorption requires the concerted interaction of O atoms with Ni(OH)₃ (broken orange spikes) and H atoms with Pt (broken magenta spikes) at the boundary between the Ni(OH)₃ and Pt domains. The Ni(OH)₂-induced stabilization of the hydrated cations (AC⁻) (broken dark blue spikes) likely occurs through noncovalent (van der Waals-type) interactions. The hydrated AC⁺ can interact further with water molecules (broken yellow spikes), which alters the orientation of water as well as the nature and strength of the interaction of the oxide with water. Reproduced from Reference [50] with permission from AAAS.*

*Figure 6. Linear sweep voltammograms over (a) Pt(111) and (b) Au(111) disk electrodes in 0.1 mol L⁻¹ potassium perchlorate at various pH levels (1–13) at a disk-rotation speed of 1600 rpm, recorded at a scan rate of 50 mV s⁻¹. Reproduced from Reference [118] with permission from Macmillan Publishers Ltd (copyright 2013).*
in acidic solutions of pH \( \leq 2 \) and at alkaline pH (pH > 10), only sharply increasing cathodic currents are obtained. In contrast, a two-step reduction is observed at near-neutral pH levels. The first reduction is observed below approximately 0 V on the RHE scale, which reaches a constant value at approximately –300 mV on the SHE scale, and a further increase in the reduction current is obtained below approximately –700 mV on the SHE scale.

The interpretation of the influence of pH on the HER current–potential relationship (Figure 6) is still under debate. Mayrhofer and co-workers reported that the Nernst–Planck equation well reproduces the \( j–E \) relationship for the Pt electrocatalyst with the assumption of electric currents determined by the diffusion limitation of \( H^+ \) and \( OH^- \). In their calculation, the following equilibrium is also assumed [Eq. (34)]:

\[
K_w = [H_2O]_{\text{diss}}/[H_2O]_{\text{diss}}
\]

in which \( K_w \) is the equilibrium constant of water molecule dissociation into formation from a proton and hydroxide ion. Simply, the fact that the calculation based on the Nernst–Planck equation matches with the experimental observation indicates that the thermodynamics and mass transport are solely responsible for the \( j–E \) relationship of the HER/HOR when the kinetically facile Pt electrode is used. In this framework, the two-step reduction for the HER at near-neutral pH can be rationalized by the local pH gradient, and all of the cathodic events originate from the hydronium ion reduction.

On the other hand, Markovic and co-workers claimed that a microkinetic description, in conjunction with Fick’s law for the HER (hydronium ion reduction and water molecule reduction), and the HOR (hydrogen oxidation with water molecule and hydroxide ion) matches the experimental observation. Similarly to the previous case, the initial reduction events at a lower overpotential and near-neutral pH are attributed to the diffusion-limited hydronium ion reduction. However, in their scenario, a further increase in the reduction currents below approximately –700 mV versus SHE at near-neutral pH levels is attributed to water molecule reduction at near-neutral pH, which kinetically does not depend on the pH. In their study, Au(111) was also investigated under identical conditions, which showed a similar two-step reduction at near-neutral pH, as depicted in Figure 6b. As Au is not as active as Pt, the thermodynamics and the consideration of diffusion cannot solely explain the observation, and the contribution of kinetics cannot be ignored. Accordingly, the second reduction event at a larger overpotential in the near-neutral pH solutions should be explained by water molecule reduction, which kinetically does not depend on the pH. The proposed reduction of the water molecule is also supported by the observations for polycrystalline Ni and Ni-modified Pt. Furthermore, the difference between the performance for the HER observed in acidic and alkaline environments clearly suggests the significance of kinetics in the HER even when Pt is used, which implies the occurrence of water molecule reduction. Importantly, in both cases, the two-step reduction at near-neutral pH is rationalized by the lack of hydronium ion activity in close proximity to the surface. In particular, because the hydronium ion activity at near-neutral pH is insufficient to result in substantial reaction rates, for example, –10 mA cm\(^{-2}\), the cathodic reaction is limited by the mass transport of the hydronium ion as the overpotential increases. This rationale leads to one strategy for improving the HER at near-neutral pH: maintaining the local pH to avoid the diffusion limitation of hydronium ions.

