Designing Electrochemical Systems for Energy Conversion

Dissertation by
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Doctor of Philosophy

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ABSTRACT

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Keisuke Obata

Electrochemical water splitting to hydrogen and oxygen is an attractive approach to store and convert intermittent renewable energy sources. Energy efficient, cost effective and durable electrochemical systems are highly required. Firstly, CeO$_x$ coated oxygen evolution electrocatalysts were developed to improve the stability. Unique permselectivity of the CeO$_x$ layer was disclosed, which helps to prevent dissolution of active metal site. Because oxygen evolution reaction requires a higher overpotential than hydrogen evolution reaction, kinetically facile oxidation of soluble redox ions was proposed as an alternative anodic reaction, in which the oxidized redox ions can be used for succeeding homogeneous reactions, such as treatment of H$_2$S. How to tune the thermodynamics and the diffusion of candidate redox ions is discussed for a desired application. In addition to the anodic reaction, cathodic hydrogen evolution reaction has to be optimized. To maximize hydrogen evolution performance in near-neutral pH buffered conditions, concentration overpotentials from local pH and hydrogen on a Pt cathode are distinguished by mass transport modelling. Finally, stand-alone module was developed to perform solar-driven redox-mediated H$_2$S splitting to H$_2$ and S under natural solar irradiation.
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LIST OF ABBREVIATIONS

AEM anion exchange membrane
AM 1.5G air mass 1.5 global solar spectrum
AQDS anthraquinone disulfonate
CIGS Cu(In,Ga)(Se,S)₂
CV cyclic voltammogram
DOS density of state
EC electrochemical
EDTA ethylenediaminetetraacetic acid
EV electric vehicle
FC fuel cell
FCV fuel cell vehicle
FIB focused ion beam
FTO fluorine doped tin oxide
GC gas chromatography
HEDTA hydroxyethylethylediaminetriacetic acid
HER hydrogen evolution reaction
HOR hydrogen oxidation reaction
ICP inductively coupled plasma
L ligand
LCOE levelized cost of energy
LCOH levelized cost of hydrogen
MEA membrane electrode assembly
NTA nitrilotriacetic acid
<table>
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<th>Abbreviation</th>
<th>Description</th>
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<td>oxygen evolution reaction</td>
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<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
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<tr>
<td>PC</td>
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<td>PEM</td>
<td>proton exchange membrane</td>
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<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>RDE</td>
<td>rotating disk electrode</td>
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<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
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<td>SAED</td>
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<tr>
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1. Introduction

1.1. Energy Demand and Renewable Energy Sources

Our population in the world is 7 billion and is predicted to keep increasing to 9 billion by 2050.\textsuperscript{1} Due to the growing population, industrialization and improvement of the living standard, especially in developing countries, our energy demand is expected to keep increasing. Our energy consumption was 18 TW-years on 2018 and predicted to increase to 23 TW-years by 2040.\textsuperscript{2} Fossil fuels have played a major role to supply energy because of their easiness to transport and high energy density per unit mass and volume (Figure 1. 1). They are definitely expected to keep contributing to our daily life and industries.\textsuperscript{3} Although the fossil fuels have strongly contributed our industrialization since 18\textsuperscript{th} century, unavoidable emission of CO\textsubscript{2} started to trigger negative impacts towards the global climate, ecosystem and human life.\textsuperscript{4} CO\textsubscript{2} is a greenhouse gas (GHG) which absorbs an infrared radiated from the earth surface and re-radiate back to the earth. Even though CO\textsubscript{2} is a minor component in the atmosphere, the concentration of CO\textsubscript{2} has increased from 270 ppm to 400 ppm after the industrial revolution.\textsuperscript{5} As a consequence, the global temperature has increased by 1 °C during this period. Without any effort, the concentration and global temperature are predicted to increase up to 900 ppm and by 4 °C, respectively, due to the dramatically increasing energy demand, which will further damage our environment.\textsuperscript{5} To achieve sustainable society, the Paris agreement on 2015 targets to limit the temperature increase by 2 °C from preindustrial period, which requires global CO\textsubscript{2} emission free by 2100. Since the fossil fuels are essential for our
development, it is an ambitious challenge while maintaining the economic growth. Although every countries have decided targets to contribute the 2 °C scenario, the planned efforts are not satisfactory, which will results in the temperature increase by 3 °C. Disruptive improvement of energy efficiency, deployment of CO₂ emission free energy source and reconstruction of our energy systems are highly desired to achieve the ambitious target.

![Figure 1.1. Global energy consumption by energy source. Adapted from U.S. Energy Information Administration.](image)

Last few decades, there is a growing interest towards renewable energy sources, such as solar energy, wind power and biomass feedstock, which have less CO₂ emission or CO₂ emission free during energy harvesting compared with fossil fuels. International Energy Agency suggested that deep penetration of renewable sources reaching 70% for the electricity generation by 2060 to achieve the 2 °C scenario. In addition to the electricity generation, all the energy sectors, industry, transportation and building, have to develop CO₂ emission systems. Incentive and supports from government can be expected due to its carbon free process, which helps further deployment of renewables. Currently, limited amount
of global CO₂ emissions is going through carbon taxes which is usually less than $10/ton CO₂. To satisfy the two-degree scenario, it is estimated that carbon tax has to be $50-100/ton CO₂ by 2030, which will push the transition from CO₂-emitting fossil fuel based society to carbon-free renewable based sustainable society. Their levelized cost of energy (LCOE), which determines the average total cost including manufacturing and operation to produce the electricity during lifetime, is a common measure to compare variety of energy source. The LCOEs for renewable sources have continuously kept declining from $360/MWh to $50/MWh for utility scale solar cell and from $135/MWh to $45/MWh for wind power in some regions from 2009 to 2017, and they are predicted to further decrease by increasing their market. The LCOEs from renewable sources are becoming comparable with those from conventional power generation techniques using coal ($60/kWh) and gas combined cycle ($102/kWh). Among the renewable energy sources, solar energy has a great potential in terms of the amount of energy supplied. The solar energy reaching to the surface of our earth is 173,000 TW-years, which is 8,000 times higher than our energy consumption (Table 1.1).

**Table 1.1.** Total recoverable reserves for finite resources and potentials for renewable energy sources estimated on 2015.

<table>
<thead>
<tr>
<th>Total recoverable reserves / TWyear</th>
<th>Potential for renewables / TW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum</td>
<td>220</td>
</tr>
<tr>
<td>Natural gas</td>
<td>335</td>
</tr>
<tr>
<td>Coal</td>
<td>830</td>
</tr>
<tr>
<td>Uranium</td>
<td>90-300</td>
</tr>
</tbody>
</table>
One of the problems associated with the solar energy is its low energy density. Standard energy density of solar irradiation is $1 \text{ kW m}^{-2}$ (Air Mass 1.5 Global (AM 1.5G)), which means large area is required to capture sufficient energy and efficient system is desired to minimize the area and required devices. Another disadvantage is its daily and seasonal intermittency, which means the power output from photovoltaic (PV) cells can oscillate and potentially lead the existing electricity grid to fluctuate out of control. This intrinsic intermittency limits further deployment of renewable energy sources. Therefore, energy storage or conversion techniques are highly required for the renewable energy sources to develop a sustainable society.

1.2. Energy Storage and Conversion

Energy can be stored by variety of foams, such as mechanical energy, electrical energy, electrochemical energy, thermal energy and chemical energy. Pumped hydro storage, compressed air energy storage and flywheels store electricity as mechanical energies through the height of water level, pressure, and inertia of rotating mass, respectively. Currently, pumped hydro storage is the only one commercialized technique to store energy with large scale to balance low and high electricity demand. Its storage capacity is more than 100 GW, which occupies 99% of share for the current energy storage. But, the capacity is still less than 5% of the global energy demand. Because pumped hydro is a bulk storage approach, it is not suitable for frequency-response demands. Electrochemical approaches store electricity by electrochemical reactions with electrode materials or ions in electrolyte solutions. Variety of batteries, which
depends on the choice of electrodes and electrolytes, are developed and commercialized such as lead-acid, lithium-ion, redox flow and sodium-sulfur batteries. Batteries are getting more popular for mobile applications, like laptop, phones, and automobiles. As the electrical storage, superconducting magnetic energy storage and supercapacitor reserve electricity as a magnetic field and a polarization at the interface between electrodes and electrolyte, respectively. The electrical storage shows a good response to the fluctuating supply and demand which helps to improve the quality of electricity. Energy can be stored as chemical bonds in hydrogen, hydrocarbon and ammonia through, for instance, electrochemical approach. After the storage, they can be easily transported between different locations by existing infrastructure and distribution systems. The produced chemicals can be used as an energy source to produce electricity or heat. Otherwise, they can be feedstocks for other valuable chemicals.

Variety of parameters, such as energy density, power density either weight based or volume based, life time, self-discharging rate, round-trip efficiency etc, are compared among these techniques to find out suitable systems for specific application. Because of their advantages and disadvantages, above mentioned techniques are not always competing each other, they are complementary techniques to develop an efficient society through best mix.

In this thesis, electrochemical hydrogen production is discussed to store and convert energy. Because of its molecular weight, hydrogen has the highest energy density per unit mass compared with conventional fossil fuels (Table 1. 2). On the other hand, its energy density per unit volume is low at ambient condition,
which requires compression or liquidation to minimize the volume. Alternative hydrogen storage/carrier techniques, metal hydride, ammonia, hydrogen absorbing alloy, are investigated although they sacrifice energy density per unit mass.

**Table 1.2. Energy density per unit mass and volume at 0 °C**

<table>
<thead>
<tr>
<th></th>
<th>Energy density by mass (MJ/kg)</th>
<th>Energy density by volume (MJ/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>142</td>
<td>0.0128</td>
</tr>
<tr>
<td>Natural gas</td>
<td>54.0</td>
<td>0.0403</td>
</tr>
<tr>
<td>Propane</td>
<td>50.2</td>
<td>0.0254</td>
</tr>
<tr>
<td>Gasoline</td>
<td>46.5</td>
<td>34.6</td>
</tr>
<tr>
<td>Lithium ion battery</td>
<td>0.54-0.76</td>
<td>1.6</td>
</tr>
</tbody>
</table>

In addition to energy capacity, discharging rate is an important factor, which determines how efficiently energy can be stored for long periods when it is not connected to external loads. For instance, batteries are not suitable for long term storage more than a day because of the self-discharging through the electrolyte. Because hydrogen is a stable chemical, storage for long periods more than a day is possible, which is suitable for seasonal storage. However, the round-trip efficiency, which determines the efficiency between input electricity and output one, for H₂ storage followed by fuel cell is low (30%) because of the energy loss through the electrolyzers and fuel cells. Meanwhile, the efficiencies of Li-ion battery and pumped hydro storage are 90 and 80%, respectively. Therefore, improvement of the efficiencies for electrolyzers and fuel cells is highly required.
The produced hydrogen can be utilized for variety of applications, not only for electricity regeneration, but also for transportation and chemical feedstock. Electricity can be regenerated by fuel cells, which is a reverse reaction of water splitting. Variety of fuel cells (FCs), such as proton exchange membrane (PEM) FC, solid oxide fuel cell (SOFC) etc, are developed and commercialized. Based on their own pros and cons, the type of FC is chosen for specific purpose in term of required scale, cost and lifetime. In a short term, the energy storage application of H₂ is proposed for isolated remote area, which has a limited accessibility to the electricity grids and high electricity price.

Some countries are trying to limit or ban conventional fossil fuel cars. For example, Norway is targeting all new passenger cars and light vans sold on 2025 to be CO₂ emission-free cars. Fuel cell vehicles (FCVs) has an advantage to travel longer distance than electric vehicles (EVs) due to the high weight based energy density of H₂. FCVs do not produce NOₓ and SOₓ like fossil fuel cars. On-site generation of H₂ from renewable energy sources at the fuel stations is predicted to have a cost advantage compared with the centralized production of H₂ by steam reforming which requires additional cost to distribute H₂ to the stations. Public transportation, shipping by heavy duty trucks, forklift, nonelectrified diesel train can get benefit effectively than personal FCVs because they have routine routes or bases which can be easily coupled with H₂ fuel station.

In addition to electricity generation and transportation, building sector including residential and commercial is another major energy consumer in which
energy is used to control temperature of living spaces, water and food. Currently, natural gas, coal and oil are the major energy source which release CO\(_2\). In order to achieve 2 °C scenario, 50 % of CO\(_2\) emission from this sector has to be decreased by 2050.\(^2\)\(^2\) Besides improving the energy efficiencies of buildings, it is required to replace conventional fossil fuels to low-carbon energy source. 5-20% of H\(_2\) can be blended in the existing natural gas infrastructure,\(^2\)\(^2\) which will reduce the carbon footprint in the building sector if H\(_2\) is produced by environmentally friendly technique. Fuel cell is an attractive option for cogeneration of electricity and heat.

Currently, more than 50 % of produced H\(_2\) are used as a chemical feedstock for ammonia synthesis by Haber-Bosch process to produce urea and fertilizer.\(^2\)\(^3\) There is a potentially big market for renewable derived H\(_2\) for the chemical industry. H\(_2\) and CO\(_2\) can be also a feedstock for hydrocarbon, such as methane.\(^2\)\(^4\)–\(^2\)\(^7\) For example, methane is produced by Sabatier reaction. Light olefins are synthesized by Fischer-Tropsch process from syngas that are produced from CO\(_2\) and H\(_2\) by reverse water gas shift reaction. The synthesized hydrocarbon can get benefit from the existing infrastructures and facilities. The great advantage of H\(_2\) produced from water is its high purity (>99.9%) obtained without auxiliary purification equipment compared with that produced by conventional steam reforming of methane. In addition to above mentioned chemical synthesis, food, pharmaceutical industry and cosmetics would appreciate the high purity H\(_2\) derived from water.
1.3. Hydrogen Production via Electrochemical Water Splitting

1.3.1. Thermodynamic of Water Splitting

In order to design and evaluate the electrochemical systems, what we have to take into account first is thermodynamics. The process which converts chemical energy to electric and thermal energy is described by the fundamentals of thermodynamic.\textsuperscript{28,29} The required energy for water splitting (Equation 1.1) is determined by the enthalpy change (\(\Delta H\)) at given temperature and pressure. The corresponding electrical work and heat are described by the Gibbs’ free energy change (\(\Delta G\)) and the entropy term (\(T\Delta S\)), respectively.

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \quad (1.1)
\]

The relationship among the above thermodynamic values are expressed in the following equation

\[
\Delta G = \Delta H - T\Delta S \quad (1.2)
\]

When the heat is managed by the surrounding of electrochemical cells, reversible voltage (\(V_{\text{rev}}\)) is the required voltage (Equation 1.3).

\[
V_{\text{rev}} = \frac{\Delta G}{nF} \quad (1.3)
\]

where \(n\) is the number of required electron moles to produce one mole of hydrogen (\(n = 2\)). \(F\) represents Faraday constant (96,485 C/mol). If the heat (\(T\Delta S\)) is also provided by the electricity, the minimum voltage for water splitting is
thermo-neutral voltage \((V_n)\). In an ideal process, \(V_n\) is described by the following equation.

\[
V_n = \frac{\Delta H}{nF}
\]  

(1.4)

Usually, heat is provided by Ohmic loss and overpotentials on electrocatalysts during water splitting.

At standard condition (298.15 K and 1 atm), \(\Delta H^0 = 285.84 \text{ kJ/mol}\), \(\Delta G^0 = 237.21 \text{ kJ/mol}\), and \(\Delta S^0 = 0.1631 \text{ kJ/mol K}\). Standard voltages \(V_{rev}^0\) and \(V_{tn}^0\) are 1.23 and 1.48 V, respectively. Water splitting is an endothermic reaction \((\Delta H > 0)\) and nonspontaneous \((\Delta G > 0)\) reaction, which requires energy input to perform the reaction. Its reverse reaction is an exothermic reaction \((\Delta H < 0)\) and spontaneous \((\Delta G < 0)\) reaction, which is how we obtain the electricity from fuel cell.

In the presence of sufficient voltage to split water, reduction reaction takes place on a cathode to produce hydrogen \((\text{HER: Equations 1.5 and 1.7})\), and oxygen is evolved from an anode by oxidation reaction \((\text{OER: Equations 1.6 and 1.8})\). In fuel cells, their reverse reactions, i.e., hydrogen oxidation reaction \((\text{HOR})\) and oxygen reduction reaction \((\text{ORR})\), happen to regenerate electricity.

(Acid)

Cathode: \(2H^+ + 2e^- \rightleftharpoons H_2\)  

(1.5)

Anode: \(4H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-\)  

(1.6)
(Alkaline)

Cathode: \(2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-\) \(1.7\)

Anode: \(4OH^- \rightleftharpoons O_2 + 2H_2O + 4e^-\) \(1.8\)

Herein, it is convenient to investigate anodic and cathodic half reactions individually. Energy loss associated with either anode or cathode can be identified, which helps us to establish research directions for anode and cathode independently. To study half reactions, it is helpful to determine equilibrium potentials for individual half reactions and discuss electrochemical reactions against their equilibrium potentials. Standard redox potential \(E^0\) can be defined by standard Gibbs energies of formation \(\Delta_fG^0\). For instance, the standard potential for Equation 1.5 \(E^0(H^+/H_2)\), in which activity of proton and partial pressure of hydrogen are unity, is described by the following equation.

\[
2\Delta_fG^0(H^+) + 2FE^0(H^+ / H_2) = \Delta_fG^0(H_2) \quad (1.9)
\]

Because \(\Delta_fG^0(H^+)\) and \(\Delta_fG^0(H_2)\) are zero, the standard potential for Equation 1.5 \(E^0(H^+/H_2)\) is zero. This equilibrium is called standard hydrogen electrode (SHE) and frequently used as a reference for other half reactions. Therefore, equilibrium of Equation 1.5 takes place at 0 V vs. SHE at standard condition. Accordingly, the standard potential for oxygen reaction in Equation 1.6 is 1.23 V vs. SHE based on the standard Gibbs energy of formation for water \(\Delta_fG^0(H_2O)\), which is \(-237\) kJ/mol. Standard potential is determined at standard condition where activities of all the species are unity. Because equilibrium can shift by the
activities, the equilibrium potential \( (E_{eq}) \) at given condition is described by following Nernst equation with corresponding standard potential \( (E^0) \),

\[
E_{eq} = E^0 + \frac{RT}{nF} \ln \left( \frac{a_{ox}}{a_{red}} \right)
\]

(1.10)

where \( a_i \) represents the activity of species \( i \). This Nernst equation results in the well-known potential-pH diagram of hydrogen and oxygen reactions with a slope of \(-59 \text{ mV/pH}\). The equilibrium potential of hydrogen reaction at given pH is also used as another reference potential, which is called reversible hydrogen electrode (RHE).

### 1.3.2. Overpotentials during Water Splitting

In addition to the above mentioned thermodynamics, additional overpotentials are required to drive reactions at certain reaction rate.

\[
V = V_{rev} + \eta_{kin,HER} + \eta_{kin,OER} + \eta_{con,HER} + \eta_{con,OER} + \eta_{Ohmic}
\]

(1.11)

\( \eta_{kin} \) is a kinetic overpotential to activate electrocatalyst to obtain a certain current density. \( \eta_{con} \) is a concentration overpotential which comes from unavoidable concentration gradients between the bulk solution and the electrode surface during reaction. \( \eta_{Ohmic} \) is Ohmic potential drop arising from resistance of solutions, electrodes and electrocatalysts. All these overpotentials depends on the current density and they increase at high current density. It is essential to identify their contributions and find out measures to minimize the energy loss, for example,
developing outperforming electrocatalysts, engineering the electrolyte and designing electrochemical device configuration.

**Kinetic overpotential**

Electrode kinetics is determined by standard Gibbs energy of activation ($\Delta^\dagger G^0$) which is required to reach a transition state and symmetry factor ($\alpha$) which is a value between 0 and 1 and determines the symmetry of potential energy surface against the reaction coordinate. The activation energy changes with the applied electrode potential and the corresponding symmetry factor, which results in potential dependent rate constants ($k$) following Arrhenius equation.

$$k_{\text{ox}} = A_{\text{ox}} \exp\left[\left\{ -\Delta^\dagger G_{\text{ox}}^0 + (1-\alpha) F (E - E^0) \right\}/RT \right] \quad (1.12)$$

$$k_{\text{red}} = A_{\text{red}} \exp\left[\left\{ -\Delta^\dagger G_{\text{red}}^0 - \alpha F (E - E^0) \right\}/RT \right] \quad (1.13)$$

where $A$ is the pre-exponential factor. Herein, it is convenient to describe the potential from the equilibrium potential where the observed current density is zero.

$$\eta = E - E_{eq} \quad (1.14)$$

where $\eta$ is an overpotential. The observed reaction rate, or current density, comes from a sum of the reaction rates of anodic and cathodic direction, which results in the description of Butler-Volmer equation,

$$j = j_0 \left[ \frac{a_{\text{red,surface}}}{a_{\text{red,bulk}}} e^{(1-\alpha)\eta} - \frac{a_{\text{ox,surface}}}{a_{\text{ox,bulk}}} e^{-\alpha\eta} \right] \quad (1.15)$$
in which \( j_0 \) is an exchange current density. The exchange current density is often used as an indicator to compare different electrocatalysts. The first and second exponential terms in Equation 1.15 are anodic and cathodic contributions, respectively. It has to be noted that the overpotential in Equation 1.15 is the sum of the kinetic overpotential \( (\eta_{\text{kin}}) \) and the concentration overpotential \( (\eta_{\text{con}}) \) for the half reaction in Equation 1.11. As shown in Equation 1.15, the activities at the electrode surface also determine the current density in addition to the electrode potential. The gradient of activities between the bulk solution and the electrode surface during reaction is the origin of the concentration overpotential \( (\eta_{\text{con}}) \).

The above Butler-Volmer equation is developed for single charge transfer processes. Water splitting reaction takes place through multiple electron transfer with adsorbed intermediate, which makes the description of reaction rate further complicated. For example, hydrogen evolution reaction (Equation 1.5) goes through formation of an adsorbed hydrogen by Volmer step (Equation 1.16) followed with either Heyrovsky (Equation 1.17) or Tafel recombination (Equation 1.18).

\[
\text{Volmer} \quad M + H^+ + e^- \rightleftharpoons M-H \quad (1.16) \\
\text{Heyrovsky} \quad M-H + H^+ + e^- \rightleftharpoons M + H_2 \quad (1.17) \\
\text{Tafel} \quad 2M-H \rightleftharpoons 2M + H_2 \quad (1.18)
\]

where \( M \) denotes an empty catalytic site. It is known that heterogeneous kinetics for electrocatalytic reactions, like HER/HOR and OER/ORR, are highly
dependent on the electrode material. For instance, the exchange current density, which is an indicator for electrode kinetics, differs orders of magnitude depending on the electrode materials. Extensive studies have been performed to identify the descriptor for the activity trend. Trasatti found a volcano shaped dependence of the exchange current density against the adsorption energy between metal and hydrogen locating platinum group metals at the top,\textsuperscript{30} which is also confirmed by DFT calculation.\textsuperscript{31} The idea behind the volcano shaped trend is that moderate binding energy is required to form the intermediate from the reactant and to desorb as the product, which follows Sabatier principle for heterogeneous catalysis. This approach considers only the thermodynamics of adsorption and does not take into account the kinetic activation barriers. The kinetic barriers are assumed to scale with the corresponding thermodynamic barrier following Brønsted-Evens-Polanyi relation,\textsuperscript{32,33} which often reproduces experimentally observed activity trends. A rigorous calculation which considers transition states between intermediates is often performed especially to describe HER/HOR in alkaline condition, which requires kinetically sluggish water dissociation.\textsuperscript{34–37} The pathway with the lowest activation barrier can be identified as a reaction pathway. The highest energy barrier in the pathway is identified as a rate determining step. Based on the finding of the volcano shaped activity trend, bimetallic catalyst was developed to control the hydrogen binding energy. J. Greeley et al. performed computational screening for over 700 bimetals.\textsuperscript{38} They theoretically and experimentally confirmed that BiPt surface alloy surpass pure Pt. Another example is from non-noble metals, in which Ti and Cu adsorb hydrogen strongly
and weakly, respectively. Finely tuned bimetal of Ti and Cu showed a suitable binding energy and outperformed Pt catalyst. Transition metal chalcogenides and phosphide are newly studied alternative non-noble metal catalysts for acid electrolysis. DFT calculation identified that the edge sites in their two dimensional structure is highly active sites with a decent adsorption energy of hydrogen while the basal plane are inactive. Following the DFT calculation, nano-structuring of chalcogenides are performed to increase the number of highly active sites. Ni based alloys are frequently employed for alkaline electrolyzers. Among the alloys studied, NiMo alloy was most active and stable in a practical operation condition (6 M KOH, 80 °C) for alkaline electrolyzer although the rationale behind the outperforming activity of NiMo is still under discussion.