### 3.4. The influence of ions on the HER at near-neutral pH

There have been a couple of studies reported regarding the HER at near-neutral pH in buffered solutions that function to maintain the local pH level. Experimentally, it was clearly demonstrated that the use of a buffered solution as a “supporting electrolyte” successfully prevented the diffusion limitation of hydronium ions at near-neutral pH levels. Figure 7 shows the polarization curves obtained by using Pt in various electrolytes (including acetate, phosphate, and carbonate buffer) on the RHE scale.

![Figure 7. Steady-state positive-going sweeps of the HER polarization curves of Pt obtained in selected \( H_2 \)-saturated buffered electrolytes. The sweep rate is 10 mV s\(^{-1}\) and the rotating speed is 1600 rpm. The polarization curves have been corrected for the solution resistance. Adapted from Reference [80].](image)

A sharp increase in the reduction current was obtained with overpotentials in buffered solutions at near-neutral pH. In the study, the M–H binding energy in various conditions was also determined by cyclic voltammograms. The investigation of the HER performance (the potential at \( \sim 1 \) mA cm\(^{-2}\)), in conjunction with the M–H binding energy strength, indicated that both the HER performance and M–H binding energy shift monotonically with the solution pH. Such an observation is in agreement with the conventional view of the reaction (the activity–binding energy relation: the Sabatier principle). Notably, when the buffered solution is used as the “supporting electrolyte”, the concentration of the electrolyte has to be carefully selected to at least provide a sufficient buffering capacity to the system. A careful investigation by Mayrhofer and co-workers clarified the requirement: 10 mM is sufficient to prevent altera-
tion of the local pH up to 1 mA cm$^{-2}$. Other than maintaining the local pH, it should be noted that the presence of buffered species can introduce additional parameters required for describing the electrocatalytic kinetics, as discussed in Section 2. As noted by Markovic and co-workers, an additional chemical equilibrium can be introduced to the surface reaction because hydronium and hydroxide ions are the reactants/products, which can react with supporting ions through protonation/deprotonation steps. This rationale indicates that the choice of buffered species can have a drastic impact on the reaction performance. In addition, a recent theoretical study by Rossmeisl and co-workers predicted a large contribution from the entropic barrier present for the HER, in which electrolyte ions should play a significant role.

3.5. The influence of ions on the HER at near-neutral pH under densely buffered conditions

The use of buffering action leads to improved HER performances at near-neutral pH, as discussed in Section 3.4. However, the study focused on a low current density region (ca. 1 mA cm$^{-2}$) which is much smaller than the target for solar fuel production (8.2 mA cm$^{-2}$ or 10 mA cm$^{-2}$). Thus, as a next step, studies of the HER in more practical conditions are necessary. This section introduces our recent work at near-neutral pH, which shows the significance of ions for the HER in buffered conditions with regards to the mass transport.

Conventionally, two possibilities are proposed for rationalizing the improved HER observed in buffered conditions in the literature: phosphate behaves as a proton source by either 1) releasing its proton in close proximity to the surface or 2) being directly decomposed on the surface. In both cases, the activity of phosphate in the solution is presumably correlated with the kinetics, indicating that a higher phosphate concentration improves the HER performance. This rationale had previously been confirmed by experiments only up to 0.5 mol L$^{-1}$. Of note, the salt added to the system is typically up to 0.5 mol L$^{-1}$ to improve the conductivity of the solutions. These considerations predict that further increasing the solute concentration of buffered solutions above 0.5 mol L$^{-1}$ would result in improved HER performance.

Thus, the impact of the phosphate concentration on the HER over a wide concentration range was investigated. In Figure 8, the overpotential distribution for the HER when using a Pt disk electrode in 0.5–3.0 mol L$^{-1}$ sodium phosphate solution at pH 5 is depicted (at −10 mA cm$^{-2}$). In the low concentration regime, the HER performance increased with increasing concentration, then reached a maximum at approximately 2.0 mol L$^{-1}$, and decreased in more highly concentrated solutions, which is a clear volcano-shaped trend. In general, there are at least three critical parameters that affect the overall performance of an electrochemical reaction:

1) Kinetic overpotential: the surface reaction;
2) Concentration overpotential: the concentration gradient;
3) Ohmic loss: the solution resistance.