To design electrocatalysts, it is also important to identify the reactants. As shown in Equations 1. 5 and 1. 7, reactant for HER switches from proton to water with increasing electrolyte pH. In an unbuffered condition, the reactant switching from proton to water molecule for HER occurs at pH ~1.6 at a current density of ~10 mA cm$^{-2}$ in a static condition without convection. It is known that the kinetics for HER in alkaline solution is two orders of magnitude lower than that in acidic condition due to the additional kinetic penalty to break OH bond in reactant water. Therefore, strategy to improve HER activity in alkaline is guided to introduce a functionality to support the kinetically sluggish dissociation of water. For example, oxophilic materials, like Ni(OH)$_2$ and Ru,
deposited on HER electrocatalysts are reported to facilitate water dissociation step and leave reactive hydrogen on electrocatalysts.⁴⁷,⁵⁰,⁵¹

Oxygen evolution reaction (OER) is more difficult reaction than hydrogen evolution reaction due to the number of electrons transferred and involved reaction intermediates. The overpotential for OER is more than 200 mV to reach 10 mA cm⁻² with finely tuned catalysts in highly alkaline condition, while HER requires less than 100 mV with best performing catalysts. A variety of reaction mechanisms are proposed, for example single site mechanism shown in Equations 1.19 - 1.23.⁵²-⁵⁵

\[
\begin{align*}
M + H_2O & \rightleftharpoons M-OH + H^+ + e^- \quad (1.19) \\
M-OH & \rightleftharpoons M-O + H^+ + e^- \quad (1.20) \\
M-O + H_2O & \rightleftharpoons M-OH + H^+ + e^- \quad (1.21) \\
M-OH & \rightleftharpoons M-O^- + H^+ \quad (1.22) \\
M-O^- & \rightleftharpoons M + O_2 + e^- \quad (1.23)
\end{align*}
\]

Strategies to describe the reactivity towards OER are also guided by the absorption energies between metal site and those reaction intermediates like performed for HER. Volcano shaped activity trend is reproduced using adsorption energies of oxygenates for a variety of single metal oxides and perovskites showing RuO₂, Co₃O₄, LaNiO₃, SrCoO₃ as optimal.⁵⁴,⁵⁵ A complexity appears for
OER because binding energies for multiple intermediates have to be taken into account while HER is purely described with the binding energy of hydrogen. The binding energies for oxygenate intermediates are often related each other, so called scaling relationship. Due to the scaling relationship between intermediates, the thermodynamically required overpotential to produce $O_2$ through intermediates will never be zero unlike HER. Co and Ni doping to RuO$_2$ is calculated to break the limitation by introducing functionality to the neighboring inert sites and experimentally showed an improved OER activity compared with pristine RuO$_2$.\textsuperscript{56}

In acidic solutions, options for OER electrocatalysts are limited to noble metals due to the corrosion of various transition metals in the acid environment. Ir and Ru based oxides works well. But, due to the scarcity of these precious metals, it is desired to minimize the loading amount or to replace to non-noble metal catalyst while maintaining the activity and stability for acid environment. Alkaline conditions provide more options because of the formation of passivation layer in this condition. Earth abundant transition metal based electrocatalysts, especially, Ni, Co, Fe and Mn, are extensively studied for alkaline electrolysis. Among them, Fe-doped transition metal oxides, like NiFeO$_x$, are a state of the art electrocatalysts. Small amount of Fe, which comes from trace impurity in electrolyte, significantly improves the OER activity from undoped transition metal oxides.\textsuperscript{57–60}

Conductivity of electrocatalysts is also an important parameter. Basically, metals are oxidized under harsh oxidative conditions during OER, which results
in formation of the corresponding oxide, hydroxide and oxyhydroxide. These oxidized metals usually have a semiconducting characteristic leading to Ohmic loss within electrocatalysts while Ir and Ru oxides are exception showing a metallic conductivity. Therefore, deposition of semiconducting oxide on conductive supports are required to minimize the Ohmic loss. Alternatively, core-shell structures are studied with catalytically active oxide shells and metallic conductive cores from chalcogenides, pnictides, and carbides.

Stability of electrocatalysts is also a critical factor to determine the energy efficiency during operation. Deactivation of electrocatalysts leads to increase the overpotentials. For instance, impurities, such as metal cations and sulfur containing compounds, in electrolytes may deposit and block catalytic active sites, which leads to decrease current density per geometric area. Corrosion of electrocatalysts is a severe issue especially for OER, in which metals are oxidized to high oxidation states. These highly oxidized metals can be precursors for OER and decomposition to dissolved metal ions. In acidic solution, Ru based oxide works best for OER, but suffers from its poor stability due to the corrosion under the strong oxidative condition. Therefore, Ir based catalysts are preferred for water electrolysis in acid conditions because of its superior stability than Ru catalysts.

Concentration overpotential

Above mentioned voltage losses comes from the identities of electrocatalysts, which is classified as kinetics of catalysts. Meanwhile, an additional voltage loss appears due to the mass transport of reactants and products
through electrolyte solutions. In an ideal situation where the activities of involved species at the electrode surface are maintained to those in the bulk solution during reactions, the reaction rate purely comes from intrinsic kinetics of electrode materials, which is the maximum performance that the electrode can achieve in a given electrolyte. However, in real operating conditions, reactants at the electrode surface depletes from the bulk solution while products accumulate during electrochemical reactions. As shown in Equation 1.15, the reaction rate is also determined by the activities of involved species at the electrode surface. Deficiency of reactants decreases forward reaction rate and increased local products push backwards reaction, which results in reduction of overall reaction rate, i.e. an additional overpotential, which is called concentration overpotential ($\eta_{\text{con}}$), is required compared with the ideal mass transport free condition. As long as the morphology of electrodes are the same, the gradient of activities between the electrode surface and the bulk solution is independent to the electrode materials at given current density and reaction conditions. Therefore, the gradient is purely determined by the mass transport in the electrolyte. The electrolyte and reaction condition which can maintain local activities more close to that in the bulk solution is preferable to minimize concentration overpotential.

There are couples of driving forces to transport ions and molecules. For instance, ions and molecules move from high concentration to low concentration, which is called diffusion and follows Fick’s law. Electric field built between anode and cathode can drive ions depending on their charge, which is called
migration. Certainly, convection like stirring helps to push the bulk solution to the electrode surface.

Governing parameters in the electrolyte solution are diffusion coefficient and viscosity. Diffusion coefficient determines molar flux in the presence of gradient of concentration and electric potential. Diffusion coefficient is described by the following Stokes-Einstein equation.

\[ D = \frac{k_B T}{3\pi d\mu} \]  

(1.24)

where \( k_B \) is the Boltzmann constant, \( d \) is the effective hydrodynamic diameter of the hydrated ion (Stokes diameter), which includes all the H_2O molecules carried in the hydration sphere, and \( \mu \) is the dynamic viscosity of the electrolyte. Therefore, less viscous solution and high temperature help to improve the mass transport. Viscosity also has an influence on the convection. Because the diffusion coefficients in liquid phase are two orders of magnitude lower than those in gas phase, the energy loss from mass transport appears more severely in liquid phase than in gas phase. Therefore, commercialized electrochemical systems are often operated at elevated temperature because reaction temperature improves all these parameters.

**Ohmic loss**

Due to the electric field during electrochemical reactions, charged ions or electron are moving towards certain direction through conducting phases, such as electrodes, electrolyte, current collector and ion exchange membrane. Because of
the scattering of charged species with surrounding atoms, applied energy is lost as random movements (heat) which is called Ohmic loss. Ohmic voltage loss ($\eta_{\text{Ohmic}}$) has a linear relationship to the current density while kinetic overpotential a logarithmic relation as shown in Equation 1. Therefore, the Ohmic loss appears more severely at high current density.

1.3.3. Water Electrolysis Devices

Main components of water electrolyzer are cathode, anode, electrolyte, and separator which prevents short circuit and gas crossover between anode and cathode. Variety of electrolyzers exist depending on the choice of electrolyte and their configuration.

Alkaline water electrolyzers which literally use highly alkaline solution (25-30 wt% KOH) are commercially available mature technique. More than 400 units were already operated by 1902. High production capacity (760 Nm$^3$H$_2$/h) can be achieved which corresponds to electricity consumption of 5.3 MW. Noble metal catalysts are not required because transition metal based electrodes are stable under alkaline conditions. A porous diaphragm based on ZrO$_2$ composite is employed as a separator between anode and anode. Due to the Ohmic loss through the diaphragm, its operating current density is currently limited to approximately 400 mA cm$^{-2}$. Alkaline electrolyzer is not suitable to track highly fluctuating power input and operation in low current density ($<100$ mA cm$^{-2}$). Operation range is usually 25-100 % of the capacity to avoid forming the flammable gas mixture.
Meanwhile proton exchange membrane (PEM) electrolyzers are relatively new technique, which was first developed by General Electric on 1966 and commercialized on 1978. Instead of liquid electrolyte, proton conducting polymer is assembled as an ion conductor between anode and cathode. Because the ion selective membrane is used instead of porous separators, high purity of $\text{H}_2$ can be obtained from PEM electrolyzer compared with alkaline one. Because ion exchange membranes separate $\text{H}_2$ and $\text{O}_2$ more effectively than diaphragm, it can be operated at low current density which corresponds to 5% of production capacity. Thanks to the high conductivity and the thickness (<0.2 mm) of membrane, high current density (>1 A cm$^{-2}$) and high efficiency can be achieved. Because of the presence of highly acidic sulfonic acid functional group in the membrane, acid stable electrocatalysts are required, currently Pt and Ir for commercial system. Because of the degradation of membrane and contamination of cations, lifetime of PEM electrolyzer is usually 7 years, which is shorter than that for alkaline one (10 years). Inspired by the advantages of PEM electrolyzer, anion exchange membrane (AEM) electrolyzer is under development, in which hydroxide anions conduct through polymer membranes instead of proton. The alkaline environment of AEM allows earth-abundant materials as electrodes. However, conductivity and stability of polymer in alkaline condition still need to be improved.

Solid oxide electrolyzer (SOE) is an analogous of SOFC, which operates at high temperature (600 – 900 °C) and utilize oxygen ion conducting zirconia based ceramics as solid electrolyte. Although SOE is still under developing stage, higher
efficiency is expected due to advantageous reduction of reversible voltage at elevated temperature. For example, the reversible voltage decreases to 0.91 V at 1000 °C, which helps to reduce the electricity consumption during electrolysis. Geothermal energy or effluent high temperature gas from nuclear reactors are proposed as required heat source.\textsuperscript{93–95} Main challenges are the thermal stability of materials and the purification from mixture of hydrogen and steam.

Because above mentioned electrolyzers are operated at extreme conditions which require corrosion resistant materials, electrolyzers in near-neutral pH conditions are attractive options regarding the safety and choice of materials. But, the water splitting in near-neutral pH conditions is quite challenging and remains far from commercialization because electrode kinetics and conductivity in neutral-pH conditions are inferior to those in the commercialized harsh conditions.\textsuperscript{96–98} pH gradient can easily build up even at low current density (\(<10 \text{ mA cm}^{-2}\)), which results in large concentration overpotential even in the presence of proton donating/accepting buffer ions.\textsuperscript{99–102} Fundamental understandings and strategies towards water electrolysis in near-neutral pH condition will certainly also help the development of seawater splitting and electrochemical CO\textsubscript{2} reduction in carbonate buffer solution.

Currently, high purity of water feed is required to avoid blockage of separators and deactivation of electrodes from impurities. Impurity tolerant electrolyzer, ultimately seawater as a feed, is preferable to minimize purification cost. For instance, electrocatalysts for seawater splitting are studied.\textsuperscript{103–107}
Membrane free electrolyzers using microfluid dynamics or buoyancy effect are proposed, which also helps simplification of device architecture.\textsuperscript{96,108,109}

The status and future targets of the commercially available electrolyzers are summarized in Table 1.3.\textsuperscript{77} Obviously, improvements of energy, cost efficiency and durability are highly demanded.

**Table 1.3. Comparison between alkaline and PEM electrolyzers\textsuperscript{77}**

<table>
<thead>
<tr>
<th></th>
<th>Alkaline electrolyzer</th>
<th>PEM electrolyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity input / kWh kg\textsubscript{H\textsubscript{2}}\textsuperscript{-1}</td>
<td>54</td>
<td>50</td>
</tr>
<tr>
<td>Current density / A cm\textsuperscript{-2}</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>System cost / euro kW\textsuperscript{-1}</td>
<td>1,100</td>
<td>580</td>
</tr>
<tr>
<td>Stack life time / h</td>
<td>75,000</td>
<td>95,000</td>
</tr>
</tbody>
</table>

Alkaline and PEM electrolyzers cost €1,000-1,200/kW and €1,900-2,300/kW as capital cost including gas conditioning and balance of plant, respectively.\textsuperscript{77} More than 50% of system cost comes from stack of electrolyzers.\textsuperscript{77} The cost of stacks are further broken down in Figure 1.2. Bipolar plates occupy 50% in PEM electrolyzer because of the large stacking structure. Besides bipolar plates, anode and cathode catalysts cost more than 30%. Improvement of performance shown in Table 1.3 will decrease the contribution of the stack cost within the H\textsubscript{2} production cost during its lifetime.
To develop solar fuel devices based on the electrochemical approach, light absorbing semiconductors are essential to produce electron and hole pairs which perform electrochemical reactions at the electrolyte interface. Due to the band gap within semiconductors, excited electron and hole pairs are produced by light irradiation. Variety of semiconductors are synthesized and characterized, some of them are employed for practical applications, like photovoltaic (PV) cells. The important criteria for semiconductors is to produce a sufficient photovoltage to perform desired electrochemical reactions.

There are couples of options to combine semiconductor and electrochemical system (Figure 1. 3a-c). Semiconducting materials are immersed in electrolyte solutions for particulate photocatalysis (PC, Figure 1. 3a) and photoelectrochemical (PE, Figure 1. 3b) system. Both oxidation and reduction reactions take place on the surface of semiconductors or electrocatalysts deposited on semiconductors in PC system (Figure 1. 3a). In PE system (Figure 1. 3b), only
half reaction occurs on a photoelectrode and counter reaction happens on a counter electrode which can be either a metal electrode or another photoelectrode. In photovoltaic + electrolyzer (PV+EC, Figure 1.3c) system, semiconductor is completely isolated from electrolyte and connected via wires to electrodes in the electrolyte.

Figure 1.3. Various types of solar-driven water splitting systems. (a) Particulate photocatalysis (PC), (b) photoelectrochemical (PE) system, and (c) photovoltaic + electrolyzer (PV+EC). (d) Reported solar-to-hydrogen energy conversion efficiencies. Reproduced from Ref. 110 with permission from The Royal Society of Chemistry

Particulate photocatalysis systems allows simplicity to the solar-driven water splitting because it requires semiconductor particles and reactor to disperse
particles in solution. However, the solar-to-hydrogen (STH) energy conversion efficiency of PC systems remains low as shown in Figure 1.3d because all the requirements, such as light absorption, charge separation, catalytic kinetics and stability have to be satisfied on a single particle for successful solar driven water splitting. Furthermore, it has a risk to produce explosive gas mixture and requires separation of product gases.

Photovoltaic cell and electrolyzer are mature techniques and commercially available, which can be easily assembled to solar fuel device. Because there is no risk from the degradation of semiconductor in corrosive solutions, a variety of semiconductor can be applied. Light absorbers and electrochemical systems can be optimized independently. Gaseous products are easily separated by separators (ion exchange membrane or diaphragm). Its STH energy conversion efficiency is reached more than 30% using highly efficient triple junction PV and PEM electrolyzer under 42 sun.\textsuperscript{111}

PE is a system between PC and PV+EC. Semiconductors are still immersed in electrolyte, counter reaction is spatially isolated which helps the separation of products from anode and cathode. Anodic and cathodic reactions can be optimized independently. However, the PE systems also suffer from the stability of semiconductors in aqueous solutions like PC systems, which limits the choice of semiconducting materials and electrolyte solutions. The STH energy conversion efficiency is also between PC and PV+EC systems (Figure 1.3d).

Levelized cost of H\textsubscript{2} (LCOH) per unit mass is a measure to compare H\textsubscript{2} production costs among techniques including their capital and operating costs
during their lifetime. Currently, more than 90% of H₂ is produced by steam reforming of methane (SRM) from fossil fuel with releasing CO₂. Its LCOH is $1.5/kg_{H₂}, which serves as a benchmark for the solar driven water splitting.\textsuperscript{112} Although the estimated LCOHs based on the renewables vary depending on the locations, efficiencies and choice of technique, hydrogen from renewables are still higher than that from SRM. For instance, the LCOH of hydrogen production from PV+EC systems costs $5-11/kg_{H₂}.\textsuperscript{77,113} Because the energy is provided from renewable sources, capacity factor, which compares actual output and maximum output with continuous operation, also plays a role.\textsuperscript{108,113,114} Usually, the capacity factors of photovoltaic and wind power are 25% and 35%, respectively,\textsuperscript{115} which means that there is a large dead time against prepared maximum capacity of electrolyzers leading to the increase of H₂ production cost. Further cost reduction and improvement of efficiency and lifetime are highly desired in addition to subsidies for CO₂ free H₂ production techniques. Meanwhile, because of the simple device architecture of PC system, LCH of PC system is predicted to be potentially $1.6 / kg_{H₂}, which is significantly lower than those of PEC and PV+EC.\textsuperscript{116} But, the prediction assumed STH energy conversion efficiency and lifetime to be 10% and 20 years. Therefore, disruptive breakthrough is essential from the current STH efficiency of PC system (~2%).\textsuperscript{117,118}

1.5. Alternative Approach for Electrochemical Hydrogen Production

As mentioned in this introduction, solar-driven water splitting remains many challenges to compete with conventional hydrogen production via steam reforming of methane. One of the main challenges is the kinetically sluggish
oxygen evolution reaction (Figure 1.4). It requires more than 200 mV of overpotential in highly alkaline or acidic condition with finely tuned electrocatalysts, sometimes even noble metals, Ir or Ru, are required. Although oxygen evolution is an energy consuming reaction, the economical value of O$_2$ is one order of magnitude lower than H$_2$.

![Figure 1.4. Schematic comparison between water splitting and hydrogen production with an alternative oxidation reaction](image)

Alternative direction for electrochemical hydrogen production is to produce value-added chemicals on anodes.\(^{119,120}\) For instance, chlorine is produced on anodes while cathodes produce hydrogen in commercialized chlor-alkaline process.\(^{121}\) Chlorine and hydrolyzed hypochlorite (ClO\(^-\)) are frequently used for pulp and paper bleaching, bleach in laundry and treatment of wastewater. Its chemical price is 250 and 33 times higher than that of oxygen and hydrogen, respectively.\(^{119}\) There is attempts to produce hydrogen peroxide from water by electrochemical oxidation.\(^{122,123}\) Hydrogen peroxide is another attractive oxidizing
agent because it produces just environmentally friendly water or oxygen after utilization. Its value is 140 and 18 times higher than that of oxygen and hydrogen, respectively. Hydrogen peroxide is commercially synthesized from H₂ and O₂ in the presence of anthraquinone catalyst. Electrochemical oxidative upgrading of biomass feedstocks to valuable chemicals is another option.  

5-hydroxymethylfurfural (HMF) is a dehydration product from C6 carbohydrate and regarded as an important biomass feedstock for wide range of valuable commodities. HMF can be oxidized to 2,5-furandicarboxylic acid (FDCA) which is one of top 12 valuable products from biomass. FDCA is a building block for a biobased plastic called polyethylene furanoate (PEF) by esterification with ethane-1,2-diol, which is a potential candidate to replace petrochemical based polyethylene terephthalate (PET). Promising alternative reaction is an electrochemical oxidation of soluble redox ions, Fe, vanadate, halide ions, TEMPO, heteropoly molybdo phosphophate, followed by homogeneous reactions, like upgrading of HMF to FDCA or oxidation of H₂S. H₂S is a toxic byproduct from refineries and fossil fuel wells. Fossil fuel producing countries are serious to effectively process and better utilize harmful H₂S. For example, Shah field in Abu Dhabi contains more than 20% of H₂S in natural gas. Conventionally, H₂S is treated by Claus process to produce water and solid sulfur.  

Because above mentioned electrochemical oxidation reactions require smaller number of electron transferred than that for OER, their kinetics is expected to be faster than that of OER, which helps to decrease kinetic
overpotential (Figure 1.4). Ubiquitous electrode materials, such as carbon, nickel and stainless steel, may be sufficient to perform the reactions.

Thanks to the tunability of redox potentials of anodic reactions (Figure 1.4), variety of combinations between semiconductors and electrochemical systems can be possible. For example, in case of Si-PV, which have open-circuit voltage approximately 0.6 V, three Si-PVs are required in series to obtain sufficient photovoltage to split water. By tuning the redox potential, one or two PV may be able to produce hydrogen, which helps to increase the hydrogen production rate per unit area of light irradiation.

Because some oxidative products, especially strong oxidizing agents, are not stable to distribute long distance, there may be an advantage from on-site generation compared with current centralized production and distribution.

1.6. Scope of the Dissertation

Electrochemical hydrogen production is an attractive approach for energy storage and conversion of intermittent renewable energy sources. Improvements of its efficiency and durability is highly demanded for deep penetration of the renewables and development of a sustainable society. In this dissertation, strategies are guided by controlling mass transport and tuning thermodynamics for electrochemical production of H\textsubscript{2} from H\textsubscript{2}O and H\textsubscript{2}S.

Chapter 2 contributes to develop a novel approach to improve the stability of anodes for OER, in which electroinactive CeO\textsubscript{x} layer was formed on OER electrocatalysts by an electrochemical anodic deposition. To identify the
functionality of the layer, various kinds of probe molecules are introduced in the electrolyte solution. Permselectivity of redox ions and molecules through the CeO$_x$ layer is discussed, which are correlated with the improvement of the stability of OER catalysts.

In Chapter 3, oxidation of a soluble redox ion is proposed as an alternative anodic reaction instead of the kinetically sluggish oxygen evolution reaction, which can be combined with the treatment of H$_2$S to achieve redox-mediated H$_2$S splitting. The redox potential of metal complex is estimated by its stability constant and the standard potential of free metal ion. The estimated potential pH diagram helps to identify promising candidates from thermodynamic perspective. To minimize concentration overpotential in near-neutral pH region, diffusion of redox ions is further optimized by solubility or redox ions, supporting buffer and operating temperature.

Maximizing HER performance in near-neutral pH solution is important not only for above mentioned redox-mediated H$_2$S splitting but also for photocatalytic water splitting. Chapter 4 contributes to identify the mass transfer contribution in near-neutral pH buffered solution during HER. An advanced mass transport model is developed, in which diffusion of H$_2$ and proton carriers is considered at the same time. Concentration overpotentials from pH and H$_2$ gradient are distinguished, which highly depends on the electrolyte identity and molarity.

Combining the knowledge obtained from Chapter 2 - 4, a stand-alone module was developed for solar-driven redox-mediated H$_2$S splitting in Chapter
5. A photovoltaic module was directly connected to an electrochemical module, in which anodes oxidize Fe$^{2+}$-HEDTA redox ion and cathodes produce H$_2$. Unique membrane-free device was fabricated by coating permselective CrO$_x$ layer on cathode. The stand-alone device was demonstrated to produce H$_2$ under natural light irradiation. Sulfide ion was oxidized to solid sulfur in the succeeding homogeneous reaction with Fe$^{3+}$-HEDTA, which confirmed the proof of concept for the present system. The main challenge was the stability of CrO$_x$ nanomembrane layer on cathode. The stability of CrO$_x$ layer is discussed based on the thermodynamics in the target electrolyte solutions.

The present dissertation clearly demonstrates the importance for regulating the mass transport of ions and molecules by the electrolyte engineering and the coating with permselective layers to improve energy efficiency and stability. Estimation of redox potential is fundamental but demonstrated to be a powerful tool to design electrochemical reactions and to choose stable materials for target reactions. The approaches studied in this dissertation will contribute to the development of various kinds of electrochemical applications, such as electrochemical CO$_2$ reduction, photocatalytic water splitting, redox flow batteries, and so on.
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2. Improving the Stability of Oxygen Evolution Electrocatalysts by a Permselective CeO$_x$ Layer$^a$

Electrochemical oxygen evolution reaction is a major energy loss during water electrolysis. Its deactivation under harsh oxidative conditions severely affect the overall cell voltage for water splitting. In this chapter, electrochemical anodic deposition of CeO$_x$ layer was applied on OER catalysts. Its functionalities for OER and permselectivity of reducing agents are discussed.

2.1. Introduction

The anodic oxygen evolution reaction (OER) is a kinetically sluggish reaction, requiring a substantial overpotential during the water electrolysis unlike the hydrogen evolution reaction (HER) conducted on the cathodic side. Highly active, durable and cost-effective electrocatalysts for OER are desired for the development of an efficient water splitting device. NiFeO$_x$ is one of the most active electrocatalysts for OER in alkaline conditions, and while it is known that Fe plays a critical role in the improved activity,$^1$ the origin of the enhancement of the OER kinetics by Fe doping is still under debate. Although many studies have been devoted to decreasing the overpotential via the development of an LDH structure,$^{4-6}$ compositional control,$^7$ or deposition on a conductive support with high surface area,$^7,8$ few reports have discussed the stability under harsh oxidative conditions.$^9$ Görlin et al. reported a significant overpotential increase (approximately 30 mV) on Ni$_{0.65}$Fe$_{0.35}$O$_x$ over 20 h during a constant current

$^a$ This chapter was adapted from K. Obata and K. Takanabe, *Angew. Chem. Int. Ed.*, 2018, DOI: 10.1002/anie.201712121
electrolysis at 10 mA cm$^{-2}$. Speck et al. observed that the iron content in the Ni$_{0.5}$Fe$_{0.5}$O$_x$ catalyst decreased from the loss of FeO$_4^{2-}$ species after the overpotential increased by approximately 200 mV during the stability test at 200 mA cm$^{-2}$ for 24 h. FeOOH is also known to dissolve as FeO$_4^{2-}$ during OER in alkaline solutions.

Unique functionalities can be introduced by a surface modification on electrocatalysts. A variety of surface layers are proposed especially for HER catalysts, such as CrO$_x$, MoO$_x$, TiO$_x$ and SiO$_x$. These layers are reported to suppress undesired side reactions, like oxygen reduction reaction, and poisoning by impurities while producing hydrogen. The functionalities originate from the suppressed diffusion of unwanted reactants through the layers while allowing proton and hydrogen to go through. Meanwhile, an effective layers for OER catalysts are not explored, in which the layers have to be stable under harsh oxidative condition. The above mentioned layers developed for cathodic sites may not be applicable for OER electrocatalysts because those layers are often formed by an electrochemical cathodic deposition, which can be oxidized back to soluble ions in the anodic condition. Therefore, layers different from those for HER electrocatalysts are required for OER catalysts, which is preferably deposited by an electrochemical anodic process.

In this chapter, the stability issue of an active OER electrode by coating the electrode with a protective thin layer that allows the evolved O$_2$ to penetrate, without losing dissolved ion species from the active surface into the solution. Herein, an anodically deposited CeO$_x$ layer successfully realizes this unique
permselectivity that results in a highly stable performance of the NiFeO\textsubscript{x} catalyst. The functionality of the deposited CeO\textsubscript{x} layer was investigated by introducing a variety of probe molecules in the electrolyte.

\textbf{2.2. Results and discussion}

\textbf{2.2.1. Synthesis and Characterization of CeO\textsubscript{x}-coated NiFeO\textsubscript{x}}

NiFeO\textsubscript{x} was prepared on a Au substrate by a conventional cathodic deposition\textsuperscript{20,21} and was used as the base electrode. The CeO\textsubscript{x} layer was formed on the NiFeO\textsubscript{x} by applying a constant anodic potential of 1.7 V vs. the reversible hydrogen electrode (RHE) in the deposition solution containing 0.4 M cerium nitrate and 0.4 M ammonium acetate (pH = 7).\textsuperscript{22} Acetate ion helps to stabilize Ce\textsuperscript{3+} in the deposition solution. The optimal deposition time was found to be 6 h (vide infra). In the deposition solution, Ce\textsuperscript{3+} is oxidized and precipitates on the anode due to the lower solubility of Ce\textsuperscript{4+} compared to Ce\textsuperscript{3+} as shown in the following equations.\textsuperscript{22}

\begin{align*}
\text{Ce(CH}_3\text{COO)}^- + \text{H}_2\text{O} &\rightarrow \text{Ce}^{\text{3+}} + \text{CH}_3\text{COOH} + \text{OH}^- \quad (2.1) \\
\text{Ce}^{\text{3+}} + 2\text{OH}^- + \text{H}_2\text{O} &\rightarrow \text{Ce(OH)}_2^{\text{2+}} + \text{e}^- \quad (2.2) \\
\text{Ce(OH)}_2^{\text{2+}} + 2\text{OH}^- &\rightarrow \text{CeO}_2 + \text{H}_2\text{O} \quad (2.3)
\end{align*}

Ce\textsuperscript{3+} can be also oxidized by O\textsubscript{2} evolved from the anode, making the Ce deposition process rather complex.\textsuperscript{23}
Because Ni(OH)$_2$ matrix becomes conductive only after oxidation to NiOOH$^{24}$ more anodic potential (1.7 V vs. RHE) was applied than that for the oxidization of Ce$^{3+}$ (1.0 V vs. RHE) to deposit CeO$_x$ on top of NiFeO$_x$ (Figure 2.1a and b), where oxygen is also evolved.

![Figure 2.1](image-url)

**Figure 2.1.** Cyclic voltammograms for (a) the Au substrate and (b) NiFeO$_x$ electrode in 0.4 M Ce(NO)$_3$ + 0.4 M CH$_3$COONH$_4$ (pH = 7) under an Ar atmosphere (conditions: 20 mV s$^{-1}$ and 298 K). (c) Chronoamperogram of the NiFeO$_x$ electrode at 1.7 V vs. RHE during the deposition process of CeO$_x$ in 0.4 M Ce(NO$_3$)$_3$ + 0.4 M CH$_3$COONH$_4$ (pH = 7) under an Ar atmosphere.

In the cyclic voltammogram of the Au substrate in the deposition solution (Figure 2.1a), oxidation of Ce$^{3+}$ appeared at approximately 1.0 V vs. RHE in the 1st cycle and disappeared from the 2nd cycle, consistent with a previous report.$^{22}$ Oxidation of Ni$^{2+}$ appeared at 1.65 V vs. RHE in the deposition solution (Figure 2.1b).

Therefore, the potential for deposition was determined to be 1.7 V vs. RHE for
the deposition of CeO$_x$ on the oxidized conductive NiFeO$_x$ matrix. The deposition
time was fixed to 6 h unless specified otherwise. A representative
chronoamperogram is shown in Figure 2. 1c, which shows that the total charge
passed during the deposition was 13±1 C cm$^{-2}$, corresponding to 150±11 μmol
cm$^{-2}$ of electrons. Using inductively coupled plasma (ICP), the total amount of
deposited Ce was measured to be 1.9±0.2 μmol cm$^{-2}$ (Before stability test in
Table 2. 1). Therefore, only less than 10% of total charge (150±11 μmol cm$^{-2}$ of
electrons) was utilized for the deposition process.

**Table 2. 1.** Compositions of bare and CeO$_x$-coated NiFeO$_x$ as measured by ICP.
Compositions were obtained before and after stability test at 20 mA cm$^{-2}$ for 96 h.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Ni/μmol cm$^{-2}$</th>
<th>Fe/μmol cm$^{-2}$</th>
<th>Ce/μmol cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before stability test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFeO$_x$</td>
<td>1.3±0.3</td>
<td>0.8±0.3</td>
<td></td>
</tr>
<tr>
<td>CeO$_x$/NiFeO$_x$</td>
<td>1.2±0.3</td>
<td>0.9±0.3</td>
<td>1.9±0.2</td>
</tr>
<tr>
<td>After stability test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFeO$_x$</td>
<td>1.0±0.1</td>
<td>0.6±0.1</td>
<td></td>
</tr>
<tr>
<td>CeO$_x$/NiFeO$_x$</td>
<td>1.4±0.1</td>
<td>0.86±0.20</td>
<td>1.8±0.2</td>
</tr>
</tbody>
</table>

Top-view scanning electron microscopy (SEM) images of bare NiFeO$_x$
and the CeO$_x$-coated NiFeO$_x$ electrodes are shown in Figure 2. 2a and b,
respectively, and the cross-sectional image of the latter is shown in Figure 2. 2c.
Figure 2.2. Top-view SEM images of (a) bare NiFeO\textsubscript{x} and (b) CeO\textsubscript{x}-coated NiFeO\textsubscript{x}. (c) Cross-sectional (milled by focused ion beam (FIB)) SEM images of CeO\textsubscript{x}-coated NiFeO\textsubscript{x}.

It can be seen that the cathodically deposited NiFeO\textsubscript{x} had a coarse structure on the Au substrate, and the CeO\textsubscript{x} layer was uniformly formed with a thickness in the 100 - 200 nm range on top of the NiFeO\textsubscript{x}. Transmission electron microscopy (TEM) image of CeO\textsubscript{x} layer revealed that approximately 5 nm of nanoparticles aggregated to form the layer consisting apparent voids between them (Figure 2. 3b). The CeO\textsubscript{x} material at the NiFeO\textsubscript{x} surface seems to be more porous than the bulk layer (Figure 2. 3a) and some lattice fringes suggest the existence of ultrafine crystalline structure of CeO\textsubscript{2}, which is confirmed by selected-area electron diffraction (SAED), forming its aggregated layer (Figure 2. 3c and d).
Figure 2.3. (a) Cross-section TEM image of CeO$_x$-coated NiFeO$_x$. (b) (c) high resolution TEM images of CeO$_x$ layer. (d) SAED of CeO$_x$ layer

Raman spectra show an O−Ce−O vibration at approximately 450 cm$^{-1}$ with the broad Ni−O vibration peak$^{25,26}$ from Ni(OH)$_2$ at approximately 560 cm$^{-1}$ (Figure 2.4a). When compared to commercial crystalline CeO$_2$, the O−Ce−O vibration was shifted toward lower wavenumber values, and the peak shape became broader. This difference can be due to the particle size or coexistence of Ce$^{3+}$.$^{27,28}$ The XRD diffraction pattern did not show any peaks from crystalline CeO$_2$ apparently because of fine crystalline particles (Figure 2.4b). It showed a broad peak at approximately 25°, indicating the coexistence of the amorphous phase. XPS spectra of Ce 3d showed a multiplet splitting composed of Ce$^{3+}$ and Ce$^{4+}$,$^{26,29,30}$ indicating that Ce$^{3+}$ precipitated together with Ce$^{4+}$ (Figure 2.4c). O
1s spectra showed two main peaks at 529 eV and 532 eV, characteristic of oxide and hydroxide\textsuperscript{29–31}, respectively (Figure 2. 4d).

![Figure 2. 4.](image)

(a) Raman spectra of bare and CeO\textsubscript{x}-coated NiFeO\textsubscript{x} electrode and commercial CeO\textsubscript{2}. Raman spectra were obtained before and after the stability test at 20 mA cm\textsuperscript{−2} for 96 h. (b) XRD diffractograms of the substrate (Au/Ti/FTO), NiFeO\textsubscript{x}/substrate and CeO\textsubscript{x}/NiFeO\textsubscript{x}/substrate. (c) (d) XPS spectra of the freshly prepared CeO\textsubscript{x} layer: (c) Ce 3d and (d) O 1s.
2.2.2. Electrochemical Measurements of CeO$_x$-coated OER Catalysts

Figure 2. 5a shows a stability test of uncoated and CeO$_x$-coated NiFeO$_x$ at 20 mA cm$^{-2}$ in 1 M KOH.

Figure 2. 5. (a) Electrocatalytic stability test by controlled current electrolysis at 20 mA cm$^{-2}$. Cyclic voltammograms of bare NiFeO$_x$ and CeO$_x$/NiFeO$_x$ electrodes before and after the stability test. (c) Tafel plot taken from cyclic voltammograms. Scans (20 mV s$^{-1}$) in the negative direction are shown. (d) Peak positions of the Ni reduction peak taken from the cyclic voltammograms. All the measurements were conducted in purified 1 M KOH at 298 K with O$_2$ bubbling.

Uncoated NiFeO$_x$ reached 20 mA cm$^{-2}$ at 1.53 V vs. RHE in the beginning of the stability test, but the overpotential increased with time by more than 60 mV over 96 h. The uncompensated resistance which comes from the resistance of solution and electrode did not change before and after the stability test, which
implies that delamination of electrocatalysts from the substrate and the resultant increase of resistance are not the reason for the increased overpotential. On the other hand, CeO$_x$-coated NiFeO$_x$ maintained its overpotential for 96 h, while the potential to achieve 20 mA cm$^{-2}$ was similar to the uncoated NiFeO$_x$ at the initial stage.

In the cyclic voltammogram (CV) measured immediately after the stability test (96 h), a slight recovery of the current toward OER was observed at the second cycle, without going back completely to the original current density measured prior to the stability test on the bare NiFeO$_x$ electrode (Figure 2. 5b). It is often reported that a cathodic sweep or resting potential help to recover the current of deactivated NiFeO$_x$ to some extent, but the reason for this still remains unclear. In contrast, although a slight increase of the overpotential (~10 mV) was observed during the stability test for CeO$_x$-coated NiFeO$_x$, by potential sweeping, the OER current recovered completely to the original value that was measured prior to the stability test (Figure 2. 5b). This full recovery was in marked contrast to the behavior observed for the bare NiFeO$_x$ electrode.

Importantly, the Tafel slope remained $\approx$40 mV dec$^{-1}$ after the CeO$_x$ deposition (Figure 2. 5c), clearly suggesting that the CeO$_x$ layer did not affect the reaction mechanism of NiFeO$_x$ toward OER. A comparison of the redox peaks of Ni$^{2+/3+}$ in the CVs measured before and after the stability test showed that the redox peaks exhibited a similar negative shift after anodic polarization on bare and CeO$_x$-coated NiFeO$_x$ (Figure 2. 5d) despite their different stabilities. This indicates that
the redox peak position of Ni\textsuperscript{2+/3+} does not reflect the OER activity, in agreement with a previous report.\textsuperscript{32}

Examination of the Raman spectra obtained after the stability test shows that a broad peak due to NiO\textsuperscript{25} appeared at approximately 670 cm\textsuperscript{-1} on the bare and CeO\textsubscript{x}-coated NiFeO\textsubscript{x} (Figure 2. 4a). The O–Ce–O vibration remained broad and shifted to lower wavenumber compared to commercial CeO\textsubscript{2}. XPS spectra also showed that the coexistence of Ce\textsuperscript{3+} and Ce\textsuperscript{4+} was retained, along with the coexistence of the oxide and hydroxide, after anodic polarization (Figure 2. 6a and b). These results indicate that the CeO\textsubscript{x} layer did not show a significant change in its crystal nature after the OER. From ICP measurement, the amount of Fe in the bare NiFeO\textsubscript{x} remained unchanged after stability test (Table 2. 1) in contrast with the previous report observing content of Fe dropped from 50% to 25%.\textsuperscript{10,12} It is consistent with the claim in the literature that only limited amount of Fe was highly active sites\textsuperscript{32–34} and those sites were lost, which could not be quantified by our ICP measurement. Alternatively, the amount of Ce remained unchanged after long current electrolysis, suggesting that CeO\textsubscript{x} layer was not a sacrificial layer. Top-view SEM images of CeO\textsubscript{x}-coated NiFeO\textsubscript{x} electrode after the stability test also shows that CeO\textsubscript{x} layer maintained similar morphology compared with that before the stability test (Figure 2. 2b and Figure 2. 6c).
Figure 2.6. XPS spectra of (a) Ce 3d and (b) O 1s for CeO$_x$ layer after chronoamperometry at 20 mA cm$^{-2}$ for 5 h. (c) Top-view SEM image of CeO$_x$-coated NiFeO$_x$ after stability test for 96 h.

Impedance spectra of the bare and CeO$_x$-coated NiFeO$_x$ electrodes show a single semicircle that arises from the parallel connection of the charge transfer resistance ($R_{CT}$) toward OER and the double layer capacitance ($C_{dl}$) (Figure 2.7a and c). The corresponding transition appeared at approximately 100 Hz in the Bode plot (Figure 2.7b). A thick oxide film was often reported to show an additional semicircle in the Nyquist plot and the corresponding peak of the phase and step of log|Z| at approximately 1 kHz in the Bode plot. This additional semicircle is assigned to the parallel connection of the resistance ($R_f$) and capacitance ($C_f$) from the oxide film$_{35-38}$ (Figure 2.7d) and induces a potential drop through the oxide film. CeO$_x$-coated NiFeO$_x$ did not show any other
observable semicircle, which also implies that the CeO$_x$ layer itself did not cause a potential loss through the layer in alkaline conditions.

![Nyquist and Bode plots](image)

**Figure 2. 7.** (a) Nyquist plots and (b) Bode plots of bare NiFeO$_x$ and CeO$_x$/NiFeO$_x$ at 20 mA cm$^{-2}$ in purified 1 M KOH at 298 K with O$_2$ bubbling. Equivalent circuit for (c) Randles circuit and (d) Voigt circuit.

An electrode with CeO$_x$ directly deposited on Au without NiFeO$_x$ did not exhibit any appreciable current at ~1.5 V vs. RHE, confirming that CeO$_x$ itself is not relatively active for OER (Figure 2. 8a). When the deposition process was conducted in the absence of the Ce$^{3+}$ precursor, the stability of the NiFeO$_x$ was not improved, also confirming that the deposition of the CeO$_x$ layer is essential for obtaining a stable OER performance (Figure 2. 8b), i.e., either acetate or ammonium ions in the deposition solution alone did not contribute to the improved stability.
Another possibility to cause improved stability is that the Ce species alters the nature of NiFeO\textsubscript{x}. Doping of Ce into the Ni-based catalyst is reported to improve the kinetics of OER and 3-5 nm of segregated CeO\textsubscript{2} was reported after electrochemical measurements even though the contribution of CeO\textsubscript{2} to the improved kinetics is still under investigation.\textsuperscript{39-41} Therefore, different compositions of NiFeCeO\textsubscript{x} electrodes were also prepared by adding Ce(NO)\textsubscript{3} into the solution for cathodic deposition of oxide catalysts. The compositions of deposition solutions and deposited electrocatalysts are shown in Table 2. 2, demonstrating the successful incorporation of the Ce species into NiFeO\textsubscript{x}. 

**Figure 2.8.** (a) Cyclic voltammograms of the bare and CeO\textsubscript{x}-coated Au/Ti/FTO electrodes in 1 M KOH (conditions: 20 mV s\textsuperscript{-1} and 298 K). (b) Chronoamperogram of bare NiFeO\textsubscript{x} and NiFeO\textsubscript{x} treated by chronoamperometry in solution without Ce precursor (0.4 M CH\textsubscript{3}COONH\textsubscript{4} pH = 7). (conditions: 1 M KOH and 298 K).
Table 2.2. Compositions of NiFeCeO₃ measured by ICP. The NiFeCeO₃ electrodes were prepared by cathodic deposition in the solution containing 50 mM NH₄OH, 25 mM H₂SO₄, 9 mM NiSO₄, 9 mM FeSO₄ and x mM Ce(NO₃)₃.

<table>
<thead>
<tr>
<th>x / mM</th>
<th>Ni / μmol cm⁻²</th>
<th>Fe / μmol cm⁻²</th>
<th>Ce / μmol cm⁻²</th>
<th>Composition of deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.3±0.2</td>
<td>0.22±0.07</td>
<td>0.03±0.01</td>
<td>Ni₀.₈₄Fe₀.₁₄Ce₀.₀₂Oₓ</td>
</tr>
<tr>
<td>6</td>
<td>0.6±0.2</td>
<td>0.12±0.04</td>
<td>0.05±0.02</td>
<td>Ni₀.₇₉Fe₀.₁₅Ce₀.₀₆Oₓ</td>
</tr>
<tr>
<td>9</td>
<td>0.6±0.1</td>
<td>0.09±0.02</td>
<td>0.07±0.01</td>
<td>Ni₀.₇₈Fe₀.₁₃Ce₀.₀₉Oₓ</td>
</tr>
</tbody>
</table>

Ni₀.₈₄Fe₀.₁₄Ce₀.₀₂Oₓ indeed exhibited improved OER performance (both onset and current) compared to NiFeOₓ without Ce incorporation (Figure 2.9a and b). The introduction of an additional CeO₃ layer did not alter the initial OER performance but largely improved the stability (Figure 2.9c).
Figure 2. 9. (a) Cyclic voltammograms measured at 10 mV s\(^{-1}\) and (b) chronoamperograms of bare NiFeO\(_x\), NiFeCeO\(_x\) and CeO\(_x\)/NiFeO\(_x\) in 1 M KOH. (c) Electrocatalytic stability tests by controlled current electrolysis at 20 mA cm\(^{-2}\) of the electrodes in purified 1 M KOH. (Conditions: 298 K, with bubbling of O\(_2\))
2.2.3. Evaluation of Permselectivity through CeO\(_x\) layer

The permselectivity of the CeO\(_x\) layer in the presence of various kinds of reducing agents, which can be oxidized on NiFeO\(_x\), was investigated by electrochemical measurements. Figure 2. 10a shows representative cyclic voltammograms of the bare and CeO\(_x\)-coated NiFeO\(_x\) electrodes in 1 M KOH with and without 0.2 M K\(_4\)Fe(CN)\(_6\). In the alkaline solution with the ferrocyanide redox ions, bare NiFeO\(_x\) displays the oxidation and reduction peaks of ferrocyanide and ferricyanide, which has the redox formal potential at 1.33 V vs. RHE in pH 14, followed by the redox peaks of Ni\(^{2+/3+}\). On the other hand, CeO\(_x\)-coated NiFeO\(_x\) does not show any redox peaks of the ferrocyanide ions, and only the redox peaks from Ni\(^{2+/3+}\) as if ferrocyanide ions are absent were observed, implying that the CeO\(_x\) layer blocked the permeation and charge transfer of ferrocyanide. Then, CeO\(_x\)-coated NiFeO\(_x\) electrodes with different deposition times were prepared and tested for the same experiment (Figure 2. 10b). Comparing the currents at 1.4 V vs. RHE where ferrocyanide oxidation contribution is obvious, CeO\(_x\)-coated NiFeO\(_x\) with 2 h of deposition detected a higher current for the oxidation of ferrocyanide. This indicates that more than 4 h of deposition are necessary to obtain sufficient permselectivity. This permselectivity was also confirmed by gas quantification of O\(_2\) during controlled current electrolysis at 10 mA cm\(^{-2}\) (Figure 2. 10c). In the case of bare NiFeO\(_x\), oxygen was not detected in the initial 3 h, indicating that the oxidation of the redox mediator dominated on the bare NiFeO\(_x\) surface rather than OER. After 3 h of electrolysis, oxygen started to evolve only gradually due to the decreasing
concentration of redox species during the electrolysis and resultant diffusion limitation of redox species. On the other hand, >90% of the faradaic efficiency to O₂ was maintained on CeOₓ/NiFeOₓ after 7 h.

**Figure 2.10.** (a) Cyclic voltammograms for the bare and CeOₓ-coated NiFeOₓ electrodes at 20 mV s⁻¹ (CeOₓ deposition time: 6 h) (b) Linear sweep voltammograms of the CeOₓ-coated NiFeOₓ electrodes with different deposition times (2, 4, and 6 h) at −20 mV s⁻¹. (c) Faradaic efficiency of O₂ at 10 mA cm⁻² for the bare and CeOₓ-coated NiFeOₓ electrodes. All the measurements were performed in in 1 M KOH solution with and without 0.2 M K₄Fe(CN)₆ under Ar atmosphere at 298 K. (d) Cyclic voltammograms for the bare and CeOₓ-coated FTO electrodes (CeOₓ deposition: 10 μA cm⁻², 1 h) in 0.5 M K₁.₆H₁.₄PO₄ (pH = 7) with and without 5 mM K₄Fe(CN)₆.