The contribution of each component can be quantified by a rational elucidation of the reaction performance.

In a typical chemical engineering model, the chemical reaction can be represented by the mass transport and the surface reaction, with the mass balance considered. Figure 9 shows a schematic illustration of the model that describes the HER in densely buffered conditions.

The protonated species (HA; for example, a monobasic phosphate) is equilibrated with the counter anion (A$^−$; for example, a dibasic phosphate) and proton in the bulk of the electrolyte. The protonated species reach the surface of the electrode, where they are deprotonated for the surface reaction, and the produced deprotonated species then diffuse back to the bulk of the electrolyte. By considering both the kinetics and mass transport, the following continuity equation can be developed, which describes the mass transport and consumption/regeneration of buffered species [Eq. (35)]:

$$\frac{\partial a_{HA,b}}{\partial t} = \frac{D_{HA}}{\delta} (a_{HA,b} - a_{HA,s}) + (-r_{HER} + r_{HOR})$$  (35)
The calculation results are presented quantitatively in Figure 8. The analysis predicts that the overall performance is strongly dependent on the concentration overpotential in buffered near-neutral pH conditions: the concentration overpotential exceeds 50%, and the kinetic overpotential accounts for less than 10% of the overall potential. These characteristics suggest that the HER in buffered near-neutral pH conditions is predominantly governed by the mass transport of weak acid species. The mass transport during the reaction is not related to the electrode identity but is solely determined by the electrolyte properties; therefore, it is inferred that fine-tuning of the electrolyte, or electrolyte engineering, to minimize the concentration overpotential leads to the improved apparent HER performance in the buffered near-neutral pH solutions. The associated electrolyte properties are as follows:

a) diffusion coefficient:
   i) effective ion size (hydrated ion size);
   ii) viscosity;

b) mean activity coefficient.

The significance of electrolyte engineering at near-neutral pH for the HER is summarized in Figure 10.

**Figure 10.** Experimentally observed Ir-free overpotential (kinetic and concentration overpotentials) at 10 mA cm$^{-2}$ over a polycrystalline Pt disk electrode in 0.5 mol L$^{-1}$ sodium sulfate (pH 4.0), 0.1 mol L$^{-1}$ NaH$_2$PO$_4$ (pH 4.4), and 1.5 mol L$^{-1}$ potassium phosphate solution [K$_2$H$_2$PO$_4$; KHPPO$_4$; K$_2$HPO$_4$; H$_2$PO$_4$; NaH$_2$PO$_4$], recorded at a scan rate of ~50 mV s$^{-1}$, at a disk rotation speed of 3600 rpm and at 298 K. Adapted from Reference [127].

When a typical supporting electrolyte, such as sodium sulfate solution, is used at pH 5, a two-step reduction is observed (Figure 6a), in which an overpotential of approximately 500 mV is required to achieve 10 mA cm$^{-2}$. Once the significance of the reactant switching is realized, the buffered solution can be used as a “supporting electrolyte”. In this case, 10 mA cm$^{-2}$ is achieved at an overpotential of approximately 120 mV in 0.1 mol L$^{-1}$ NaH$_2$PO$_4$ when using a Pt disk electrode. The HER in the solutions is predominantly governed by the significant concentration overpotential, which can be minimized by fine tuning of the electrolyte properties. In the optimized electrolyte of 1.5 mol L$^{-1}$ potassium phosphate (monobasic/dibasic = 80:20), an overpotential of only 40 mV is sufficient to achieve 10 mA cm$^{-2}$. Under these conditions, the performance is much better than that in alkaline solution (0.1 mol L$^{-1}$ KOH), and it is almost comparable to that in acidic solution (0.1 mol L$^{-1}$ HClO$_4$). These findings demonstrate the promise of near-neutral pH conditions for the HER. It should be emphasized that the solution resistance originates from the migration of ions, which is highly correlated with the diffusion of ions, as discussed in Section 2. Thus, as expected, the electrolyte composition that maximizes ion diffusion (optimum conditions for the HER in buffered conditions) also minimizes the solution resistivity in buffered near-neutral pH conditions.