Above mentioned measurements are performed without any drying process after deposition. The permselectivity of CeOₓ layer is sensitive to the drying as shown in Figure 2.10d performed with FTO in 0.5 M K₁.₆H₁.₄PO₄ (pH = 7). After the deposition of CeOₓ layer on FTO substrate, the oxidation peak
from ferrocyanide above 1 V vs. RHE is effectively suppressed. After drying CeO\textsubscript{x}/FTO at 110 °C for 7 h in air, oxidation current above 1 V vs. RHE increased which indicates that the permselective functionality was lost most likely due to the formation of cracks and voids. These comparisons implies that measurements or imaging performed in dried or vacuum condition, such as BET and TEM imaging, may not represent the layer during operation without drying process.

To further investigate the permselectivity of the CeO\textsubscript{x} layer, Faradaic efficiencies of O\textsubscript{2} in the presence of different kinds of reducing agents, such as iodide, methanol, ethanol, isopropanol, lactate and malate, were further evaluated and are summarized in Figure 2. 11 with the corresponding Stokes radii of reducing agents, which were estimated from the corresponding diffusion coefficients in aqueous solution.\textsuperscript{42,43}

In alkaline solutions, all reducing agents used are more thermodynamically preferred to be converted than.\textsuperscript{44–46} Among different alcohols, bulkier i-PrOH reaction was more suppressed than smaller MeOH by the CeO\textsubscript{x} layer. A clear improvement of selectivity toward O\textsubscript{2} was observed in the solution with redox anions rather than neutral alcohols. Notably, while lactate anion and isopropanol have similar Stokes radii, significant improvement for OER selectivity was obtained in the presence of lactate anion, suggesting that charges of reactants play a significant role to the permeation through the CeO\textsubscript{x} layer. This trend suggests that diffusion of the reducing agents is impacted not only by their sizes but also by their charges. Since the isoelectronic point of CeO\textsubscript{2} is reported to be approximately 7,\textsuperscript{47,48} the CeO\textsubscript{x} layer should be negatively charged and repulse
anions, resulting in the more effective suppression of the diffusion of the anion through the layer in alkaline conditions. Although OH$^-$ ions are also negatively charged, the CeO$_x$ layer electrodeposited by anodic polarization was reported to have a hydrous disordered structure,$^{49}$ which could contribute to the diffusion of OH$^-$ to the NiFeO$_x$ catalyst underneath the layer.

![Figure 2.11. Faradaic efficiency of O$_2$ during controlled current electrolysis at 10 mA cm$^{-2}$ for the bare and CeO$_x$-coated NiFeO$_x$ electrode in 1 M KOH solution in the presence of different kinds of reducing agents with the corresponding Stokes radii](image)

Confinement effect is reported to provide a unique reaction environment between the catalysts and overlayers, which results in a different catalytic activity.$^{50}$ For example, enhanced activity towards oxidation of CO and methanol is reported on Pt encapsulated with SiO$_x$ overlayer. In the present comparison between bare NiFeO$_x$ and CeO$_x$/NiFeO$_x$, confinement effect towards the measured Faradaic efficiency is expected to be negligible because improved Faradaic
efficiency by CeO, deposition was observed regardless of organic anions and inorganic anions. Therefore, permselectivity towards the anionic species supposed to play a major role rather than the altered reactivity of catalysts in the presence of overlayer.

Effective diffusion coefficient can be roughly calculated using Fick’s law in the electrolyte and through the layer.\(^5\) Herein, diffusion coefficient of ferrocyanide anion, whose diffusion coefficient in aqueous solution is 4.8×10\(^{-5}\) cm\(^2\) s\(^{-1}\),\(^4\) is discussed based on the measured Faradaic efficiency shown in Figure 2. 10c. Because the gas quantification was performed in a static condition, convection in a mass-transport equation is ignored. Migration which is a movement of charged species driven by an electric field is also ignored in the present estimation for simplification. The remaining driving force to move molecule is diffusion which comes from Fick’s law caused by concentration gradient of individual species. The resultant current density is described by the following equation,

\[
j_i = FD_{i,\text{liq}} \frac{\partial c_i}{\partial x} = FD_{i,\text{liq}} \frac{c_{i,\text{bulk}} - c_{i,\text{surface}}}{\delta_{\text{liq}}} \tag{2. 4}\]

where \(F\) and \(x\) are Faraday constant and distance from the electrode. \(D_{i,\text{liq}}\) and \(c_i\) represent the diffusion coefficient in aqueous solution and concentration of species \(i\), respectively. Subscribe bulk and surface represent the concentration in the bulk solution and at the electrode surface, respectively. \(\delta_{\text{liq}}\) is the diffusion layer thickness in the aqueous solution.
Figure 2.12. Simplified schematic imaging representing diffusion from the bulk solution (a) without and (b) with CeO$_x$ overlayer.

Using the results from bare electrode, O$_2$ started to evolve after 2 h of electrolysis in the batch reactor, which means that the diffusion limiting current density for ferrocyanide reached to 10 mA cm$^{-2}$ after 2 h. The concentration of remaining ferrocyanide is estimated to be 0.18 M from the measured Faradaic efficiency of bare electrode, the electrolyte volume and the initial concentration. The diffusion limiting current density is obtained when $c_{i,\text{surface}}$ becomes zero as shown in Figure 2.12a, which results in the diffusion layer thickness ($\delta_{liq}$) to be 80 $\mu$m in the present electrolyte solution calculated from equation 2.4.

The estimated diffusion layer thickness in the solution ($\delta_{liq}$) is applied to the measurement with CeO$_x$/NiFeO$_x$ electrode and the thickness of CeO$_x$ layer is assumed to be uniform ($\delta_{film} = 100$ nm) for simplification in the present estimation. From the gas quantification, the diffusion limiting current density in the presence of CeO$_x$ layer was 1 mA cm$^{-2}$. The diffusion limiting current density (1 mA cm$^{-2}$) has to be applied in the solution and through the layer, which results in the following equation,
\[ j_i = F D_{i,\text{liq}} \frac{(c_{i,\text{bulk}} - c_{i,\text{int}})}{\delta_{\text{liq}}} = F D_{i,\text{film}} \frac{(c_{i,\text{int}} - 0)}{\delta_{\text{film}}} \]  (2.5)

where \( c_{i,\text{int}} \) denotes the concentration at the interface between the electrolyte and the layer. Theoretically, the concentration equilibrium between the electrolyte and the layer at the interface has to be considered, which is called partition coefficient.\(^5^2\) In the present estimation, the partition coefficient is assumed to be unity and \( c_{i,\text{int}} \) is applied to the electrolyte and the layer at the interface as shown in Figure 2.12b. The second term and the last term in the equation 2.5 represent the description of the current density in the electrolyte and through the layer, respectively. \( D_{i,\text{film}} \) of ferrocyanide is estimated to be \( 6.0 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \). This value is in a reasonable range comparing with the reported diffusion coefficient of proton in SiO\(_x\) layer \( (10^{-10} - 10^{-11} \text{ cm}^2 \text{ s}^{-1}) \).\(^5^2\)

The coating of the CeO\(_x\) layer can be applied to water splitting in the presence of Cl\(^-\) to improve the stability of the NiFeO\(_x\) catalysts. The overpotential of NiFeO\(_x\) increased by more than 60 mV in 6 h in the solution with 1 M KCl, while it increased by 30 mV in the solution without KCl (Figure 2.13). No oxidation of Cl\(^-\) was observed in alkaline conditions because the corresponding redox potential is reported to be 1.72 V vs. RHE,\(^5^3\) which is higher than the observed potential. Cl\(^-\) appears to facilitate the deactivation of NiFeO\(_x\), as was also observed in a previous study,\(^5^3\) even though the reason of the promoted degradation is not well-understood. On the other hand, the overpotential of CeO\(_x\)-coated NiFeO\(_x\) increased only by 15 mV in 6 h, which was comparable to that for bare NiFeO\(_x\) at the beginning of the stability test.
Figure 2.13. Electrocatalytic stability tests of the bare and CeO\(_x\)-coated NiFeO\(_x\) electrodes by controlled current electrolysis at 20 mA cm\(^{-2}\) in 1 M KOH with and without 1 M KCl at 298 K with O\(_2\) bubbling.

Suppressed anion diffusion was also observed in near-neutral 0.5 M K\(_{0.6}\)H\(_{2.4}\)BO\(_3\) solution (pH = 9.4). The overpotential toward OER increased drastically due to the deposition of CeO\(_x\), while those in 1 M KOH for bare and CeO\(_x\)-coated NiFeO\(_x\) were quite similar (Figure 2.14). In neutral pH (< 11), buffer anions are required to continuously remove the protons produced from water during OER because the insufficient amount of OH\(^-\) induces reactant switching from OH\(^-\) to water.\(^{54}\) The increased overpotential due to the CeO\(_x\) layer also indicates that the presence of the CeO\(_x\) layer prevented the diffusion of the buffer anion, which unfortunately limits the applicability of CeO\(_x\) in buffered condition at least when the layer is thick.
Figure 2.14. Cyclic voltammograms of (a) the bare and (b) CeO$_x$-coated NiFeO$_x$ electrodes in 1 M KOH (pH = 14) and 0.5 M KBi (K$_{0.6}$H$_{2.4}$BO$_3$, pH = 9.4) under bubbling of O$_2$ (condition: 10 mV s$^{-1}$ and 298 K).

In an alternative approach, the deposition of CeO$_x$ was also conducted on CoO$_x$ nanoparticles (SEM images are shown in Figure 2.15).

Figure 2.15. Top-view SEM images of (a)CoO$_x$/FTO and (b)CeO$_x$/CoO$_x$/FTO.
An accelerated stability test was performed by cyclic voltammetry in 0.5 M phosphate buffer solution (pH = 7) (Figure 2. 16). Bare CoOₓ showed a drastic decrease of the current and a positive shift of the onset potential with potential cycles that were attributed to the gradual loss of the Co species from the electrode surface. The CeOₓ coating did not alter the initial onset, i.e., the electrocatalytic activity of CoOₓ. These observations are attributed to the confinement introduced by the layer where the dissolved Co species is maintained within the layer, assisting self-healing. Thus, the essential role of the additional CeOₓ layer for the stability was confirmed to be universal regardless of the OER catalysts.

Based on these results, the CeOₓ layer is confirmed to show permselectivity, which prevents the detrimental redox species from diffusing through. Figure 2. 17 summarizes the permselective functionality of the CeOₓ layer. In particular, the layer suppresses the diffusion of dissolved Fe species from catalyst to the electrolyte, resulting in the preservation of the active sites in NiFeOₓ during anodic polarization.
Figure 2.17. Schematic image of the improved stability and selectivity achieved by the deposition of CeO$_x$ on the OER catalyst.

2.3. Summary

In conclusion, a highly durable NiFeO$_x$ OER electrocatalyst was successfully developed by the anodic deposition of a CeO$_x$ layer on it. The CeO$_x$ consisted of a mixed oxide and hydroxide layer, which prevented the diffusion of redox ions while allowing OH$^-$ and evolved O$_2$ to permeate through. The improved stability of the OER catalysts was attributed to permselectivity, which can regulate the diffusion of redox ions, such as iodide, ferrocyanide and dissolved metal ion species, between the electrolyte and OER catalysts. CeO$_x$ protection is also applicable to other OER materials and obviously to corrosion inhibition without electrocatalysis, demonstrating the universality of the permselective function applicability. This finding demonstrates a promising novel approach for introducing an inorganic layer by anodic deposition for highly active and durable OER catalysts that operate in harsh oxidative conditions.
2.4. Experimental methods

Materials

The following chemicals were used: NiSO$_4$$\cdot$7H$_2$O (99.999%: Sigma-Aldrich), Ni(NO$_3$)$_2$$\cdot$6H$_2$O (99.999%: Sigma-Aldrich), FeSO$_4$$\cdot$7H$_2$O (≥99%: Sigma-Aldrich), Ce(NO$_3$)$_3$$\cdot$6H$_2$O (≥99%: Sigma-Aldrich), cobalt phthalocyanine (99.999%: Sigma-Aldrich), CH$_3$COONH$_4$ (≥99%: Sigma-Aldrich), KOH (99.99%: Sigma-Aldrich), KCl (99.999%: Sigma-Aldrich), H$_3$BO$_4$ (≥95%: Sigma-Aldrich), K$_2$HPO$_4$ (≥99%: Sigma-Aldrich), KH$_2$PO$_4$ (≥98%: Sigma-Aldrich), K$_4$Fe(CN)$_6$$\cdot$3H$_2$O (99.5%: Sigma-Aldrich), KI (99.999%: Sigma-Aldrich), methanol (99.8%: Sigma-Aldrich), ethanol (99.96%: VWR chemicals), isopropanol (100%: VWR chemicals), Lactic acid (85%: Fisher Scientific), Malic acid (≥99%: Sigma-Aldrich), H$_2$SO$_4$ (99.999%; Sigma-Aldrich), NH$_4$OH (≥25%: Sigma-Aldrich), and 4 M NaOH solution (Sigma-Aldrich). Commercial tetragonal CeO$_2$ (>99%) as a reference for Raman spectra was obtained from Daiichi Kigenso Kagaku Kogyo Co. Ltd.

Preparation of materials

A Au substrate was prepared on fluorine-doped tin oxide (FTO) by sputter-coating 20 nm of Ti followed by 190 nm of Au. Electrodeposition of NiFeO$_x$ on the Au-coated FTO substrate was performed by cathodic electrochemical deposition adapted from the literature.$^{20,21}$ A current density of −20 mA cm$^{-2}$ was applied for 2 min in the electrolyte solution containing 50 mM NH$_4$OH, 25 mM H$_2$SO$_4$, 9 mM NiSO$_4$$\cdot$7H$_2$O and 9 mM FeSO$_4$$\cdot$7H$_2$O with a
carbon paper as a counter electrode. The pH of the deposition solution was adjusted to 2.5. When NiFeCeO$_x$ was prepared, 3, 6 or 9 mM of Ce(NO$_3$)$_3$·6H$_2$O was also added to the deposition solution.

The CeO$_x$ layer was formed on the NiFeO$_x$ electrode by anodic deposition in the electrolyte containing 0.4 M Ce(NO$_3$)$_3$·6H$_2$O and 0.4 M CH$_3$COONH$_4$ adapted from a previous report. A constant anodic potential of 1.1 V vs Ag/AgCl was applied for 6 h with a resting period of 1 min for every 30 min. The deposition solution was stirred by magnetic stirring during the deposition. The pH of 0.4 M CH$_3$COONH$_4$ was adjusted to 8 using 4 M NaOH solution and was changed to pH 7 after adding Ce(NO$_3$)$_3$·6H$_2$O. When CeO$_x$ was formed on the Au substrate, a constant anodic current of 0.4 mA cm$^{-2}$ was applied for 6 h. The deposition solutions were bubbled with Ar (99.9999%) for at least 30 min before adding metal salts, and an Ar atmosphere was maintained during deposition.

CoO$_x$ was prepared on the FTO substrate following a previous report. A thin film of cobalt phthalocyanine was deposited by thermal evaporation for 10 min at room temperature. The deposited cobalt phthalocyanine was transformed to CoO$_x$ by annealing in air at 400 °C for 30 min. CeO$_x$ deposition was conducted on the CoO$_x$ electrode following the deposition procedure mentioned above. A constant anodic current (10 μA cm$^{-2}$) was applied for 1 h under an Ar atmosphere.

Physical characterization

X-ray diffraction (XRD) data were collected with a Bruker D8 Advanced A25 diffractometer in the Bragg–Brentano geometry (with Cu K$_\alpha$ radiation at 40 kV and 40 mA). The data sets were acquired in the continuous scanning mode
over the 2θ range of 0−80°. Raman spectra were obtained by an Olympus BXFMILHS microscope with a He/Ne laser with excitation at 633 nm. X-ray photoelectron spectroscopy (XPS) spectra were obtained with an AMICUL KRATOS using an Al anode at 10 kV and 15 mA. The C 1s peak maximum at 284.8 eV was used as an internal standard to correct the binding energies. To obtain the loading of the catalysts on the substrates, the catalysts were dissolved in 1 mL of aqua regia for 12 h and then diluted in 9 mL of Milli-Q water. Inductively coupled plasma (ICP) measurements were performed for the solutions using an ICP-OES Varian 72 ES. Scanning electron microscopy (SEM) images were obtained with Nova Nano 630 scanning electron microscope from FEI Company. Cross-section views were taken using an FEI Helios NanoLab 400S FIB/SEM dual-beam system equipped with a Ga+ ion source. Transmission electron microscopy (TEM) was performed on a FEI Titan 80-300 ST at 300 kV equipped with a Gatan Image Filter (model GIF-Quantum 966). The electrode surfaces were covered by C and Pt layers by electron and ion beams to protect the sample from the milling.

Electrochemical measurement

A 1 M KOH solution (pH = 14), 0.5 M K\textsubscript{1.6}H\textsubscript{1.4}PO\textsubscript{4} (pH = 7) and 0.5 M K\textsubscript{0.6}H\textsubscript{2.4}BO\textsubscript{3} solution (pH = 9.4) were prepared from KOH, H\textsubscript{3}BO\textsubscript{4}, K\textsubscript{2}HPO\textsubscript{4}, KH\textsubscript{2}PO\textsubscript{4} and Milli-Q water (18 MΩ cm). Purification of the 1 M KOH solution was conducted following the procedure described in the literature\textsuperscript{9}, and the solution was used as an electrolyte as specified. Electrochemical measurements were performed using a BioLogic VMP3 potentiostat. A Pt wire and Ni foam
were used as the counter electrodes in purified KOH and other solutions, respectively. Hg/HgO (1 M KOH) (ALS CO., Ltd) and Ag/AgCl (Saturated KCl) (ALS CO., Ltd) were used as the reference electrodes in KOH solution and neutral buffer solutions, respectively. All potentials are reported with respect to the reversible hydrogen electrode (RHE). The potentials were reported with $iR$-correction unless otherwise specified. Solution resistance $R_s$ was measured by impedance spectroscopy (100 mHz – 10 kHz, 10 mV amplitude). Before and during all the measurements, Ar (99.9999%) or O$_2$ (99.999%) gas was continuously supplied to the electrochemical cell.

Product gas from a gas tight electrochemical cell was quantified with a gas chromatograph (GC-8A; Shimadzu Co. Ltd.) equipped with a TCD detector and a molecular sieve 5A column using Ar (99.999%) as the carrier gas. Ar was flowed at 22 sccm in the electrochemical cell, and the outlet gas was connected to a sampling loop in the GC.
2.5. References


(6204), 1593–1596.


3. Electrochemical Oxidation of a Highly Soluble Redox Mediator in Aqueous Solution for Energy Conversion

Although the stability of OER catalysts were significantly improved by newly developed coating with permselective layers in chapter 2, its overpotential still remains large (> 200 mV at 10 mA cm⁻²). Chapter 3 proposes oxidation of soluble redox ions as an alternative anodic reaction instead of kinetically sluggish oxygen evolution reaction, in which oxidized redox ions can be used for the treatment of H₂S to achieve redox-mediated H₂S splitting. The redox potentials of various kinds of metal complexes are estimated by its stability constant and the standard potential of free metal ion. The estimated potential pH diagram helps to identify promising candidates thermodynamically. To minimize concentration overpotential in near-neutral pH region, diffusion of redox ions is further optimized by solubility, supporting buffer and operating temperature.

3.1. Introduction

The electrochemical production of hydrogen has gained tremendous attention to store intermittent renewable energy sources, such as solar and wind power. A lot of efforts have been devoted to developing water-splitting devices in which a hydrogen evolution reaction (HER) takes place on a cathode and an oxygen evolution reaction (OER) happens on an anode to decrease the required voltage, improve stability, and develop ubiquitous-element electrodes. The

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components that determine the required voltage for water splitting are thermodynamics (1.23 V), kinetic overpotential on the electrocatalyst, diffusion overpotential and Ohmic loss. Tandem- or series-connected solar cells are, therefore, required to achieve enough voltage\textsuperscript{1–3} when solar energy is used as a renewable feedstock. It is well known that the kinetics of the OER requires additional overpotential compared to the HER and that the overpotential for OER required to achieve 10 mA cm\textsuperscript{−2} is approximately 200 mV with finely tuned electrocatalysts on high surface area substrates immersed in a highly alkaline aqueous solution at ambient temperature.\textsuperscript{4,5} In fact, to achieve electrochemical hydrogen evolution, anodic reaction is not limited to the OER. For example, in the commercialized chloro-alkaline process, chloride ion is oxidized to chlorine while hydrogen evolves on the cathode. Alternative anodic reactions during the HER have been proposed in the literature, such as oxidative upgrading of biomass feedstock\textsuperscript{6–8} and production of oxidizing agents like hydrogen peroxide or per oxydisulfate anion.\textsuperscript{9–11} In this chapter, oxidation of soluble redox species is discussed, which can potentially serve as redox mediators for successive homogeneous reactions. By choice, some redox electrochemical reactions do not require adsorption on electrode materials due to its outer sphere electron transfer nature. In such cases, fast kinetics can be achieved, especially in contrast to that of the electrocatalytic OER. Since adsorption on electrocatalysts is not involved during electron transfer, non-noble metals and earth-abundant materials are applicable for electrodes, such as carbon, steel and nickel. Redox potential can be
tunable by choice with versatile options to combine with a variety of output voltage originating from renewable energy sources.

Redox species oxidized on an anode can be regenerated via various homogeneous reactions; for example, the oxidation of hydrogen sulfide (or more specifically sulfide ions). Hydrogen sulfide is a by-product (often waste) from wells of crude oil and natural gas, which is essential to be adequately treated. The Clauss process is commonly applied to convert toxic hydrogen sulfide to sulfur and water (Equation 3.1).

\[ 2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + 2\text{H}_2\text{O} \quad (3.1) \]

As an alternative commercialized technique, redox chemistry in liquid phase is applied for the treatment of hydrogen sulfide (Equation 3.2).

\[ \text{H}_2\text{S} + 2\text{Ox} \rightarrow \text{S} + 2\text{H}^+ + 2\text{Red} \quad (3.2) \]

where Ox and Red denote the oxidized and reduced redox species, respectively. The redox potential must be positive enough compared to the oxidation potential of the hydrogen sulfide. Iron-complexes with aminopolycarboxylic acid, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and hydroxyethyleneaminetriacetic acid (HEDTA) are introduced to Sulferox process and LO-CAT process while anthraquinone-based redox is applied for the Stretford process.\textsuperscript{12,13} The reduced redox is subsequently re-oxidized by bubbling oxygen (Equation 3.2)

\[ \text{Red} + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Ox} + \text{OH}^- \quad (3.3) \]
The overall reaction from Equations 3.2 and 3.3 during the process is shown in Equation 3.4, which is the same as the Clauss process.

\[ 2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + 2\text{H}_2\text{O} \quad (3.4) \]

In this process, the redox species are not consumed and serve as an electron mediator between the sulfide and oxygen.

Instead of bubbling oxygen, redox species can be electrochemically re-oxidized on the anode (Equation 3.5) while producing hydrogen on the cathode (Equation 3.6).

\[ \text{Red} \rightarrow \text{Ox} + e^- \quad (3.5) \]

\[ 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2 \quad (3.6) \]

By combining Equations 3.5 and 3.6, the overall reaction becomes Equation 3.7, which is the splitting of hydrogen sulfide to hydrogen and sulfur.

\[ \text{H}_2\text{S} \rightarrow 2\text{H}_2 + \text{S} \quad (3.7) \]

Hydrogen sulfide has a great advantage as feedstock of hydrogen compared to water due to its thermodynamics. The redox potential of sulfide to sulfur is approximately 0.14 V relative to the reversible hydrogen electrode (RHE),\textsuperscript{14} which indicates that single silicon solar cells can be potentially applied to produce hydrogen. Since the direct oxidation of sulfide ion on an anode may cause precipitation of insulating solid sulfur on the surface of anode\textsuperscript{15,16}, the redox-mediated process is an attractive approach. A variety of redox ions, such as
Fe-based redox, iodide, vanadate and heteropoly molybdophosphate, are investigated.\textsuperscript{17–21}

The present work provides detailed insight on the thermodynamics and kinetics for potential candidates of Fe redox species, Fe-EDTA and Fe-HEDTA in addition to anthraquinone-2,6-disulfonate (AQDS) as an organic form. From a thermodynamic point of view, a near-neutral pH was effectively selected to provide suitable voltage range, but it requires the use of supporting buffers to minimize local pH shift during proton-coupled electron transfer reactions. Near-neutral pH also has an advantage compared to acidic conditions to provide potential candidates for a non-noble metal cathode for HER. Although the presence of redox couple can potentially hinder HER on cathode, selective HER can be achieved by incorporation of ion exchange membranes or membrane coated electrodes to prevent side reactions.\textsuperscript{22–25} Due to the highly reversible kinetics of redox species, mass transport represents a major contribution to the current response. Fe-HEDTA has a high solubility (1 mol kg\textsuperscript{-1}), which helps to overcome the diffusion problem. In addition, temperature and the supporting buffer were also examined to improve the diffusion-limitation of redox species.
3.2. Results and discussion

3.2.1. Thermodynamics of Redox Species

The redox potential of the 0.1 M redox species\textsuperscript{26-28} from the standard hydrogen electrode (SHE) is compared to the potential of S\textsuperscript{2-/0} species\textsuperscript{14} and HER/hydrogen oxidation reaction (HOR) in Figure 3. 1a. The redox potential of the iron-based complex can be described by the standard potential of the Fe\textsubscript{aq}\textsuperscript{2+/3+} ion, the corresponding formation constant of the metal complex (\(\beta_{\text{ox}}\) and \(\beta_{\text{Red}}\)) and the activity of the responsible species (\(a_{\text{ox}}\) and \(a_{\text{Red}}\)),\textsuperscript{29,30} as shown in Equation 3. 8.

\[
E = E_{\text{Fe}^{2+}/\text{Fe}^{3+}} - \frac{RT}{n} \ln \frac{\beta_{\text{ox}}}{\beta_{\text{Red}}} + \frac{RT}{n} \ln \frac{a_{\text{ox}}}{a_{\text{Red}}} \quad (3. 8)
\]

where \(n\) denotes the number of charges transferred for the corresponding redox reaction, and \(R\) and \(T\) represent the universal gas constant and temperature, respectively. The first two terms in the right side of the Equation 3. 8 are derived from the thermochemical cycle shown in Figure 3. 1b where the Gibbs free energy of the metal complex redox couple (\(\Delta G_4\)) can be obtained from the corresponding Gibbs free energy of the metal redox couple (\(\Delta G_1\)) and the formation of the metal complex (\(\Delta G_2\) and \(\Delta G_3\)). The Gibbs free energy change is independent of the reaction pathway, which gives Equation 3. 9

\[
\Delta G_1 + \Delta G_3 = \Delta G_2 + \Delta G_4 \quad (3. 9)
\]
Therefore, the Gibbs free energy change of the redox reaction for the metal complex can be determined as shown in Equation 3.10.

$$\Delta G_i = \Delta G_t - \Delta G_2 + \Delta G_3 \quad (3.10)$$

**Figure 3.1.** (a) Potential-pH diagram of total 0.1 M of Fe$^{2+/3+}$-based redox species (50% oxidized and 50% reduced) with the S$^{2−/0}$ species and the HER/HOR. The redox potential of 1 mM of AQDS was reproduced from the literature. 26 (b) Thermochemical cycle describing the change in Gibbs free energy of the metal complex. (c) (d) Speciation distribution diagram of Fe$^{2+}$ and Fe$^{3+}$ in the solution containing 0.05 M Fe$^{2+}$, 0.05 M Fe$^{3+}$, and (c) 0.1 M HEDTA$^{3−}$ and (d) 0.1 M EDTA$^{4−}$ obtained from the HySS program. The formation constants are shown in Table A1.

The last term in Equation 3.8 is to compensate for the activities of the oxidized and reduced species following the Nernst equation. The speciation distribution of the redox couple is obtained from the corresponding equilibrium constants. The distribution of the Fe$^{2+/3+}$-HEDTA and Fe$^{2+/3+}$-EDTA species is shown in Figure 3.1c and 1d, respectively and the corresponding equilibrium constants$^{29,31–34}$ are shown in Table A1. As can be seen from Equation 3.8, the formation constants of
the metal complex can shift the redox potential considerably from the potential of
the free Fe\textsubscript{aq}\textsuperscript{2+/3+} ion couple. EDTA derivatives have a negatively-charged oxygen
in their carboxylic group that stabilizes the Fe\textsuperscript{3+} more than the Fe\textsuperscript{2+}, making the
reduction of ferric ion more energetically-demanding, while phenanthroline
serves as a π-acceptor that delocalizes the electron from Fe\textsuperscript{2+} resulting in a
positive shift of redox potential from the Fe\textsubscript{aq}\textsuperscript{2+/3+} couple.

The potential-pH diagram shows that all of the redox species shown can
thermodynamically oxidize hydrogen sulfide to sulfur. The following order is the
requirement of thermodynamics to demonstrate the HER with the oxidation of the
redox in the neutral pH range (4-7).

AQDS < Fe-EDTA < Fe-HEDTA < Fe(CN)\textsubscript{6}

Although EDTA and HEDTA have similar structures, as shown in Figure
1a, different slopes were observed in the pH range from 3 to7. Fe-EDTA has pH-
independent redox potential in this range because proton transfer is not required in
the redox reaction for the predominant species shown in Figure 1d. Therefore, the
thermodynamic voltage for the HER and oxidation of Fe-EDTA is pH-dependent
and slightly acid conditions (pH 3-4) are thermodynamically favorable. On the
other hand, Fe-HEDTA had a slope of 59 mV pH\textsuperscript{-1} because proton transfer was
also involved in the reaction. The thermodynamic voltage required for the HER
and oxidation of Fe-HEDTA is constant to be \(~0.50\) V in a wide range within
neutral region from pH 3 to 8 (Figure 3. 1). This constant value can be an
advantage to design the overall process which is not influenced by the pH,
including the choice of cathode material and the subsequent homogeneous reaction with \( \text{H}_2\text{S} \). On the other hand, Fe-EDTA exhibits small but various voltages (~0.32-0.50 V) in the same pH range, which requires additional care of the operation. It should also be noted that electrochemical reaction for Fe-HEDTA involves the proton-coupled electron transfer reactions; i.e., an additional voltage loss due to the local pH shift (concentration overpotential) needs to be minimized upon the steady state electrochemical operation. In this context, a use of supporting buffer is essential to minimize the local pH shift, which will be discussed later. While the oxidation of the sulfide ion to sulfur is the primary target in this chapter, the tunability of the redox potential through the formation of a metal complex allows for various applications towards homogeneous reactions and energy storage.

### 3.2.2. Electrochemical Measurements of Redox Species

The cyclic voltammograms of candidate redox (Fe-EDTA, Fe-HEDTA, AQDS, and \( \text{Fe(CN)}_6 \)) were measured using a glassy carbon rotating disk electrode, as shown in Figure 3. 2a and the anodic current at 900 rpm are compared in Figure 3. 3a. A total 0.1 mol kg\(^{-1}\) of redox species, 50% in a reduced form and 50% in an oxidized form, were introduced into a 0.5 mol kg\(^{-1}\) citrate-buffered solution at pH 5. First, the onset potentials of the redox species appeared in the order below.

\[
\text{AQDS} < \text{Fe-EDTA} \approx \text{Fe-HEDTA} < \text{Fe(CN)}_6
\]
The estimated potential for Fe-EDTA (0.13 V vs. SHE in Figure 3.1a) agreed well with the measured onset potential (approximately 0.14 V vs. SHE, 0.44 V vs. RHE at pH 5). In contrast, for Fe-HEDTA, there was a slight difference between the estimated and the measured potentials (~0.1 V). In this estimation, the activity coefficients of the oxidized and reduced species are assumed to be in unity in the potential-pH diagram. Relatively dense redox solutions (0.1 mol kg\(^{-1}\)) used may cause the strong ion interaction, such as oligomerized Fe\(^{3+}\)-HEDTA formed at pH 5, alkali ions, and buffer ions. Indeed, a potential shift of more than 100 mV from the standard potential for the Fe(CN)\(_6\)\(^{4-/3-}\) redox couple was reported due to an association with alkali cations;\(^{35-37}\) e.g., the association constants with potassium cation are reported to be 10\(^{1.46}\) and 10\(^{2.35}\) for Fe(CN)\(_6\)\(^{3-}\) and Fe(CN)\(_6\)\(^{4-}\), respectively.\(^{38}\) The lower formation constant of Fe\(^{3+}\)-HEDTA (log \(\beta\) = 20) than that of Fe\(^{3+}\)-EDTA (log \(\beta\) = 25) (Table A1) might cause additional complex formation with citrate, which may in turn lead to the potential shift.
Figure 3.2. (a) Cyclic voltammograms measured using a glassy carbon rotating disk electrode in a solution containing a total of 0.1 mol kg$^{-1}$ redox species (Fe-EDTA, Fe-HEDTA, AQDS or Fe(CN)$_6$) with 0.5 mol kg$^{-1}$ citrate buffer. Redox solutions have 50% reduced species and 50% oxidized ones. (50 mV s$^{-1}$, 298 K). (b) Corresponding Koutecký-Levich plot.
Figure 3.3. (a) Anodic current at 900 rpm shown in Figure 3.2a with the isolated kinetic current obtained from the Koutecký-Levich plot. (b) Tafel plot of kinetic current.

The cyclic voltammograms in Figure 3.2a clearly show the anodic and cathodic diffusion-limiting current of redox species. For Fe-HEDTA, the second step reduction was observed at more negative potential than 0 V vs. RHE. In the cyclic voltammogram of analogous redox, V-HEDTA, sequential reduction peaks were accordingly assigned to the reduction of the monomer and dimer species, respectively, considering the homogeneous dissociation rate limitation. In Figure 3.2a, the reduction of the monomer Fe-HEDTA takes place at 0.44 V vs. RHE while the dimer species started to be reduced at 0 V vs. RHE. The cyclic voltammograms in Figure 3.3a show that the current of AQDS increased slowly, while the one for Fe(CN)$_6^{3-}$ shows a sharp increase. As a diffusion-limiting current was observed, the observed current-potential relationship contains contributions from diffusion and kinetics on the electrode. The Koutecký-Levich analysis was applied to isolate their contributions following Equation 3.11 and the corresponding Koutecký-Levich plots are shown in Figure 3.2b,
\[ \frac{1}{j} = \frac{1}{j_{\text{kin}}} + \frac{1}{j_{\text{lim}}} \]  

(3.11)

where \( j \), \( j_{\text{kin}} \), and \( j_{\text{lim}} \) represent the measured current density, kinetic current density on the electrode, and diffusion-limiting current density at a given rotation speed, respectively. The diffusion-limiting current density is given by the Levich equation (Equation 3.12).

\[ j_{\text{lim}} = 0.62nF \gamma cD^{2/3} v^{-1/6} \sigma^{1/2} \]  

(3.12)

where \( n \) is the number of required electrons, \( F \) is Faradaic constant, \( \gamma \) is the activity coefficient, \( c \) is the concentration of redox, \( D \) is the diffusion coefficient, \( v \) is the kinematic viscosity, and \( \omega \) is the rotation speed. Tafel plots of the obtained kinetic current densities are shown in Figure 3.3d, which clearly shows that Fe(CN)\(_6\) has facile kinetics toward electrochemical oxidation while AQDS has poor kinetics. Due to the considerable differences in their structure and charge, a fair comparison of the reaction rate is difficult among these redox species. In this chapter, the comparison is limited between Fe-EDTA and Fe-HEDTA, which have similar structures. According to the Marcus theory,\(^{40,41}\) the activation free energy at standard potential (\( \Delta G^*_0 \)) is determined by the reorganization energy (\( \lambda \)) as shown in Equation 3.13.

\[ \Delta G^*_0 = \frac{\lambda}{4} = \frac{\lambda_i + \lambda_o}{4} \]  

(3.13)

where \( \lambda_i \) and \( \lambda_o \) denote the inner and outer reorganization energy, respectively. The inner reorganization energy represents the vibrational contribution of the
structure while the outer reorganization comes from the surrounding dipole solvent. The predominant reactions at pH 5 are shown in Equations 3.14 and 3.15.

$$\left[\text{Fe(II)-EDTA}\right]^{2-} \rightarrow \left[\text{Fe(III)-EDTA}\right]^{-} + e^- \quad (3.14)$$

$$\left[\text{Fe(II)-HEDTA}\right] + \text{H}_2\text{O} \rightarrow \left[\text{Fe(III)-HEDTA}\right]^{-} + \text{H}^+ + e^- \quad (3.15)$$

While Fe-EDTA is a simple electron transfer reaction, Fe-HEDTA shows proton-coupled electron transfer. Therefore, the inner reorganization energy of Fe-HEDTA is expected to be higher than that of Fe-EDTA, which might have resulted in the poor kinetics of Fe-HEDTA compared to Fe-EDTA.

Even though the potential to reach 10 mA cm$^{-2}$ was 0.5 V vs. RHE at 900 rpm in the presence of Fe-EDTA, which is the most negative among the redox species investigated, the diffusion-limiting current is only 11 mA cm$^{-2}$ even with vigorous rotation (900 rpm) at room temperature. Using a glassy-carbon electrode, Figure 3.3a also shows isolated kinetic current densities. From this figure, it is clear that the diffusion overpotential, which is the difference between kinetic overpotential and measured overpotential, plays a major role as the current increases. This diffusion overpotential is expected to increase when it is operated in static or practical operational conditions, suggesting that the engineering of the electrolyte rather than the electrode material is the key to improvement. The diffusion overpotential is determined by the diffusion-limiting current, according to Fick’s law shown in Equation 3.16.
\[ J_{\text{lim}} = nFD \frac{\partial a}{\partial x} \] (3. 16)

where \( n \) is the required number of redox reactions, \( F \) is the Faradaic constant, \( D \) is the diffusion coefficient, \( a \) is the activity in the bulk solution, and \( x \) is the thickness of the diffusion layer. Increasing the concentration of the redox species is a simple approach to improve the diffusion-limiting current for practical applications. Cyclic voltammetry and chronoamperometry at the potential where the diffusion-limiting current was observed were performed with a variety of concentrations of redox solutions containing only reduced species (Fe\(^{2+}\)-EDTA and Fe\(^{3+}\)-HEDTA), as shown in Figure 3. 4a and b, respectively.

**Figure 3. 4.** (a) Cyclic voltammograms measured using a glassy carbon rotating disk electrode in a solution containing Fe\(^{2+}\)-EDTA or Fe\(^{2+}\)-HEDTA with 0.5 mol kg\(^{-1}\) citrate buffer (pH = 5, Ar, 50 mV s\(^{-1}\), 900 rpm, 298 K). (b) Corresponding I-t profile measured at the potential where the diffusion-limiting current was observed.

Up to 0.4 mol kg\(^{-1}\) of Fe\(^{2+}\)-EDTA, the diffusion-limiting current density increased to 70 mA cm\(^{-2}\) and this is higher than that observed in Figure 3. 3a suggesting that the concentration of reactant plays an important role, as shown in Equation 3. 16. When the concentration of Fe\(^{2+}\)-EDTA reached 0.45 mol kg\(^{-1}\), the
diffusion-limiting current density did not change from that in 0.4 mol kg$^{-1}$ (Figure 3. 4a) and a considerable decay of the current density, which approached close to 0 mA cm$^{-2}$, started to appear during chronoamperometry (Figure 3. 4b). After the chronoamperometry in 0.45 mol kg$^{-1}$ of Fe$^{2+}$-EDTA, precipitation was observed on the anode resulting in the disappearance of anodic current, which comes from less soluble Fe$^{3+}$-EDTA (< 0.2 mol kg$^{-1}$). On the other hand, constant current density above 70 mA cm$^{-2}$ was observed in the presence of Fe$^{2+}$-HEDTA above 0.5 mol kg$^{-1}$ that can exceed the diffusion-limiting current density of Fe$^{2+}$-EDTA (70 mA cm$^{-2}$ with 0.4 mol kg$^{-1}$), as shown in Figure 3. 4b. These results indicate that the solubility of both the oxidized and reduced redox species must be considered to determine the concentration of the redox solution. Noticeably, Fe-HEDTA showed sufficient solubility (> 1 mol kg$^{-1}$) regardless of the oxidation state of Fe, which makes it possible to operate the proposed system at high concentrations. The diffusion-limiting current density did not increase when the concentration was increased from 0.75 to 1.0 mol kg$^{-1}$. This could stem from the diffusion-limit of citrate buffer since the oxidation of Fe-HEDTA is proton-coupled electron transfer and the concentration of the buffer was limited to 0.5 mol kg$^{-1}$, which is smaller than that of the redox species, in this series of measurements. Optimization of the supporting buffer is further discussed in the following section. The high solubility is likely associated with the soluble characteristics of the ligand itself, where the solubility of HEDTA-Na$_3$ is > 2.5 mol kg$^{-1}$ while that of EDTA-Na$_2$ is only 0.4 mol kg$^{-1}$. It is interesting to note that the difference in the structure between these ligands is that one carboxylic
functional group on EDTA is substituted with an alcohol group on HEDTA, as shown in Figure 3. 1a. Although Fe(CN)$_6$ is also well soluble (~0.4 mol L$^{-1}$) and proposed for redox flow batteries,$^{42,43}$ the onset potential of Fe-HEDTA (0.43 V vs. RHE) appears more negative than that of Fe(CN)$_6$ (0.75 V vs. RHE) at pH 5 as shown in Figure 3. 3c, which is a great advantage to reduce the overall cell voltage when HER is also performed on a cathode. Therefore, Fe-HEDTA is identified as a suitable candidate for this study because of the remarkable solubility, which helps to overcome diffusion issues, and pH-independent thermodynamic voltage to perform redox oxidation and HER (approximately 0.43 V) in a nearly neutral pH range (2-8). Further studies on Fe-HEDTA were performed in the following section under dense redox conditions.
3.2.3. Electrochemical Measurements of Dense Fe-HEDTA at Various pH Values

The redox potential estimated from the speciation distribution with different concentrations is shown as a solid line in Figure 3. 5a assuming that the activity coefficients of Fe-HEDTA are one. The redox potential estimated based on the equilibrium constants shifted toward negative by increasing the concentration of Fe-HEDTA, likely due to an increase in the fraction of dimerized Fe$^{3+}$-HEDTA, which has more negative standard potential compared to that of the monomer. The formal potential with a total of 1.0 mol kg$^{-1}$ Fe-HEDTA was obtained by open circuit potential measurement at different pH by introducing 0.5 mol kg$^{-1}$ of excess HEDTA as a buffer, which is also shown in Figure 3. 5a as scattered points. The measured potential appeared more negative than the estimated potential, which was also observed with a total of 0.1 kg$^{-1}$ redox shown in Figure 3. 1a and Figure 3. 3a.
Figure 3.5. (a) Estimated redox potential obtained from speciation distribution with different concentrations of Fe-HEDTA and the open circuit potential (OCP) measured using a glassy carbon disk electrode in a solution containing 0.5 mol kg$^{-1}$ of Fe$^{2+}$-HEDTA, 0.5 mol kg$^{-1}$ of Fe$^{3+}$-HEDTA, and 0.5 mol kg$^{-1}$ of HEDTA-Na$_3$ under Ar atmosphere. (b) Cyclic voltammograms measured using a glassy carbon rotating disk electrode in a redox solution (900 rpm, 50 mV s$^{-1}$, 298 K). (c) Tafel plot of kinetic current obtained after the Koutecky-Levich analysis.

Electrochemical measurements at different pH were conducted using a glassy carbon rotating disk electrode and the cyclic voltammograms are shown in Figure 3.5b. Similar anodic diffusion-limiting current densities were observed in the pH range from 9 to 4, while the diffusion-limiting current density decreased in the acidic pH range (< 3). The decreased diffusion-limiting current density in acid is ascribed to the formation of Fe$_{aq}^{2+}$, which started to be oxidized at higher potentials as observed in the solution at pH 0.9. A Tafel plot of the kinetic current,
which was obtained after Koutecký-Levich analysis, is shown in Figure 3. 5c. This shows that superior kinetics were observed in pH 4 – 6 while more acidic and alkaline conditions require higher overpotential. Non-linear behavior in the Tafel plot at pH 2.9 may arise from the coexistence of various reduced species as shown in Figure 3. 1c. Due to the local pH shift at high overpotential, the major reactant can switch to FeHL or Fe\textsubscript{aq}\textsuperscript{2+}, the reactions with which require additional overpotential, as in the case of the reaction at pH 0.9 in Figure 3. 5c.

The pH dependence of the kinetics was also investigated on a Pt rotating disk electrode (Figure 3. 6). Although approximately 3 – 6-fold higher kinetic current was observed on the Pt compared to the glassy carbon electrode in the pH range investigated, similar pH-dependence was also observed on the Pt, which suggests that the obtained pH-dependence came from the redox species itself in the electrolyte rather than the surface nature of the electrode materials. Under acidic conditions, the Fe\textsuperscript{2+} species starts to form Fe\textsubscript{aq}\textsuperscript{2+} or neutral Fe(II)HL. Obviously, the oxidation of Fe\textsubscript{aq}\textsuperscript{2+} requires higher inner reorganization energy through the formation of Fe(III)L (Equation 3. 17) compared to the reaction at medium pH (Equation 3. 15).

\[
\text{Fe}^{2+} + \text{HEDTA}^{3-} \rightarrow \text{Fe}^{3+} - \text{HEDTA} + e^- \quad (3. 17)
\]

The oxidation of neutral Fe(II)HL is anticipated to require more outer reorganization energy compared to the negatively charged Fe(II)L\textsuperscript{−} because negatively charged species can form a larger solvation shell through the polarization. Although more alkaline conditions (pH > 6) can form more
negatively-charged Fe(II)(OH)L$^{2-}$, which is expected to have a larger solvation shell compared to Fe(II)L$^-$, the kinetic current started to decrease. This may be ascribed to the increase in local concentration of highly-hydroxylated Fe(III)(OH)$_2$L$^{2-}$ during anodic polarization, which has a potential risk of precipitation.

**Figure 3.6.** (a) Cyclic voltammograms measured by a platinum rotating disk electrode in the solution containing total 1.0 mol kg$^{-1}$ Fe-HEDTA with 0.5 mol kg$^{-1}$ of HEDTA. Redox solutions have 50% of reduced species and 50% oxidized species. (b) Tafel plot of kinetic current density after Koutecký-Levich analysis.

RDE measurements were obtained using Pt and glassy carbon electrodes in the solution containing Fe$_{aq}^{2+/3+}$ under acidic conditions and compared to Fe-HEDTA (Figure 3. 7). The onset potential of Fe-HEDTA appeared more negative than of Fe$_{aq}$ as discussed in the previous section (Figure 3. 1a), which is the advantage of the present system to demonstrate the coproduction of hydrogen.
Figure 3.7. (a) Cyclic voltammograms measured by a glassy carbon and a platinum rotating disk electrode in the solution containing total 1.0 mol kg$^{-1}$ Fe$^{2+/3+}_{aq}$ in 0.5 mol L$^{-1}$ of H$_2$SO$_4$ or total 1.0 mol kg$^{-1}$ Fe-HEDTA in 0.5 mol kg$^{-1}$ of excess HEDTA. Redox solutions have 50% of reduced species and 50% oxidized species. (b) corresponding Tafel plot after Koutecký-Levich analysis.