This section reviews an attempt to understand and elucidate the complicated influence of ions and the application of this knowledge to improve the HER performance. The findings summarized in this section shed light on the newly developing field of water splitting at near-neutral pH, which is a critical aspect in the construction of a sustainable society in the future. It should be emphasized that the significance of the electrolyte properties seems critical in systems that involve electrochemical reactions. In integrated solar fuel production systems of photocatalytic and photoelectrochemical water splitting, it is possible that mass transport is the limiting factor of the overall performance, particularly in buffered conditions.

### 4. Oxygen Evolution Reaction (OER)

The OER is the other half-reaction that composes the water splitting reaction, which typically requires a greater overpotential to achieve a substantial reaction rate than the HER. This section reviews the general aspects of the OER at extreme pH, which is followed by a discussion on the influences of ions at various pH levels on its performance.

#### 4.1. OER at extreme pH: general aspects and introduction to the influence of ions

The OER performance is also correlated with the volcano-shaped trend for various specific activity descriptors (the Sabatier principle). The correlation between the mass activity for the OER and the enthalpy of the transition from a lower to a higher oxide was initially reported in 1984 in which IrO$_2$ and RuO$_2$ are at the top of the volcano. As introduced in Section 2, the OER through the PCET scheme involves four surface intermediates: M, MOH, MO$_2$, and MOOH. A recent computational study has revealed that scaling relationships exist among the binding energies of these species, which can be represented by the number of outer electrons. Owing to this relationship, the volcano-shaped trend is obtained when the OER performance is plotted against only one M-adsorbate descriptor. Similarly, a volcano plot is reported, for example, among the perovskite-structured oxides, which is correlated with the $e_g$ electron. Among the oxides composed of earth-

abundant materials, nickel–iron (oxy)hydroxide has been recently reconfirmed as a promising electrode in alkaline media. In 2016, superior OER performance was revealed for the Ni–Co–W mixed oxyhydroxide, which requires an overpotential of only 191 mV to reach 10 mA cm\(^{-2}\) in 1.0 mol L\(^{-1}\) NaOH and for Au-supported NiCoO\(_x\) which reaches 10 mA cm\(^{-2}\) at an overpotential of 271 mV in 1.0 mol L\(^{-1}\) NaOH.

In principle, the volcano-shaped relationship indicates that a simple oxide composed of earth-abundant elements cannot outperform IrO\(_x\) and RuO\(_x\) in OER performance. One strategy to achieve a higher performance than the volcano limit is the introduction of inhomogeneity in the active sites because the volcano relationship is predicted for the single-site mechanism. One successful example of this is the addition of a noble metal to the transition metal oxide.

Improving not only the activity but also the stability is a challenge for OER electrodes, particularly in acidic and near-neutral pH environments. A trade-off between the activity and stability is reported for the OER in acidic environments, even for the most active oxides, IrO\(_x\) and RuO\(_x\). As expected from the Pourbaix diagram shown in Figure 11, the cationic state of the metals is thermodynamically more favored at lower pH levels, which is consistent with the nature of their dissolution into solution. In addition to the influence of pH (the activity of free H\(^+\)) on the OER, the supporting ions that coexist in the electrolyte have been reported to have a significant impact on the performance, which needs to be considered to rationalize and improve the OER performance, as will be discussed in the following sections.

4.2. The influence of ions on the OER at extreme pH

Contrary to the HER, the OER does not proceed on the metallic surface but on the oxide surface. The oxide can sustain local positive/negative charges on the surface, as discussed in Section 2, which allows decoupled pathways (i.e., PT and ET) to occur. An example of the decoupled ET and PT path for the OER is reported by Koper, Smith, and co-workers. In situ surface-enhanced Raman spectroscopy was employed in their study, the spectra of which indicate the presence of superoxo-type species formed by the PT step. Such a decoupled pathway not only complicates the reaction mechanism itself but also results in ions participating in the reaction scheme.