A higher diffusion-limiting current density was observed with Fe$_{aq}$ compared to Fe-HEDTA, which came from their molarities (0.34 mol L$^{-1}$ and 0.44 mol L$^{-1}$, respectively) and their diffusion coefficients. The diffusion coefficient is described by the Stokes-Einstein equation (Equation 3.18).

$$D = \frac{kT}{3\pi d \mu} \quad (3.18)$$

where $k$ is the Boltzmann constant, $d$ is the effective hydrodynamic diameter of the hydrated ion (Stokes diameter), which takes into account all the H$_2$O molecules carried in the hydration sphere, and $\mu$ is the dynamic viscosity of the electrolyte. Although the Stokes diameter of Fe$^{2+}$-HEDTA has not been reported, those for Fe$^{2+}_{aq}$ and Fe$^{2+}$-EDTA are reported to be 6.8 and 8.4 Å, respectively.$^{44,45}$

The charge of the ion is also known to play a role to the hydration. Since the predominant ferrous complexes are Fe-HEDTA$^-$ and Fe-EDTA$^{2-}$ at pH 5, the Stokes diameter of Fe-HEDTA$^-$ may be smaller than that of Fe-EDTA$^{2-}$. The
measured dynamic viscosities were 6.0 and 1.6 mPa s for the solutions containing Fe-HEDTA and Fe aq, respectively. As a result, the diffusion coefficient of Fe²⁺HEDTA is expected to be lower than that of Fe²⁺aq mainly due to the dynamic viscosity. The kinetic current was evaluated using Koutecký-Levich analysis and the resulting Tafel plot is shown in Figure 3. 7b. The kinetic current densities were similar between Fe aq and Fe-HEDTA. The kinetic current of Pt appeared approximately four to six times higher than that of the glassy carbon for both redox couples. The ratios of the rate constant on glassy carbon against platinum are reported to be 0.15-0.28, 0.13, and 0.20 for Fe²+/³⁺, Ce³+/⁴⁺, and Fe(CN)₆⁴⁻/³⁻ redox couples, respectively, which agrees with the observed difference for Fe-HEDTA between the glassy carbon and platinum in this study. The intrinsic difference between Pt and glassy carbon may arise from the density of state (DOS) of the electrode materials, which is explained in a quantum mechanical manner, rather than adsorption energy of intermediate, which is often employed for electrocatalytic reactions, such as hydrogen evolution. That detail is out of the scope of the present study because the diffusion overpotential has a major contribution even with the glassy carbon.
3.2.4. Electrochemical Measurements in Various Buffers

Because Fe-HEDTA provides a pH-independent thermodynamic voltage to perform redox oxidation and HER in the pH range from 2 to 8 and the kinetic current becomes highest in the medium pH range (4-6), as shown in Figure 3. 1a and Figure 3. 5c, respectively, this study focuses on neutral pH 5 where the supporting buffer is required to minimize the local pH shift during the proton-coupled electron transfer. The impact of the supporting buffer species towards the diffusion-limiting current and the kinetic current is here studied. Under unbuffered conditions, hysteresis was observed during cyclic voltammetry, which could not be minimized by decreasing the scan rate (Figure 3. 8a), while buffered conditions provide steady-state current regardless of the scan direction and buffer species except for 0.5 mol kg\(^{-1}\) malonate (Figure 3. 8b). Although phosphate is a popular buffer for water splitting under neutral pH conditions, it cannot be applied to the current system because it precipitates with metal cations. It is clear that the smaller organic buffer showed the higher diffusion-limiting current. Koutecký-Levich analysis was performed to isolate the contribution of the diffusion and kinetic currents. Since the activity coefficients of the concentrated redox are difficult to determine, \(Dy^{3/2}\) was obtained from the slope of the Koutecký-Levich plot and used as an indicator of the diffusion contribution. The obtained \(Dy^{3/2}\) are shown in Figure 3. 8c with the corresponding dynamic viscosities. The obtained \(Dy^{3/2}\) shows a linear dependence respective to the reciprocal of the dynamic viscosity, in agreement with the Stokes-Einstein equation (Equation 3. 18).
Figure 3.8. Cyclic voltammograms measured using a glassy carbon rotating disk electrode in a solution containing a total of 1.0 mol kg\(^{-1}\) Fe-HEDTA (a) without supporting buffer and (b) with different buffers (HEDTA, citrate, and malonate). Redox solutions have 50% reduced species and 50% oxidized species (pH = 5, 900 rpm, 50 mV s\(^{-1}\), 298 K). (b) The relationship between \(D\gamma^{3/2}\) and the dynamic viscosity. (c) Tafel plot of kinetic current obtained after the Koutecký-Levich analysis.

There was no clear dependence of the kinetics on the viscosity in Figure 3.8d despite a kinetic viscosity effect, where the viscosity of solution alters the relaxation time of their outer solvation shell, was reported with Fe(CN)\(_6^{4-}\) and Cr-EDTA\(^{49}\), as shown in Equation 3.19.

\[
k^0 = A\mu^B\exp(-\Delta G_0^a/RT) \tag{3.19}
\]

where \(k^0\) is the rate constant of electron transfer and \(A\) and \(B\) are constants (0 < \(B\) < 1). The absence of a kinetic viscosity effect may arise from a larger inner sphere
activation barrier or weak adiabaticity\textsuperscript{50,51} for Fe-HEDTA redox, which agrees with the poor kinetics compared to Fe(CN)\textsubscript{6} observed in Figure 3. 3b.

### 3.2.5. Temperature Effects on Fe-HEDTA Redox Electrochemistry

Controlling the temperature of the electrolyte is an alternative approach to improving the diffusion and the kinetics. Since commercialized homogeneous processes to oxidize H\textsubscript{2}S in liquid phase operate at 40 – 60\textdegree{}C,\textsuperscript{12,52} it is reasonable to perform the electrochemical regeneration of redox at elevated temperatures. Here, temperature dependence was investigated with 1.5 mol kg\textsuperscript{-1} malonate buffer (Figure 3. 9b) because hysteresis got obvious at elevated temperatures in the presence of 0.5 mol kg\textsuperscript{-1} malonate buffer (Figure 3. 9a).
Figure 3. 9. (a) (b) Cyclic voltammograms from the glassy carbon disk electrode in 0.5 mol kg\(^{-1}\) of Fe\(^{2+}\)-HEDTA and 0.5 mol kg\(^{-1}\) of Fe\(^{3+}\)-HEDTA solution measured at 50 mV s\(^{-1}\) under Ar atmosphere at different temperatures. (a) 0.5 mol kg\(^{-1}\) and (b) 1.5 mol kg\(^{-1}\) of malonic acid was added as a buffer and the pH was adjusted to 5. (c) Arrhenius plot of exchange current density obtained from Tafel plots. (d) Temperature dependence of \(D\gamma^{3/2}\) and dynamic viscosity. \(D\gamma^{3/2}\) estimated from 298 K and the dynamic viscosity using the Stokes-Einstein equation is shown as a dashed line.

The diffusion-limiting current clearly improved and the current increased sharply by increasing the temperature, which implies improved diffusion and kinetics at elevated temperatures. The contributions from diffusion and kinetics were further isolated by the Koutecký-Levich analysis. The apparent activation energy was obtained from an Arrhenius plot of the exchange current density (Figure 3. 9c). The activation energy obtained for Fe-HEDTA was 50 kJ mol\(^{-1}\) while that for Fe(CN)$_6$ was reported to be 31 kJ mol\(^{-1}\), which agrees with the
poor kinetics of Fe-HEDTA compared to Fe(CN)$_6$ observed in Figure 3. 3b. $D\gamma^{3/2}$ was obtained from the slope of the Koutecký-Levich plot and shown with corresponding dynamic viscosity (Figure 3. 9d). Since the viscosity decreases at elevated temperatures as shown, the diffusion coefficient is expected to increase. In order to elucidate the diffusion-contributing term $D\gamma^{3/2}$, estimation of $D\gamma^{3/2}$ was performed from the measured $D\gamma^{3/2}$ at 298 K and measured dynamic viscosity at different temperatures following the Stokes-Einstein equation (Equation 3. 18) with the assumption that the activity coefficient and the Stokes diameter are constant. The $D\gamma^{3/2}$ estimated from the Stokes-Einstein equation, which is shown as a dashed line in Figure 3. 9d, appears lower than the measured ones. This deviation between the measured values and the estimated ones suggests that elevating temperature increased not only the diffusion coefficient but also the activity coefficient, which also helps to improve the diffusion-limiting current. Controlling the operational temperature is an attractive approach that can increase the diffusion-limiting current over two-fold.

As a summary, the obtained results are compared with the various reported redox candidates in Table 3. 1. It can be found that the advantages of Fe-HEDTA among the proposed redox candidates are its relatively low redox potential ($< 0.5$ V vs. RHE) and high solubility (1 mol kg$^{-1}$) in near neutral pH condition. The impact of supporting buffer and reaction temperature towards diffusion of dense redox is also summarized in Table 3. 2, which clearly shows that low viscosity and elevated temperature help to improve diffusion term, $D\gamma^{3/2}$. 
Table 3.1. Comparison with reported redox candidates.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>$E / V$ vs. RHE</th>
<th>Supporting electrolyte or pH</th>
<th>Concentration of redox</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{2+/3+}$-HEDTA</td>
<td>0.43</td>
<td>1.5 mol kg$^{-1}$</td>
<td>1 mol kg$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>malonate buffer (pH = 5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Fe}_{\text{aq}}^{2+/3+}$</td>
<td>0.6</td>
<td>0.5 mol L$^{-1}$</td>
<td>1 mol L$^{-1}$</td>
<td>19</td>
</tr>
<tr>
<td>$\text{Fe}^{2+/3+}$-EDTA</td>
<td>0.2</td>
<td>pH = 8.5</td>
<td>0.1 mol L$^{-1}$</td>
<td>22</td>
</tr>
<tr>
<td>$\text{H}<em>{5}(\text{PMo}</em>{2}\text{Mo}<em>{10}\text{O}</em>{40})$</td>
<td>0.8</td>
<td>0.5 mol L$^{-1}$</td>
<td>0.25 mol L$^{-1}$</td>
<td>19</td>
</tr>
<tr>
<td>/ $\text{H}<em>{3}(\text{PMo}</em>{12}\text{O}_{40})$</td>
<td></td>
<td>H$_2$SO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$^-$/I$_3^-$ (Acid)</td>
<td>0.53</td>
<td>5.5 mol L$^{-1}$ HI</td>
<td>5.5 mol L$^{-1}$</td>
<td>14,54,55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(pH = 0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$^-$/IO$_3^-$ (Base)</td>
<td>1.08</td>
<td>1.6 mol L$^{-1}$</td>
<td>1.525 mol L$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(pH=14) OH$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(VO)$_2^+$/($\text{VO}_2^+$)</td>
<td>0.99</td>
<td>7 mol kg$^{-1}$ H$^+$</td>
<td>1 mol kg$^{-1}$</td>
<td>18</td>
</tr>
</tbody>
</table>
Table 3.2. Summary of the present work to improve the diffusion.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Supporting buffer</th>
<th>Temperature / K</th>
<th>Dynamic viscosity / mPa s</th>
<th>$Dy^{3/2}$ / $10^{-6}$ cm$^2$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mol kg$^{-1}$ Fe$^{2+/3+}$/HEDTA</td>
<td>1.5 mol kg$^{-1}$ excess HEDTA</td>
<td>298</td>
<td>7.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Fe$^{2+/3+}$/HEDTA</td>
<td>1.5 mol kg$^{-1}$ citrate</td>
<td>313</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1.5 mol kg$^{-1}$ malonate</td>
<td>333</td>
<td>1.5</td>
<td>4.3</td>
</tr>
</tbody>
</table>

3.3. Summary

In this study, tuning the redox potential of Fe-containing metal complexes was demonstrated based on their equilibrium constants. Quantitative analysis of the oxidation of redox species revealed that diffusion overpotential greatly contributes to the overall electrochemical performance while ubiquitous carbon electrodes have sufficient kinetics. The Fe-HEDTA redox couple was determined to be a suitable candidate due to its pH-independent thermodynamic voltage to perform redox oxidation and HER (approximately 0.43 V) and the remarkable solubility of both its oxidized and reduced species (1 mol kg$^{-1}$) in the neutral pH range, which helps to increase the diffusion-limiting current. In addition to the redox couples itself, the supporting buffer also plays an important role in determining the diffusion-limiting current density, thereby revealing that malonate buffer is suitable for the application under a neutral pH condition (pH = 5) due to its low viscosity. Elevated temperature further helps to improve not only the diffusion coefficient of the redox but also the activity coefficient. These
insights will certainly help to design an electrochemical system with a HER and the oxidation of soluble redox species to achieve redox-mediated H$_2$S splitting.

### 3.4. Experimental methods

#### Materials

All chemicals were purchased with the following purities: KOH (99.99%, Sigma-Aldrich, St. Louis, USA), NaOH (99.99%, Sigma-Aldrich), FeSO$_4$ · 7H$_2$O (99.0%, Sigma-Aldrich), Fe$_2$(SO$_4$)$_3$ hydrate (Sigma-Aldrich), FeCl$_3$ · 6H$_2$O (≥ 99%, Sigma-Aldrich), HEDTA-Na$_3$ (≥ 99%, Fisher Scientific, Pittsburgh, USA), HEDTA-Fe (99%, Phygenera, Langenberg, Germany), K$_3$[Fe(CN)$_6$] (> 99.9%, Sigma-Aldrich), K$_4$[Fe(CN)$_6$] (99.5%, Sigma-Aldrich), AQDS (> 97%, TGI), HOC(COONa)(CH$_2$COONa)$_2$ · 2H$_2$O (≥ 99.0%, Sigma-Aldrich), C$_3$H$_4$O$_4$ (99%, Alfa Aesar, Ward Hill, USA), C$_6$H$_8$O$_7$ (100.7%, Fisher Scientific). The water used in all experiments was obtained from a Milli-Q Integral system (Millipore, Burlington, USA) with a resistivity of 18.2 MΩ cm. The pH of electrolyte solutions was adjusted using H$_2$SO$_4$ (99.999%, Sigma-Aldrich), 8 M NaOH solution (Sigma-Aldrich), or KOH. A carbon felt (AvCarb G100 Soft Graphite Battery Felt, thickness 3.2 mm, Fuel Cell Store, College Station, USA) was pretreated in air at 773 K for 5 h to make it hydrophilic.$^{56}$

#### Electrochemical measurements

Electrochemical measurements were achieved using a BioLogic VMP3 potentiostat (Seyssinet-Pariset, France). Rotating disk electrodes (RDEs, 3 mm diameter, ALS CO., Ltd, Tokyo, Japan) of glassy carbon and polycrystalline Pt
were used as working electrodes. Carbon paper or Pt wire was employed as counter electrodes. Before each measurement, the disk electrodes were first polished with 1 \( \mu \text{m} \) of diamond and then with 0.05 \( \mu \text{m} \) of alumina followed by electrochemical cleaning in a 1 M HClO\(_4\) solution between −0.9 and 1.7 V vs. SHE (standard hydrogen electrode) for glassy carbon or between −0.02 and 1.8 V vs. SHE for Pt. Ag/AgCl (saturated KCl) (ALS CO., Ltd) was used as the reference electrode. The potentials were reported with \( iR_u \)-correction unless otherwise specified. Uncompensated resistance \( R_u \) was measured by impedance spectroscopy (100 mHz – 10 kHz, 10 mV amplitude). Before and during all measurements, Ar (99.999\%) was continuously supplied to the electrochemical cell. Because reduced AQDS is not commercially available, AQDS was electrochemically reduced using a carbon felt cathode at 0 V vs. RHE in a two compartment cell separated by Nafion 212 membrane (Fuel Cell Store) under Ar atmosphere assuming a reduction with 1.5 electron per molecule.\(^{57}\) The kinematic viscosity and density of the electrolyte solutions were obtained using viscometer tubes (cell constants: 0.003259 and 0.009167 mm\(^2\) s\(^{-2}\), Fisher Scientific) and a density meter (DM40, METTLER TOLEDO, Columbus, USA), respectively.
3.5. References


(41) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and


Oxidation of redox ions has been studied as an alternative anodic reaction for OER in Chapter 3. The anodic reaction condition was investigated in near-neutral pH buffered condition (pH ~5), which helps to stabilize metal complexes. In this chapter, its counter reaction, hydrogen evolution reaction (HER), is also studied in near-neutral pH buffered conditions using Pt rotating disk electrode (RDE) as a model electrocatalyst to understand the origin of overpotential and to develop a strategy for electrolyte engineering to maximize its performance.

4.1. Introduction

Electrochemical hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) are among the most studied electrocatalytic reactions from fundamental and practical points of view, such as fuel cells and water electrolyzers. The mechanism of these reactions, including the rate determining step and pH dependency, is still under debate. Exchange current densities that rely on a variety of transition metal electrodes are being investigated in acidic conditions. A ranking of the catalytic performance among various metals is the typical example of Sabatier’s principle: i.e., a volcano trend as a function of binding energy between a metal and a hydrogen as a descriptor of catalytic activity. To obtain meaningful kinetics, a compensation of mass transport is essential, as mass transport of the reactant and product can play major roles on the observed overpotential, especially for kinetically facile reactions. Classically measured data for HER exchange current density were recently questioned by
several authors.\textsuperscript{3–5} It has been well-described that an accurate measurement of the exchange current density cannot be achieved in a conventional electrochemical setup for the extremely active Pt, as diffusion contribution cannot be excluded for such cases. In an acidic solution, HER/HOR current on a Pt rotating disk electrode (RDE) is purely determined by the diffusion of H\textsubscript{2} even in the presence of vigorous rotation (3600 rpm).\textsuperscript{4,6,7} Due to facile kinetics in an acid solution and sufficient mass transport of protons, the local activity of H\textsubscript{2} at the electrode surface is equilibrated with the electrode potential of the Nernst equation; it determines the flux of H\textsubscript{2} between the electrode and the bulk electrolyte solution and the resultant HER current density, which Zheng et al. and Durst et al. defined as (Nernstian) diffusion current of H\textsubscript{2} product.\textsuperscript{4,8} In this case, it is difficult to obtain kinetic current using RDE configuration. Instead, measurement techniques are necessary that can provide sufficient mass transport of H\textsubscript{2}, such as H\textsubscript{2} pump method with membrane electrode assembly (MEA),\textsuperscript{3,5,8} ultramicroelectrode (UME),\textsuperscript{9,10} and scanning electrochemical microscopy (SECM).\textsuperscript{11,12} Durst et al. reported the exchange current density for Pt to be as high as 70 mA cm\textsuperscript{–2},\textsuperscript{5} which is 70 times higher than Trasatti’s data (1 mA cm\textsuperscript{–2}).\textsuperscript{2,13–15}

The pH dependency of proton-coupled electron transfer reactions, including HER, relates to a reactant switching from proton to water molecule, or a switching point dependent on the identity of the electrolyte.\textsuperscript{16–18} In an unbuffered condition, the reactant switching from proton to water molecule for HER occurs at pH \(~1.6\) at a current density of \(-10\) mA cm\textsuperscript{–2} in a static condition without convection.\textsuperscript{17} The reduction of water molecules, compared to proton reduction,
requires additional kinetic penalty; it is obviously associated with stable O-H bond cleavage in water molecules. Indeed, the reported exchange current density of Pt in an alkaline condition remains two orders of magnitude lower than that in an acidic condition.\textsuperscript{5,10} Buffer acts as a proton carrier and is essential to avoid the depletion of a local proton near-neutral pH condition. Our group reported the significance of “electrolyte engineering”, i.e., the optimization of introduced identity and concentration of buffer species to improve HER performance. For example, dense solute concentration of ~1.5-2.0 mol L\textsuperscript{−1} were found maximum HER current at pH 5 and ambient temperature using phosphate buffer.\textsuperscript{19,20} The observed volcano-shaped dependence in terms of buffer concentration is the trade-off between enhancing the activity and reducing diffusion coefficient of the buffer species. Increased buffer activity enhances its cathodic reactant flux, whereas too dense buffer solution becomes too viscous resulting in small diffusion coefficients of the reactants and products.

Part of the difficulty in describing the mass transport of the buffered condition at near-neutral pH is due to concurrent homogeneous chemical reactions between the deprotonation of a weak acid (HA) and the protonation of the conjugated base (A\textsuperscript{−}) within the diffusion layer,

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \frac{k_f}{k_r} \text{A}^- + \text{H}_3\text{O}^+ \quad (4.1)
\]

It is difficult to obtain an analytical solution for the heterogeneous electrochemical reaction coupled with proceeding and succeeding homogeneous chemical reactions (Equation 4.1), so a numerical solution or approximation has
been implemented in the literature to identify the local environment near the electrodes at steady state electrocatalysis. For instance, previous studies used assumptions of local equilibrium among $\text{H}_3\text{O}^+$ and buffer species within the diffusion layer, or of very high deprotonation rate constant $k_f = 10^6 \text{ s}^{-1}$ in Equation 4.1. However, separate study reported that the local equilibrium is not maintained within the diffusion layer in the presence of carbonate buffer during electrochemical CO$_2$ reduction, using reported homogeneous deprotonation rate constant of $\text{HCO}_3^-$ $k_f = 59 \text{ s}^{-1}$ in Equation 4.1. Therefore, better description of electrolyte behavior and consequent electrocatalysis is desired to quantitatively and accurately estimate the overall electrocatalytic performance.

In this work, the contribution of mass transport was integrated to simulate the HER and HOR data of Pt RDE under buffered near-neutral pH. This advanced mass transport model coupled with the homogeneous chemical reaction between buffer species demonstrated that, for both HER and HOR performances, dual mass transport contributions from buffer species and H$_2$ predominantly determines the performance, whereas intrinsic kinetics on Pt has a negligible contribution on the observed overpotential. Those concentration overpotentials are scaled based on the difference between the thermodynamic $pK_a$ of the buffering points and the actual pH of the electrochemistry. As a consequence of such electrolyte engineering, the details of the electrolyte conditions that can maximize HER performance are discussed.
4.2. Results and discussion

4.2.1. Cyclic Voltammograms of HER/HOR using Pt RDE

Electrochemical HER/HOR using a Pt RDE at 298 K was performed in various potassium phosphate buffer solutions. Four different compositions of $\text{K}_x\text{H}_{3-x}\text{PO}_4$ or different pH were selected, namely $\text{KH}_2\text{PO}_4$ (pH = 4.3), $\text{K}_{1.06}\text{H}_{1.94}\text{PO}_4$ (pH = 5.0), $\text{K}_{1.5}\text{H}_{1.5}\text{PO}_4$ (pH = 6.8) and $\text{K}_2\text{HPO}_4$ (pH = 9.5). Their linear sweep voltammograms at 3600 rpm are shown in Figure 4. 1a-d. As for a reference, the voltammogram in 1 mol L$^{-1}$ HClO$_4$ was also measured and the data are added in Figure 4. 1a.

![Figure 4. 1. Linear sweep voltammograms using a polycrystalline Pt disk electrode in different concentration of (a) $\text{KH}_2\text{PO}_4$, (b) $\text{K}_{1.06}\text{H}_{1.94}\text{PO}_4$, (c) $\text{K}_{1.5}\text{H}_{1.5}\text{PO}_4$ and (d) $\text{K}_2\text{HPO}_4$ with bubbling H$_2$. (−50 mV s$^{-1}$, 3600 rpm, 298 K) (e) Potentials required to reach −10 mA cm$^{-2}$ at 3600 rpm.](image)

Regarding the HOR, by increasing the electrode potential from 0 V vs. RHE, all voltammograms reaching a plateau above 0.05 – 0.1 V vs. RHE (Figure 4. 1a-d). The observed plateau is assigned to the diffusion-limiting current density
for H$_2$. As the buffer concentration is increased, the diffusion-limiting current density decreases in all phosphate buffers, due to decreased solubility and diffusion coefficient of H$_2$ under these conditions. The decreasing diffusion coefficient in dense viscous solutions was estimated by the Stokes-Einstein equation using measured viscosities and the corresponding diffusion coefficients at infinite dilution (Figure 4.2).

**Figure 4.2.** (a) Dynamic viscosity of buffer solutions at 298 K. (b) - (c) Diffusion coefficients estimated from Stokes-Einstein equation with the corresponding dynamic viscosities and diffusion coefficients at infinite dilution in phosphate buffer solutions at 298 K. The diffusion coefficient of H$_3$PO$_4$ and H$_2$PO$_4^-$ are overlapping.

The bulk activity of H$_2$ was determined by the diffusion-limiting current of H$_2$ ($j_{\text{lim},H_2}$) measured at 0.4 V vs. RHE (Figure 4.3a-d) and by the refined Levich equation$^{24}$ with the corresponding diffusion coefficient of H$_2$ and the kinematic viscosity at a given concentration,

$$j_{\text{lim},H_2} = 0.6205FD_H^2V^{-1/6}a_{H_2}/\left(1 + 0.2980(D_H/V)^{1/3} + 0.1451(D_H/V)^{2/3}\right) \quad (4.2)$$
The obtained bulk activities are shown in Figure 4. 3e. It can be found that the bulk activity of H$_2$ also decreases, as the buffer concentration increases.

![Figure 4. 3. Levich plot of diffusion-limiting current density for HOR measured at 0.4 V vs. RHE in (a) KH$_2$PO$_4$, (b) K$_{1.06}$H$_{1.94}$PO$_4$, (b) K$_{1.5}$H$_{1.5}$PO$_4$, and (b) K$_2$HPO$_4$. (e) Bulk activity of H$_2$ obtained by the refined Levich equation at 298 K. Viscosity and diffusion coefficient of KH$_2$PO$_4$ and K$_{1.06}$H$_{1.94}$PO$_4$ are assumed to be constant due to the similarity of composition. Dynamic viscosity of K$_2$HPO$_4$ is taken from literature.][25]

For HER, the cathodic current density monotonically increases by applying negative potential in all the solutions. Higher cathodic current was obtained in 1 mol L$^{-1}$ HClO$_4$ compared to those in the other phosphate buffer solutions at a given potential, indicative of superior kinetics and/or mass transport in HClO$_4$ solution. In all the phosphate buffer solutions, it can be found that the overpotential decreases by increasing the concentration of buffer from a diluted concentration. As the concentration was further increased, the overpotential leveled off (Figure 4. 1b) or started to increase (Figure 4. 1c,d). To make the data more visually understandable, the overpotential to reach $-10$ mA cm$^{-2}$ at 3600 rpm is summarized in Figure 4. 1e.
At a given molarity, obtained HER overpotential was in the order, $K_{1.5}H_{1.5}PO_4$ (pH = 6.8) ~ $K_{1.06}H_{1.94}PO_4$ (pH = 5.0) < $KH_2PO_4$ (pH = 4.3) < $K_2HPO_4$ (pH = 9.5), apparently not in the order of pH (i.e., free proton activity). In general, HER performance was higher in mixed phosphate buffer solutions ($K_{1.06}H_{1.94}PO_4$ (pH = 5.0) and $K_{1.5}H_{1.5}PO_4$ (pH = 6.8)) and the overpotential is almost insensitive to the concentration from 0.5 to 1.5 mol L$^{-1}$. Among the phosphate buffers studied, the lowest overpotential ~27 mV was obtained in 0.5 mol L$^{-1}$ $K_{1.5}H_{1.5}PO_4$ at 3600 rpm, close to that in an acidic HClO$_4$ solution.

With worse HER performance than mixed phosphate buffer (Figure 4. 1e), in $KH_2PO_4$ (pH = 4.3) and $K_2HPO_4$ (pH = 9.5) solution, the HER overpotential clearly decreased (by ~20 mV) by increasing the electrolyte concentrations from 0.5 to 1.5 mol L$^{-1}$, but further increase in buffer concentration increased the HER overpotential above 2.0 mol L$^{-1}$ in $K_2HPO_4$ solution. Concentrations above 1.5 mol L$^{-1}$ could not be studied for $KH_2PO_4$ due to limited solubility (1.8 mol kg$^{-1}$ at 25 °C).$^{26}$ Similar to the current data for $KH_2PO_4$ and $K_2HPO_4$, we previously reported that optimal concentration of more soluble NaH$_2$PO$_4$ (pH = 5) for HER appeared at ~1.8 mol L$^{-1}$ and that overpotential increased when the solution became denser than 2.0 mol L$^{-1}$.$^{19}$ The overpotentials in $K_2HPO_4$ appear more than 40 mV higher than other phosphate buffers.

Very similar overpotential and its trend were observed in malonate and citrate buffer solutions, which have a similar pH range (3.5-5.0) with phosphate buffer (Figure 4. 4).
Figure 4.4. Linear sweep voltammograms using a polycrystalline Pt disk electrode in various concentration of (a) KHC$_3$H$_2$O$_4$, (b) K$_{1.57}$H$_{0.42}$C$_3$H$_2$O$_4$, and (c) Na$_{2.5}$H$_{0.5}$C$_6$H$_5$O$_7$ with bubbling H$_2$ (−50 mV s$^{-1}$, 3600 rpm, 298 K). (d) Potential required to reach −10 mA cm$^{-2}$ at 3600 rpm.

As observed in phosphate buffer solutions, the diffusion-limiting current density for HOR continued to drop by increasing the buffer concentration (Figure 4. 4a-c). Regarding HER, the overpotential to reach −10 mA cm$^{-2}$ is summarized in Figure 4. 4d, which shows the volcano-shaped concentration dependence, with 0.5 mol L$^{-1}$ at the top.
Figure 4.5. Rotation speed dependent voltammograms with a polycrystalline Pt disk electrode for (a) 1 mol L$^{-1}$ HClO$_4$, (b) 0.5 mol L$^{-1}$, (c) 1.0 mol L$^{-1}$ KH$_2$PO$_4$ and (d) 1.0 mol L$^{-1}$ K$_{1.5}$H$_{1.5}$PO$_4$ ($-50$ mV s$^{-1}$, 298 K, H$_2$ bubbling). The diffusion current densities of H$_2$ (Equation 4.3 in main text) are shown as a dashed line. Potential required to reach $-10$ mA cm$^{-2}$ at different rotation speeds in (e) KH$_2$PO$_4$ and (f) K$_{1.5}$H$_{1.5}$PO$_4$ solution.
Rotation speed dependent voltammograms in HClO₄, KH₂PO₄ and K₁.₅H₁.₅PO₄ are shown in Figure 4. 5a-d. As the rotation speed increased, the overpotential for both HER and HOR decreased in all solutions associated with an increase of the diffusion-limiting current density for HOR. These results clearly indicate that mass transport contributes to the observed HER/HOR performance.

To isolate the mass transfer contribution of H₂, the measured diffusion-limiting current density of H₂ ($j_{\text{lim},\text{H}_2}$) for HOR⁴ was utilized to calculate H₂ diffusion current density ($j_{\text{diff},\text{H}_2}$), using the following equation:

$$j_{\text{diff},\text{H}_2} = j_{\text{lim},\text{H}_2} \left( 1 - \exp \left( \frac{-2F\eta}{RT} \right) \right) \quad (4.3)$$

These diffusion current densities of H₂ are also shown in Figure 4. 5a-d. Indeed, the measured current density agrees well with all the potential range in 1 mol L⁻¹ HClO₄ (Figure 4. 5a) for both HER and HOR. This agreement indicates that the kinetics for HER/HOR on Pt and the mass transport of protons are sufficiently fast when sufficient free proton is available, so that the diffusion of H₂ determines the current density for both HER and HOR.⁴,⁶,⁷ Diffusion of H₂ is definitely critical for HOR, but the contribution from H₂ product gas during HER is often overlooked. The present observation agrees with the theoretical and experimental studies for electrochemical production of gaseous products with highly active electrocatalysts by Schönfuss et al.⁶ and Losov et al.⁷ who showed the observed overpotential came from the concentration overpotential from the electrochemically produced gaseous molecule. Yet, the diffusion current density
of H$_2$ and the measured current density are largely deviated in all phosphate buffer solutions (Figure 4. 5a-d), which suggests that there are additional contributions from the kinetics and/or the mass transport of the proton donor. The overpotentials required to reach $-10$ mA cm$^{-2}$ at different rotation speeds are summarized in Figure 4. 5e and f. This deviation more severely appears in the presence of KH$_2$PO$_4$ and diluted buffer solutions. For instance, the difference of required overpotential to reach $-10$ mA cm$^{-2}$ between 900 and 3600 rpm is 24 mV in 0.5 mol L$^{-1}$ KH$_2$PO$_4$ (Figure 4. 5e), while it is 9 mV in 0.5 mol L$^{-1}$ K$_{1.5}$H$_{1.5}$PO$_4$ (Figure 4. 5f). The large rotation dependence qualitatively implies that large concentration overpotential is contained in the observed overpotential in the low concentration of buffer and pure KH$_2$PO$_4$. 
4.2.2. Numerical Simulation of Kinetics and Mass Transport

So far, the results suggest that H₂ diffusion contribution alone as in acidic condition is insufficient, but inclusion of buffer diffusion contribution is essential to describe the overall performance for HER/HOR at near neutral pH. Thus, a mass transport model which covers both buffer species and H₂ was applied (Figure 4.6) according to newly established protocol described in Experimental. Mass transport equations were numerically solved with estimated physical parameters while unknown rate constants, i.e., heterogeneous forward rate constant for Heyrovsky step ($k_{4f}^0$ in Equation 4.16) and homogeneous deprotonation rate constants of buffer ions ($k_{1f}$ in Equation 4.7 and $k_{2f}$ in Equation 4.8), are optimized to fit with experimental results.

**Figure 4.6.** Mass transport and kinetics model for hydrogen and buffer species.
Comparisons between the experimental results and the simulated voltammograms with $K_{1.5}H_{1.5}PO_4$ are shown in Figure 4.7. First, the rate constants, $k_{1f}$, $k_{2f}$ and $k_{4f}^0$ were optimized to $4 \times 10^4 \text{ s}^{-1}$, $6 \times 10^6 \text{ s}^{-1}$, and 0.66 cm s$^{-1}$, respectively.

**Figure 4.7.** Comparison between the measured and the simulated voltammograms with various concentrations of $K_{1.5}H_{1.5}PO_4$.

It is found that simulated voltammograms agree well with the measured ones for both HER and HOR branches. The slight deviation of rotation dependence in HER branch may be originated from the underestimated cathodic diffusion-limiting current density, which cannot be observed in the current range. Therefore, the optimized heterogeneous rate constant ($k_{4f}^0$) may be overestimated.
In addition, for a more rigorous treatment on the diffusion constant (assumed to be constant in this model), the Stefan-Maxwell equation must be solved for the concentrated multicomponent electrolyte, which requires cross-diffusion coefficients between interacting ions and solvent. Bubble-induced stirring effect might have promoted mass transport. Such optimizations of the model may achieve complete reproduction of the rotation dependent voltammograms.

Similarly, the simulated voltammograms among different concentrations at pH 6.8 and pH 5.5, and at 3600 rpm are shown in Figure 4.8.

![Simulated voltammograms](image)

**Figure 4.8.** Simulated voltammograms at 3600 rpm in (a) K_{1.5}H_{1.5}PO_{4} at pH 6.8 and (b) K_{1.06}H_{1.94}PO_{4} at pH 5.5.

The simulated voltammograms in Figure 4.8a aptly describe the measured voltammograms (Figure 4.1c), where the HER overpotential decreases from 0.1 to 0.5 mol L\(^{-1}\), while the HER overpotential of 1.5 mol L\(^{-1}\) becomes higher than that of 0.5 mol L\(^{-1}\). In contrast, the HER overpotential at pH 5.5 does not change when the molarity is changed from 0.5 to 1.5 mol L\(^{-1}\) (Figure 4.8b), which reproduces the trend observed in Figure 4.1b.
Then, the simulated overpotential was deconvoluted into kinetic, pH gradient (H$^+$ diffusion) and H$_2$ diffusion for HER in phosphate buffer solutions with pH 6.8 and 5.5 at 3600 rpm (Figure 4.9), and the summarized results at −10 mA cm$^{-2}$ are shown in Figure 4.10.

**Figure 4.9.** Simulated voltammograms at 3600 rpm for HER with kinetics and concentration overpotentials from pH and H$_2$ gradient under various concentrations of (a) K$_{1.5}$H$_{1.5}$PO$_4$ (pH 6.8) and (a) K$_{1.06}$H$_{1.94}$PO$_4$ (pH 5.5).
**Figure 4.10.** Simulated kinetic overpotential and concentration overpotentials from pH and H$_2$ gradient at −10 mA cm$^{-2}$ and 3600 rpm in potassium phosphate buffer solutions.

Kinetic current is how catalysts perform electrochemical reactions in mass transport free conditions, i.e., with the known bulk activity. Using the optimized rate constant and the bulk activities of H$_2$ and H$^+$, kinetic current can be obtained using Equations 4.20-4.22. It is revealed that the kinetic overpotential ($\eta_{\text{kinetics}}$) on Pt has a negligible contribution to the overall overpotential for HER, regardless of the concentration and composition. The exchange current density in pH 6.8 is estimated to be 25 mA cm$^{-2}$, which is smaller than the value reported in the acid condition, ~70 mA cm$^{-2}$, although the present rate constant ($k_{4f}^0$) and exchange current density may still be overestimated, but the extent of its contribution relative to mass transfer ones should still be minimal. The rest of the overpotential comes from the concentration overpotentials due to the mass transport of H$_2$, H$^+$ and buffer species. Significance of concentration overpotentials is frequently discussed for electrochemical CO$_2$ reduction.$^{21,29–31}$
Singh et al. defined the Nernstian potential loss due to local pH change between the bulk solution and the electrode surface described as Equation 4. 4. 21

$$\eta_{\text{pH gradient}} = \frac{RT}{F} \ln \left( \frac{a_{H_2O^{+}, s}}{a_{H_2O^{+}, b}} \right)$$  (4. 4)

Besides, there is the activity gradient of H2 between the bulk solution and the electrode surface ($\eta_{H_2 \text{ gradient}}$). Note that the contribution from the product arises only on facile (reversible) electrochemical reactions, and not on kinetically sluggish reactions: e.g., oxygen evolution reaction 32 and CO2 reduction, 21,29,30 which require an overpotential greater than 200 mV. Also, the contribution from H2 during HER does not appear on HOR inactive Au. 18 Figure 4. 10. indicates that the contribution from pH gradient clearly drops monotonically with increasing electrolyte concentration. The overpotential accounts for more than 20 mV in 1.5 mol L$^{-1}$ at pH 5.5, while it was merely 5 mV in 1.5 mol L$^{-1}$ at pH 6.8. Meanwhile, concentration overpotential from H2 gradient gradually keeps increasing with electrolyte concentration.

The pH and H2 profiles as a function of distance from electrode into electrolyte at −10 mA cm$^{-2}$ and 3600 rpm are shown in Figure 4. 11. It can be found from Figure 4. 11a that the solution at pH 5.5 suffers from the local pH shift at electrode, compared to that at pH 6.8. The local activity profiles of H2 during HER are also shown in Figure 4. 11b. The local activity of H2 increases up to 7.5 times higher than that in bulk solution. As the solute concentration
increases, diffusion coefficient decreases (Figure 4. 2b) and more H₂ accumulates, which can push the backward reaction for HER.

![Graph showing pH and H₂ profiles](image)

**Figure 4. 11.** Profile of (a) pH and (b) H₂ from the electrode surface to the bulk solution, with various kinds of buffered conditions at −10 mA cm⁻² and 3600 rpm.

### 4.2.3. The Impact of Homogeneous Deprotonation Reaction Rate for a Buffer

In the previous sections, the homogeneous deprotonation reaction rate constants in Equations 4. 7 and 4. 8 were assumed to be high value (\(k_{1f} 10^4 \text{ s}^{-1}\) and \(k_{2f} 10^6 \text{ s}^{-1}\)). In this section, the impact of the homogeneous chemical reaction between buffer species was investigated by varying the homogeneous deprotonation reaction rate constant \((k_{1f} \text{ and } k_{2f})\) in 0.5 mol L⁻¹ \(K_{1.5}H_{1.5}PO_4\) (Figure 4. 12a).
Figure 4.12. (a) Simulated voltammograms with various homogeneous reaction rates for Equations 4.7 and 4.8. Profile of (b) pH and (c) equilibrium from the electrode surface to the bulk solution.

As expected, the overpotential for HER increased by decreasing the homogeneous reaction rate constants. Because the parameter only changed is the homogeneous reaction rate between buffer species, the local activity of H$_2$ at the electrode surface should remain the same at a given current density among the simulated voltammograms. Therefore, the observed difference should arise from the limitation of the homogeneous reaction rate. The pH profile within the diffusion layer is shown in Figure 4.12b. The local pH shifts from 6.72 at the bulk to 6.85 close to the electrode surface, which is independent of the homogeneous deprotonation reaction rates. This local pH shift arises purely from
the diffusion of H\(^+\) and buffer species. At close vicinity of the electrode (< 5 nm, Figure 4.12b inset), further deviation of local pH (up to 7.8 with \(k_{1f} = k_{2f} = 10^4\) s\(^{-1}\)) is observed, which depends on the homogeneous deprotonation reaction rates. The local concentration of buffer species and H\(^+\) are normalized with the corresponding equilibrium constants (Figure 4.12c). It is found that there is a layer (< 5 nm), a so-called "reaction layer",\(^{33,34}\) where the local equilibrium is no longer maintained, due to the limitation of homogeneous chemical reaction rates. As the homogeneous deprotonation reaction rates increase, the reaction layer gets thin and the equilibrium can be maintained close to the electrode surface. Although the homogeneous chemical reaction rates for phosphate buffer have not been reported, the modeling in this study agrees with previous reports, assuming high deprotonation reaction rates \((k_{1f} = k_{2f} = 10^6\) s\(^{-1}\))\(^{23}\) or that the local equilibrium is maintained within the diffusion layer.\(^{16}\)

4.2.4. Significance of Electrolyte Engineering of Buffered Conditions

The HER/HOR on Pt in a highly acid condition is purely determined by the diffusion of H\(_2\) due to the facile kinetic and mass transport of protons. In contrast, although protons supplied by buffer ions are still the reactant, the HER in near-neutral pH buffered conditions requires unavoidable, additional overpotentials due to the transport of proton carriers. The quantitative modeling presented herein distinguishes the contributions from the protons supplied from buffer ions (i.e., local pH) and H\(_2\) during HER.
Figure 4.13. (a) pH gradient in 1.0 mol L$^{-1}$ potassium phosphate buffer solution from the bulk solution to the electrode surface at $-10$ mA cm$^{-2}$. Bulk pHs are shown as dotted points. Speciation distribution of (b) phosphate, (c) malonate, and (d) citrate buffer.

Since protonated buffer ions provide the reactant, a sufficient concentration of buffer is required at a given convection -- for instance, above 0.5 mol L$^{-1}$ at 3600 rpm. It is most effective when protonated and unprotonated buffer ions coexist (see Figure 4.13a and b); i.e., how far pH is from the p$K_a$.

Although simulation could not be performed in pure KH$_2$PO$_4$ (pH 4.3) and K$_2$HPO$_4$ (pH 9.5), further severe local pH shift is expected, which results in the strong concentration dependence observed in Figure 4.1a and d. The present consideration is consistent with the recent report by H. Dau and C. Pasquini, which exhibits the maximum OER performance at pH close to p$K_a$ in buffered
condition. Although simulation is not performed for organic buffers in Figure 4, we suspect that pH was close enough to their pK_a (Figure 4. 13b and c) to minimize the local pH shift, resulting in the similar volcano concentration dependence observed with K_1.5H_1.5PO_4. Please note that this buffer diffusion under the near-neutral pH condition is present regardless of electrocatalysts, purely determined by the electrolyte properties.

Besides the buffer diffusion, the increasing contribution from H_2 diffusion during HER must be considered with respect to the identity and concentration of the buffer when a kinetically facile electrocatalyst, such as Pt, is used. The conditions with a denser buffer or more alkaline pH lead to the decrease in diffusion coefficient of H_2 due to the increase of viscosity of the electrolyte (Figure 4. 2), which results in increased concentration overpotential, associated with H_2 diffusion during HER. In fact, a dense buffered condition also leads to a decrease in bulk activity of H_2 (Figure 4. 3). Severe local activity shift of H_2 from equilibrium takes place during HER in dense electrolyte conditions at a given current density.

Overall, fine-tuning of these contributions via electrolyte engineering is required for (photo-)electrochemical applications in near-neutral pH buffered conditions depending on the target current density and operating conditions. Because those applications are usually performed under static or mild convection, the concentration overpotential is more severe than that in the RDE configuration. For instance, at 400 rpm, where the diffusion layer thickness is close to that of the static condition, the concentration overpotential from pH gradient substantially
increases, as can be seen in Figure 4. 13a. When the concentration overpotential from pH gradient is minimized by electrolyte engineering, diffusion of H₂ becomes a major contributor of the whole overpotential in the case of Pt (Figure 4. 10). To suppress the concentration overpotential from H₂ during HER, using Pt, the strategy is aimed to improve the diffusion-limiting current for HOR, which can be described by the bulk activity of H₂ and the diffusion coefficient associated with viscosity. Less viscous buffer solution will help accelerate the diffusion of H₂. For instance, carbonate buffer is known to be less viscous than phosphate buffer.\(^{25}\) Elevating the partial pressure of H₂ is an alternative approach to decrease the concentration overpotential of H₂, but it causes shift of the equilibrium potential based on the Nernst equation. Therefore, the pressure must be carefully chosen depending on the target current density and the convection of electrolyte. Alternatively, elevating the reaction temperature will help to decrease the concentration overpotential due to the improved diffusion coefficient. Further exploration of these aspects may lead to improved performance in water electrolysis at a near-neutral pH.

The present study focused on the strategy of electrolyte engineering to minimize the concentration overpotential of HER. To develop (photo-)electrochemical water splitting devices, however, another important parameter strongly affected by the electrolyte is solution resistance and overpotential on the counter oxidation reaction, such as oxygen evolution reaction (OER).\(^{25}\) That is, conductance of KH₂PO₄ and KH₂PO₄ is shown in Figure 4. 14a.
Figure 4.14. (a) Conductance of $K_2HPO_4$ and $KH_2PO_4$ at 298 K. (b) Ohmic loss in the presence of 0.5 and 3.0 mol kg$^{-1}$ of $K_2HPO_4$.

To minimize solution resistance, a dense condition (2-4 mol kg$^{-1}$ of $K_2HPO_4$) is preferable, while the optimized condition for HER needs a more diluted condition (0.5 mol L$^{-1}$ $K_{1.5}H_{1.5}PO_4$), as concluded in this study. Ohmic loss depends on the current density, and the distance between anode and cathode (Figure 4.14b). Although the ohmic loss is merely 15 mV at 10 mA cm$^{-2}$ in 0.5 mol kg$^{-1}$ of $K_2HPO_4$ with 1 mm of distance, it reaches more than 100 mV at 100 mA cm$^{-2}$. At this high current density, a conductive electrolyte (3.0 mol kg$^{-1}$ of $K_2HPO_4$) reduces the ohmic loss to 60 mV. The ohmic loss and overpotentials from HER and OER must be finely-tuned via electrolyte engineering to minimize overall voltage for the water splitting, depending on the target current density and the device configuration.

4.3. Summary

Mass transport of $H_2$ gas molecule and buffer ions was quantitatively described during the electrochemical hydrogen evolution reaction (HER) and the hydrogen oxidation reaction (HOR) under buffered conditions at near-neutral pH.
On a Pt rotating disk electrode, kinetics for HER/HOR is so fast that the concentration overpotential dominates the observed overpotential. Although the observed overpotential for HER/HOR predominantly comes from diffusion of H₂ in highly acidic conditions, the present model in a buffered condition at near-neutral pH revealed that an additional penalty due to mass transport of buffer ions, which highly depends on the electrolyte identity and molarity. To minimize the concentration overpotential from pH gradient, the buffer concentration must be increased and the pH must be close to pKₐ. As such, the concentration overpotential from H₂ is expected to be a major contributor and increase in dense and alkaline conditions. The present model of kinetics and mass transport will guide the development of (photo-)electrochemical water splitting and CO₂ reduction via electrolyte engineering.