Indeed, a significant influence of the ions has been reported for the OER; the OER performance in 0.1 mol L\(^{-1}\) of simple alkali hydroxide solutions follows the order K\(^+\) < Na\(^+\) < Cs\(^+\) over Ba\(_2\)Sr\(_2\)Co\(_5\)Fe\(_2\)O\(_{19}\) and IrO\(_x\). Also, for MnO\(_x\) electrodes, the same order was reported. It should be noted that the order of the cations for the OER (greater performance with the cation that has a larger atomic number) is opposite to that of the HER (greater performance with the cation that has a smaller atomic number), which clearly indicates the different mechanisms present for these cases. It has been proposed that hydrated ion clusters M\(^+\) (H\(_2\)O)\(_x\) anchored on the surface are present, which modify the reaction intermediate species. A similar mechanism has also been proposed for the hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR), and alcohol oxidation. However, when the OER is evaluated in 0.05 mol L\(^{-1}\) H\(_2\)SO\(_4\) containing an alkali metal sulfate, the performance is minimally altered (except for Rb) over Pt(111), therefore, the impact of ions largely depends on the material and reaction conditions, that is, the pH, particularly for the OER.

4.3. The influence of ions on the OER at near-neutral pH

As described in the Introduction, the development of water electrolysis systems under the milder conditions of the near-neutral pH has attracted tremendous attention in this decade. Its success greatly relies on the development of active and stable OER electrodes. This section reviews the studies on the OER at various pH levels, with a focus on near-neutral pH, where significant effects of ions on the reaction performance will be discussed.

Historically, noble metal oxides such as IrO\(_x\) and RuO\(_x\) have been recognized as outstanding electrodes for the OER in both acidic and alkaline environments. In 2005, the IrO\(_x\) electrode was adopted for the OER at near-neutral pH levels (0.1 mol L\(^{-1}\) KNO\(_3\); pH 5.3) over Mn\(_2\)O\(_3\) and IrO\(_x\). However, the high-cost and scarcity of such noble metals is considered a huge issue, which has driven the exploration of non-noble metal-based OER electrodes at near-neutral pH. Among the more cost-effective elements, Co\(_x\) and Ni\(_x\) have been the subject of research studies in this decade.

A pioneering work was reported by Nocera and co-workers in 2006, which demonstrated a stable OER performance over a Co-based material in phosphate solution at near-neutral pH levels. In their study, a current density of approximately 1.0 mA cm\(^{-2}\) was achieved at 1.24 V versus SHE at pH 7.
Their follow-up study proposed a self-healing mechanism, in which the cobalt cation released into the solution can be redeposited on the electrode during the OER that occurs when the phosphate is present. Following this study, some groups attempted to elucidate and further improve the performance of Co-based materials at near-neutral pH conditions. Dau and co-workers investigated the OER performance of Co electrodes in various electrolytes (phosphate, carbonate, glycine, TRIS, acetate, HEPES, chloride, borate, and MES), which revealed a similarity between the OER–pH relationship and pH titration (Figure 12a). Based on this observation, it was proposed that the deprotonation of the surface proton that is generated during the OER is the limiting process (Figure 12b), which is assisted by the supporting ions.

A systematic investigation was also reported for Mn electrodes. When an unbuffered solution was used as a supporting electrolyte (0.5 mol L\(^{-1}\) Na\(_2\)SO\(_4\)), the onset potential for the OER was found to be independent of the solution pH on the SHE scale (Figure 13a), which interestingly coincides with the observation for the HER (see Section 3.2). The observed pH independence in their study was ascribed to the formation of Mn\(^{3+}\) from Mn\(^{2+}\). The OER–pH relationship was drastically altered when buffering action was introduced into the system. Particularly, Nocera and co-workers claimed that the self-healing mechanism was also present in the Mn–phosphate system, which results in the high stability of the Mn OER catalysts. Nakamura et al. reported a strong correlation between the OER performance and pK\(_a\) of the buffering equilibrium: even at similar pH, the performance was significantly dependent on the pK\(_a\) of the buffering action. Particularly, the larger pK\(_a\) resulted in an improved OER onset potential (Figure 13b and c). This observation indicates the involvement of the deprotonation/protonation process in the rate-determining step, which was also observed for the Co OER catalysts.

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**Figure 12.**

(a) pH dependence of the catalytic current determined at 1.35 V (versus NHE) in various buffer systems. The respective electrolytes consisted of the indicated buffer system at a concentration of 0.1 mol L\(^{-1}\). The lines were obtained by means of simulations, assuming that the catalytic activity was proportional to the relative concentration of the base. HEPES = 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid, MES = 2-(N-morpholino)ethanesulfonic acid, and TRIS = 2-amino-2-hydroxymethyl-propane-1,3-diol.

(b) The proposed situation that prevails in the CoCat material, that is, catalysis of water oxidation within the bulk of the amorphous oxide materials but proton transfer to an electrolyte buffer base (abbreviated as B\(^{-}\)) at the bulk oxide surface. Adapted from reference [162].

**Figure 13.**

(a) pH dependence of the onset potential for the oxidation current (U\(_{on}\), red squares) and optical absorption at 510 nm (U\(_{max}\), blue circles). The solid line represents the standard potential for oxygen evolution. Reproduced from [165] with permission from the American Chemical Society (copyright 2012). b) Plot of pH versus potential showing the pH dependence of the onset potential (U\(_{on}\)) defined at 130 \(\mu\)A cm\(^{-2}\) for water oxidation in the presence of the indicated bases at pH ranging from 5 to 9. Adapted from Reference [167].
Overall, at near-neutral pH, the ion largely influences the OER reaction performance if the surface proton affinity allows. The $pK_a$ of supporting ions is speculated to be the main parameter in this case, which is associated with (1) the supporting ions assisted protonation/deprotonation reaction and (2) the local pH near the electrode surface. Therefore, not only the electrode identity but also the identity and molarity of ions as well as their interaction with the electrode have to be thoroughly investigated to maximize the OER performance, which is essential for the development of efficient water splitting systems.

5. Crossover Regulation

This section introduces one example of the utilization of ions, in which a selective HER in the presence of oxygen is demonstrated. In the water splitting system, both hydrogen and oxygen evolve, which naturally results in the risk of a back reaction to form water. The evolved hydrogen can be oxidized at the anode (hydrogen oxidation reaction: HOR), and the oxygen can be reduced at the cathode (oxygen reduction reaction: ORR) when no membrane is used; for example, in the photocatalytic particulate system. These unfavorable back reactions lower the overall efficiency. In general, the anode is in the form of an oxide or hydroxide, and in most cases, it is inactive towards the dissociation of hydrogen molecules. However, the cathode material is also active for the ORR in most cases, for example, $\text{Pt}_x$ [171-173] and multi-metal electrodes [174-179] as is known for fuel cell technology. Thus, oxygen-tolerant cathodes are highly desirable. Conventional approaches to this issue include the protection of the cathode by a selective membrane [181, 182] and the preparation of an HER-selective electrolyte [183]. Herein, another approach is discussed, in which the electrolyte properties are used to regulate the oxygen mass transport flux across the cell.

5.1. The influence of ions on oxygen mass transport

When a buffered solution is used as an electrolyte at near-neutral pH, the solute concentration has a drastic impact on the dissolved gas conversion. Experimentally, it was revealed that the limiting diffusion current decreased with increasing concentration on a logarithmic scale. Theoretically, the oxygen diffusion flux is a function of the following parameters, as understood from Equations (22), (25), and (27):

- a) the oxygen concentration (solubility);
- b) the kinematic viscosity of the solution;
- c) the diffusion coefficient.

These parameters can be addressed separately.

The dependence of the gas solubility on the identity/molarity of ions is rationalized by the Sechenov equation [Eqs. (32) and (33)], which shows decreasing solubility as the solute concentration increases. The kinematic viscosity of the solution can be measured with a viscometer, and both the kinematic viscosity and the viscosity are found to increase exponentially with the solute concentration. The diffusion coefficient can be determined by using the Stokes–Einstein equation [Eq. (25)], which indicates that the diffusion coefficient decreases with increasing solute concentration owing to the increased viscosity. From these values, the mass transport-limited current density (the limiting diffusion current density) can be calculated by using Equation (27) in the RDE configuration. The calculated limiting diffusion currents were found to quantitatively reproduce the experimental observations [186,126], which demonstrates that the electrolyte properties are solely responsible for the observed oxygen mass transport flux. This finding reveals the significance of the electrolyte properties on the mass transport of the dissolved gas [146] thus, by tuning the electrolyte identity and molarity, the mass transport flux of the dissolved gas can be controlled.

5.2. Electrolyte engineering for selective hydrogen production in the presence of oxygen

This section presents a global picture of the roles of electrolytes in hydrogen production and gas diffusion in densely buffered solutions. The alteration of the molarity and identity of the ion changes the associated parameters, which in turn determines the mass transport process. As discussed in Section 3.5, the HER at near-neutral pH suffers from the slow mass transport of weak acid species. The following parameters are predominantly responsible: the ion activity, effective ion size, and kinematic viscosity. The previous section (Section 5.1) described the significance of the electrolyte properties on gas diffusion, where the following parameters are revealed as descriptors: the kinematic viscosity and gas solubility. Overall, for the HER in the presence of oxygen, the following are the governing parameters:

- a) mean activity coefficient;
- b) ion size;
- c) viscosity;
- d) gas solubility.

These parameters are dependent on each other, and they define the ion activity, diffusion coefficient, and diffusion-layer thickness, which in turn determine the mass transport flux of the weak acid and dissolved gasses, as summarized in Figure 14.

The ways in which these parameters affect the HER and oxygen diffusion are different: for example, a higher concentration results in a monotonic decrease in the oxygen diffusion flux, but the HER reaches its optimum at approximately 1.5–2.0 mol L$^{-1}$ in many cases. Therefore, there are optimum conditions where a higher HER performance and a poorer oxygen diffusion flux are achieved, for example, a selectivity as high as 90% for the HER can be achieved in 1.5 mol L$^{-1}$ $\text{K}_3\text{H}_2\text{PO}_4$ over a Pt electrode at $-50$ mV versus RHE under oxygen-saturated conditions. Of note, the additional use of a membrane in such systems can further lower the crossover loss and mitigate safety concerns. Regarding membrane use, the readers are referred to other recent journal articles.
The ion plays a critical role not only in the HER and OER but also in the dissolved gas conversion. Simple tuning of the electrolyte properties results in a drastic alteration of the electrochemical performance. The electrolyte thus needs to be carefully considered in the development of efficient solar hydrogen production systems. Notably, as such, the tuning of the electrolyte property is clearly crucial to fuel cell technology in near-neutral pH conditions, particularly for microbial fuel cells.

6. Conclusions and Perspectives

Water electrolysis plays a critical role in fuel generation from sustainable energy resources. Versatile and flexible water splitting in various electrolytes should be investigated to adapt the various reaction conditions required for (photo)electrochemical reactions and maximize their efficiency. This review lists the fundamental physical and chemical properties of electrolytes, which strongly influence the kinetics and mass transport for water electrolysis reactions.

In conventional studies, the identity of the electrode (in particular, its binding energy to the intermediate species) has been a focus of investigation to understand the electrochemical kinetics under extreme pH conditions. However, recent studies have revealed that the performance is significantly altered by the electrolyte in at least four ways:

1) Participation of ions in the surface reaction

The reaction scheme and transition state may be directly influenced by the supporting ions at the very surface. The important role of counter ions in an ionic environment is clear for the kinetic contribution.

2) Alteration of the local pH

At a near-neutral pH, buffer ions, depending on their identity and molarity, effectively regulate the local pH through protonation/deprotonation processes close to the surface, which can minimize concentration overpotential.

3) Blockage of the active sites

At an extremely acidic/alkaline pH, a slight modification of the reaction conditions, for example, the introduction of supporting ions, drastically alters the reaction performance owing to noncovalent interactions between the hydrated ions and the surface sites (or intermediates on the surface), and/or specific adsorption.

4) Regulation of mass transport

Most significantly, the mass transport of the species responsible for the surface reaction is predominantly governed by the identity and molarity of the supporting ions.

Accordingly, it is inferred that fine-tuning of the electrolyte properties, or electrolyte engineering, is a promising concept to improve the reaction performance, especially at a near-neutral pH. As shown in this review, a quantitative description of these properties enables us to precisely determine the contribution of mass transport and associated kinetics originating from the identity and molarity of the supporting electrolyte. Therefore, it is recommended to give special attention to not only the electrocatalyst material but also the electrolyte used because the performance can be strictly limited by the mass transport and not by the performance of electrocatalyst. The study of electrolyte engineering still has ample margin to be investigated for further improved water splitting performances.

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Keywords: hydrogen evolution reaction · ions · oxygen evolution reaction · solar fuel · water splitting

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