4.4. Experimental methods

Materials

All chemicals were purchased with these purities: KH₂PO₄ (99.995%, Sigma-Aldrich, St. Louis, USA), K₂HPO₄ (99.99%, Sigma-Aldrich), KOH (99.99%, Sigma-Aldrich), C₆H₈O₇ (100.7%, Fisher Scientific, Hampton, NH, USA), HOC(COONa)(CH₂COONa)₂·2H₂O (≥ 99.0%, Sigma-Aldrich), C₃H₄O₄ (99%, Alfa Aesar, Ward Hill, MA, USA). The water used in all experiments was obtained from a Milli-Q Integral system (Millipore, Burlington, MA, USA) with a resistivity of 18.2 MΩ cm.
Electrochemistry

Electrochemical measurements were performed using a BioLogic VMP3 potentiostat (Seyssinet-Pariset, France). A rotating disk electrode (RDE, 3 mm diameter, ALS CO., Ltd, Tokyo, Japan) of polycrystalline Pt were used as a working electrode. A Pt wire was employed as a counter electrode. The disk electrode was first polished with 1 μm of diamond and then with 0.05 μm of alumina followed by electrochemical cleaning in a 1 M HClO₄ solution between −0.02 and 1.8 V vs. SHE (standard hydrogen electrode) with bubbling Ar (99.999%). Ag/AgCl (saturated KCl) (ALS CO., Ltd Tokyo, Japan) was used as a reference electrode. The potentials were reported with $iR_u$-correction using reversible hydrogen electrode (RHE) scale. Uncompensated resistance $R_u$ was measured by impedance spectroscopy (100 mHz – 10 kHz, 10 mV amplitude). Before and during all measurements, H₂ (99.9999%) was continuously supplied to the electrochemical cell. Cyclic voltammograms were performed until stable voltammograms were obtained. Voltammograms for negative going scans are shown in the figures. The kinematic viscosity and density of the electrolyte solutions were obtained using viscometer tubes (cell constants: 0.003259 and 0.009167 mm² s⁻², Fisher Scientific) and a density meter (DM40, METTLER TOLEDO, Columbus, OH, USA), respectively. Conductance was measured using a conductivity meter (S230 and InLab 731-ISM, METTLER TOLEDO).

Mass transport model

To elucidate the diffusion contribution from H₂ and buffer ions, a model containing mass transport and kinetics was developed as shown in Figure 4. 6.
The mass transport equations with coupled homogeneous chemical reactions at the steady state can be written as

\[
\frac{\partial a_i}{\partial t} = D_i \frac{\partial^2 a_i}{\partial x^2} - v(x) \frac{\partial a_i}{\partial x} + R_i = 0 \quad (4.5)
\]

where \(a_i\) and \(D_i\) are activity and diffusion coefficient for species \(i\), respectively. Here, \(v(x)\) represents the velocity of the hydrodynamic fluid at given distance from the electrode surface. \(R_i\) is the homogeneous chemical reaction rate. The first term in the middle equation describes diffusion determined by Fick’s law.

The second term in Equation 4.5 represents the convection of hydrodynamic fluid. At close vicinity to the electrode, the velocity of fluid is described by the expression

\[
v(x) = (\omega \nu)^{1/2} \left[ -0.510 (\omega \nu)^{1/2} x^2 + 0.333 (\omega \nu)^{3/2} x^3 - 0.103 (\omega \nu)^2 x^4 \right] (4.6)
\]

where \(\omega\), \(\nu\) and \(x\) are the rotating disk speed, the kinematic viscosity and the distance from the electrode surface, respectively. The last term, \(R_i\), in Equation 4.5 comes from the homogeneous consumption or production rate of \(H_3O^+\) and buffer species by the homogeneous chemical reactions. In the case of phosphate buffer, the relationships are described by:

\[
\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \xrightleftharpoons[k_{r1}]{k_{f1}} \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+ \quad \frac{k_{f1}}{k_{r1}} = K_{a1} = 10^{-2.15} \text{M}^{-1} \quad (4.7)
\]

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \xrightleftharpoons[k_{r2}]{k_{f2}} \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \quad \frac{k_{f2}}{k_{r2}} = K_{a2} = 10^{-7.21} \text{M}^{-1} \quad (4.8)
\]
where \( k_f \) and \( k_r \) represent the forward (deprotonation) and reverse (protonation) rate constants, respectively. The ratio between \( k_f \) and \( k_r \) has to satisfy the corresponding equilibrium constant. The parameter \( R_i \) for \( H_2 \) is zero because there is no homogeneous chemical reaction of \( H_2 \). According to previous reports,\(^{22,23,37}\) the activity of water is assumed to be maintained as unity through the diffusion layer. Herein, electrical double layer is not considered in this mass transport model. Therefore, the electrode surface (\( x = 0 \)) represents the position immediate after the diffuse layer (Gooey layer).\(^{34}\)

Migration is another force driven by an electric field. The migration term is often neglected in the presence of relatively dense buffer solution.\(^{30,31,38}\) For instance, J. Resasco, et al. ignored migration in their mass transport model for 0.05 M KHCO\(_3\).\(^{31}\) Following the convention, migration is not considered in the present model.

Diffusion coefficient is described by the Stokes-Einstein equation

\[
D = \frac{k_B T}{3 \pi d \mu} \quad (4. 9)
\]

where \( k_B \) is the Boltzmann constant, \( d \) is the effective hydrodynamic diameter of the hydrated ion (Stokes diameter), which includes all the \( H_2O \) molecules carried in the hydration sphere, and \( \mu \) is the dynamic viscosity of the electrolyte (measured separately). From Equation 4. 9, the diffusion coefficient has a reciprocal dependence to the dynamic viscosity, assuming a constant Stokes diameter at a constant temperature. Diffusion coefficients at a given electrolyte
concentration were estimated from the diffusion coefficients at infinite dilution,\textsuperscript{26,39} the corresponding measured dynamic viscosities (Figure 4.2a) and dynamic viscosity of water (0.89 mPa s), using the reciprocal dependence. The estimated diffusion coefficients are shown in Figure 4.2b and c. As the phosphate buffer becomes more alkaline and concentrated, the viscosity increases resulting in the decreased diffusion coefficient. The diffusion coefficients are assumed to be constant within the diffusion layer, although in reality, the composition is expected to differ from the one in the bulk solution.

At the electrode surface ($x = 0$), following boundary conditions are applied

\begin{equation}
D_{H_2} \frac{\partial a_{H_2}}{\partial x} = r_{\text{HER}} - r_{\text{HOR}} \tag{4.10}
\end{equation}

\begin{equation}
D_{H_3O^+} \frac{\partial a_{H_3O^+}}{\partial x} = 2(r_{\text{HOR}} - r_{\text{HER}}) \tag{4.11}
\end{equation}

\begin{equation}
D_{H_3^-,PO_4^{3-}} \frac{\partial a_{H_3^-,PO_4^{3-}}}{\partial x} = 0 \tag{4.12}
\end{equation}

Equations 4.10 and 4.11 describe the heterogeneous consumption or production rate of H$_2$ and H$_3$O$^+$ at the electrode surface, respectively. Buffer species were assumed to be electroinactive, as shown in Equation 4.12. Although the H$_2$ bubble starts to appear and the bubble-induced stirring effect is reported on a Pt RDE below $-5$ mA cm$^{-2}$ in 5 mol L$^{-1}$ H$_2$SO$_4$,\textsuperscript{6} they are not considered in the present model for simplification. The current density is determined by pure HER reaction rate ($r_{\text{HER}}$) and pure HOR reaction rate ($r_{\text{HOR}}$), which are defined by Zheng et al.
\[ j = 2F(r_{\text{HOR}} - r_{\text{HER}}) \]  

(4.13)

where \( F \) is Faraday constant.

The other boundary \((x = \delta)\) has to be defined as a distance at which activities are assumed to be constant values in the bulk solution. Empirically, it is assigned to be three times of the highest the Levich diffusion layer thickness \( (\delta_{\text{Levich,i}}) \).\textsuperscript{37,40,41} The Levich diffusion layer thickness is given by

\[ \delta_{\text{Levich,i}} = 1.62D_i^{1/3}V^{1/6} \sigma^{-1/2} \]  

(4.14)

As the profiles will be shown in Figure 4.11, activities are maintained to the values in the bulk solution more than 20 \( \mu \)m away from the electrode surface, which confirms that sufficient distance was provided as the boundary for our simulation.

Activities of the species must be considered instead of the concentration prepared for the electrolytes to describe mass transport and reaction rate. To obtain the activity coefficient at a given composition and concentration, a simple linear estimation was performed from the reported activity coefficient for \( \text{KH}_2\text{PO}_4 \)\textsuperscript{42} and \( \text{K}_2\text{HPO}_4 \)\textsuperscript{43} as shown in Figure 4.15.
Figure 4.15. Activity coefficient estimated linearly from the reported values of KH$_2$PO$_4$ and K$_2$HPO$_4$.

Kinetic model

HER/HOR is described by either Volmer/Heyrovsky or Volmer/Tafel.

Volmer \[
M + H_2O^+ + e^- \xrightleftharpoons[k_{f,v}^0]{k_{r,v}^0} M-H + H_2O \tag{4.15}
\]

Heyrovsky \[
M-H + H_2O^+ + e^- \xrightleftharpoons[k_{f,v}^0]{k_{r,v}^0} M + H_2 + H_2O \tag{4.16}
\]

Tafel \[
2M-H \xrightleftharpoons[k_{f,v}^0]{k_{r,v}^0} 2M + H_2 \tag{4.17}
\]

with $k_{f,v}^0$ and $k_{r,v}^0$ being the standard forward and backward rate constant for the elementary steps, respectively. The Volmer step is assumed to be fast enough to be pre-equilibrated, in which forward and backward reaction rates in Equation 4.15 are equal.$^{44-46}$ Forward reaction rate ($r_{3f}$) and backward reaction rate ($r_{3r}$) of the Volmer step are described by the expressions

\[
r_{3f} = k_{3f}^0 a_{H_2O^-} (1 - \theta_H) \exp \left\{ -\alpha_3 f \left( E - E_{3f}^0 \right) \right\} \tag{4.18}
\]
\[ r_{3r} = k^{0}_{3s} a_{H_{2}O,s} \theta_{H} \exp \left\{ (1 - \alpha_{3}) f \left( E - E^{0}_{3} \right) \right\} \quad (4.19) \]

where \( E^{0}_{3} \) and \( \alpha_{3} \) are the standard potential and symmetry factor for the Volmer step, respectively. Furthermore, \( f \) is obtained from the Faraday constant, \( f = \frac{F}{RT} \). \( \theta_{H} \) is the coverage of \( H_{ad} \). Subscripts \( s \) and \( b \) represent surface and bulk, respectively.

Standard potential \( E^{0}_{3} \) is defined where activities in liquid phase are unity and \( \theta_{H} \) is 0.5, which leads to an identical rate constant between \( k_{3f} \) and \( k_{3r} \). Pre-equilibrium of the Volmer step (Equations 4.18 and 4.19) provides potential dependent coverage (\( \theta_{H} \))

\[ \theta_{H} = \frac{a_{H,O,s} \exp \left\{ -f \left( E - E^{0}_{3} \right) \right\}}{a_{H,O,s} + a_{H,O',s} \exp \left\{ -f \left( E - E^{0}_{3} \right) \right\}} \quad (4.20) \]

Succeeding reaction on Pt is still under debate\(^{45,47-49}\) including a dual pathway\(^{46,50-52}\) between Heyrovsky and Tafel, which may be potential-dependent. Moreover, the Tafel step is suggested to be a rate-determining step in a low overpotential range, where surface coverage of adsorbed hydrogen (\( \theta_{H} \)) is below unity. The Heyrovsky step becomes rate determining when \( \theta_{H} \) approaches unity.\(^{46}\) In this study, the Heyrovsky step is tentatively assumed to be a rate-determining step, as its activation barrier is reported to be smaller than that of the Tafel step by DFT calculation.\(^{45}\) Pure HER and HOR reaction rates with the Heyrovsky step as the rate-determining step is described by the expressions

\[ r_{HER} = k^{0}_{4f} a_{H,O',s} \exp \left\{ -\alpha_{4} f \left( E - E^{0}_{4} \right) \right\} \quad (4.21) \]
\[ r_{\text{HOR}} = k_{4f}^0 a_{H_2O} a_{H_2} \left(1 - \theta_H\right) \exp \left\{-(1 - \alpha_H) f \left(E - E_4^0\right)\right\} \] (4.22)

The standard potential for the Heyrovsky step \((E_4^0)\) must satisfy the condition

\[ E_3^0 + E_4^0 = E_{\text{H}+/H_2}^0 = 0 \text{ V vs. SHE} \] (4.23)

In the present model, symmetry factors \((\alpha)\) are assumed to be 0.5 and the standard potentials of the elementary steps \((E_3^0\) and \(E_4^0)\) are assumed to be \(E_{\text{H}+/H_2}^0 = 0 \text{ V vs. SHE}\). At the equilibrium potential, \(r_{\text{HER}}\) and \(r_{\text{HOR}}\) are balanced, which determines the ratio between the forward and backward reaction rate constants for the Heyrovsky step, \(k_{4f}^0\) and \(k_{4r}^0\).

The above differential equations and boundary conditions were numerically solved by bvp5c in MATLAB, while \(k_{1f}, k_{2f}\) and \(k_{4f}^0\) were optimized by least square regression for experimental results of 0.5 and 1.5 mol L\(^{-1}\) K\(_{1.5}\)H\(_{1.5}\)PO\(_4\) with various rotation speeds. Those rate constants are assumed to be constant and applied among all the phosphate buffer solution.
4.5. References


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5. A Stand-Alone Module for Solar-Driven H₂ Production Coupled with Redox-Mediated Sulfide Remediation

Oxidation of soluble redox ions was investigated in terms of their thermodynamics and diffusion in chapter 3, which identified Fe-HEDTA redox as a promising candidate for redox-mediated H₂S splitting in near-neutral pH solution. As a counter cathodic reaction, chapter 4 discussed how to maximize HER performance in near-neutral pH buffered conditions. Based on these studies for half reactions, a stand-alone module was developed for solar-driven redox-mediated H₂S splitting in this chapter. A Cu(In,Ga)(Se,S)₂ photovoltaic (CIGS-PV) module was employed as a light absorber and an electrochemical module was designed to operate with CIGS-PV. Ion exchange membrane free device was fabricated by introducing a nano-membrane layer on cathode to produce H₂ selectively. In chapter 2, CeOₓ layer was demonstrated to improve the selectivity of O₂ in the presence of redox ions, CrOₓ layer was applied as a permselective layer for cathode in this chapter. The stand-alone module was evaluated under natural light irradiation in Saudi Arabia followed by dark homogeneous reaction with sulfide. The stability of CrOₓ layer during HER is further discussed.

5.1. Introduction

During the last few decades, there is a growing interest globally for renewable energy sources, such as solar energy and wind power. Their intermittent nature, however, prevents a massive introduction of renewable based electricity to the existing electricity grids and limits their application. Therefore electrochemical energy conversion and storage technologies are required. Tremendous efforts have
been devoted to developing solar-driven water-splitting devices (Equation 5.1), such as photocatalytic, photoelectrochemical water-splitting, and photovoltaic + electrolyzer systems.

\[
\text{H}_2\text{O} \xrightarrow{h\nu} \text{H}_2 + \frac{1}{2}\text{O}_2 \quad (5.1)
\]

The overall voltage for a water-splitting device is determined by its thermodynamics (1.23 V), Ohmic losses, concentration overpotential, and kinetic overpotentials on the electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Particularly, OER requires large overpotential of more than 200 mV at 10 mA cm\(^{-2}\) in highly alkaline conditions with finely tuned electrocatalysts on a support with high surface area.\(^1\)-\(^3\)

The anodic reactions to produce hydrogen on a cathode are not limited to OER. For instance, chlorine evolves on an anode while HER takes place on a cathode in a commercialized chloro-alkaline process.\(^4\) Alternative oxidation reactions have been proposed to replace the kinetically sluggish OER to the production of valuable chemicals, such as oxidative upgrading of biomass feedstock and the production of oxidizing agents like hydrogen peroxide and peroxydisulfate anions.\(^5\)-\(^10\) Another promising anodic reaction during HER (Equation 5.2) involves oxidizing soluble redox ions (Equation 5.3), which can perform a subsequent homogeneous reaction, such as the oxidation of toxic H\(_2\)S into solid sulfur.

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (5.2)
\]
Red → Ox + e⁻ \hspace{1cm} (5.3)

Ox and Red denote the oxidized and reduced redox species, respectively. The oxidized redox ions oxidize S\(^{2-}\) in the subsequent homogeneous reaction (Equation 5.4).

\[2\text{Ox} + \text{S}^{2-} \rightarrow 2\text{Red} + \text{S} \hspace{1cm} (5.4)\]

Combining Equations 5.2 - 5.4, the overall reaction involves splitting H\(_2\)S into H\(_2\) and S (Equation 5.5), while redox ions serve as charge carriers between the anode and sulfide; that is, redox-mediated H\(_2\)S splitting.

\[\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S} \hspace{1cm} (5.5)\]

The advantage of this approach is that valuable H\(_2\) is regenerated from H\(_2\)S while conventional H\(_2\)S treatment processes such as the Claus, LO-CAT, and Sulferox processes oxidize H\(_2\)S into H\(_2\)O and S using O\(_2\) (Equation 5.6).\(^{11,12}\)

\[\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S} \hspace{1cm} (5.6)\]

Water splitting requires more than 1.23 V, which means that 3 Si photovoltaic (PV) cells in series are necessary to obtain a sufficient voltage for solar-driven H\(_2\) production because one Si-PV has merely 0.6 V as its open circuit voltage.\(^{13}\) The advantage of H\(_2\)S splitting is that it thermodynamically requires 0.14 V, which provides a variety of options to combine PVs and electrochemical (EC) cells.

Although direct electrochemical H\(_2\)S splitting, in which an anode directly oxidizes sulfide to solid sulfur, can be performed theoretically, the deposition of solid sulfur on the anode is a challenge to be overcome.\(^{14,15}\) The redox-mediated
H$_2$S splitting process requires no passivation of electrodes because the sulfur precipitation takes place through a homogeneous reaction outside the EC cell. Another advantage of the redox-mediated process is an applicability of separation and purification process to the produced sulfur from the commercialized liquid phase processes for H$_2$S treatment, such as LO-CAT and Sulferox, in which reduced redox ions after reaction with sulfide are reoxidized by bubbling O$_2$ as shown in the following equation.$^{11,12}$

\[
\text{Red} + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{Ox} + \text{OH}^- \quad (5.7)
\]

A variety of redox ions have been investigated for redox-mediated H$_2$S splitting, such as Fe-base redox, iodide, vanadate, and heteropoly molybdophosphate.$^{16-21}$ A previous chapter investigated candidate redox ions in buffered near-neutral pH condition, particularly Fe-based metal complexes.$^{22}$ Near-neutral pH conditions were chosen because there are optimal potential options for using non-noble metal cathodes, whereas acidic conditions require noble metal cathodes. In that study, Fe$^{2+/3+}$ hydroxyethylethlenediaminetriacetate (HEDTA) was identified as a suitable candidate due to its redox potential (0.43 V vs. reversible hydrogen electrode (RHE) at pH 3-8; Figure 3. 1a) and its remarkable solubility ($> 1$ mol kg$^{-1}$).

There are a few approaches to combine light-absorbing semiconductors and electrodes to perform solar-driven H$_2$ production. Photoelectrochemical and photocatalytic approaches involve immersing the semiconductors in the electrolyte, and electrochemical reactions take place on the surface of
semiconductors or electrocatalysts that are deposited on the semiconductors. A solar-to-hydrogen (STH) conversion efficiency of 16% has been reported for water splitting, but the stability of semiconductors in electrolyte remains a major challenge. Redox ions can absorb visible light and compete with the semiconductor, so these approaches are not suitable for the present application. Isolating semiconductors from the electrolyte is a reasonable approach in terms of stability and light management. Commercially available PVs can be readily employed with EC cells via direct connection or through power electronic devices such as DC-DC convertors. A DC-DC convertor with maximum power point tracker (MPPT) helps to transfer the maximum power of the PV module to the EC module, but it requires additional investment costs. On the other hand, the current and voltage have to be carefully matched between the PV module and EC module by varying their size and the number of EC cells within the module in the case of direct connections without a DC-DC convertor. A synergetic effect is expected when PV module is directly integrated on top of EC module. The efficiency of the PV module decreases at elevated temperature under light irradiation. Therefore, in the integrated device, the electrolyte is expected to cool down the PV module, while the heat transferred from the PV module to the electrolyte improves the electrochemical reaction kinetics, mass-transport, and conductivity during electrochemical reactions.

In this study, a stand-alone module was produced by directly connecting Cu(In,Ga)(Se,S)_2-PV (CIGS-PV, irradiation area: 168 cm²) module and EC module in series. The module is used to produce H₂ coupled with the oxidation of
Fe\textsuperscript{2+}-HEDTA redox under natural light irradiation for subsequent sulfide treatment (Figure 5. 1) in which Na\textsubscript{2}S solution is introduced as a model sulfide source instead of H\textsubscript{2}S gas due to the safety concern. Hydrogen is the only gaseous product from the electrochemical system, while hydrogen and oxygen are produced in water splitting devices, which require an ion exchange membrane or a diaphragm between the anolyte and the catholyte to separate the gases produced. A crossover could take place on the cathode, where oxidized Fe\textsuperscript{3+}-HEDTA ion can be reduced instead of HER. To avoid the crossover, a nano-membrane coating was applied on the HER catalyst (bottom image in Figure 5. 1), which prevents the diffusion of large redox ions to reach the electrocatalyst underneath while allowing protons and hydrogen to go through.\textsuperscript{35–42} In this work, to prove the concept of ion exchange membrane free device, CrO\textsubscript{x} was employed as a model nano-membrane layer because of its well known functionality for corrosion protection, photocatalytic water splitting and electrochemical chlorate production.\textsuperscript{35–37,43,44} The applicability of CrO\textsubscript{x} for the present application is also discussed. Since the toxicity of Cr is a major concern, alternative layers which are under development for the above mentioned applications are also expected to be applied in the present device in the future work.
5.2. Results and discussion

5.2.1. Evaluation of Individual Electrochemical Cell Performance

To evaluate the EC cell, electrochemical measurements were performed with 1.0 mol kg\(^{-1}\) of Fe-HEDTA (50 % Fe\(^{2+}\) and 50 % Fe\(^{3+}\)) and 1.5 mol kg\(^{-1}\) of malonate buffer (pH = 5) using a carbon felt anode and a CrO\(_x\)/Pt-black mesh (geometric area: 1×1 cm\(^2\)) under static conditions at room temperature (Figure 5.2a). The onset potential appears at approximately 0.41 V, which agrees with the

Figure 5.1. Schematic image of the solar driven redox mediated H\(_2\)S splitting.
previous observation in chapter 3. The current density monotonically increases when applying a positive voltage between the anode and cathode.

Figure 5.2. (a) $j-V$ curves measured by chronopotentiometry. (Anode; carbon felt, cathode; CrO$_2$/Pt-black mesh, static condition, distance between anode and cathode: ~5 mm). $j-V$ curve measured by a glassy carbon rotating disk anode is also shown as a reference. (1.0 mol kg$^{-1}$ Fe$^{2+/3+}$ in 0.5 mol L$^{-1}$ H$_2$SO$_4$, 900 rpm). All the measurements are performed in Ar and 298 K. (b) $i-V$ curve for the CIGS-PV under light irradiation with 1 sun (PV area: 168 cm$^2$, 14 PV cells in series).

A three-electrode configuration was used to measure the potential of electrodes from a reference electrode and the resistance between the anode and cathode, which can be used to evaluate the individual overpotentials for the HER, redox oxidation, and Ohmic loss. A current density of 10 mA cm$^{-2}$ was achieved within 100 mV of overvoltage to oxidize the redox ion with an ubiquitous carbon felt anode in static conditoin, whereas the kinetically sluggish anodic OER requires more than 200 mV with finely tuned electrocatalysts. This confirms that the oxidation of Fe$^{2+}$-HEDTA is a promising alternative anodic reaction to minimize the kinetic contribution. In Chapter 3, a quantitative approach using a glassy carbon rotating disk electrode (RDE), which produces a well defined vigorous convection, revealed that the majority of the overpotential observed for
the present redox ions comes from mass-transport limitatoin.\textsuperscript{22} Thus, the overpotential in the present system could be reduced by improving the mass-transport through methods such as convection and elevating the temperature. The $j$-$V$ curve was measured as a reference using a glassy carbon RDE at 900 rpm in a solution containing 1.0 mol kg$^{-1}$ of Fe$^{2+/3+}$ in 0.5 mol L$^{-1}$ of H$_2$SO$_4$. The solution for Fe$^{2+/3+}$ had to be acidic to maintain Fe$^{2+/3+}$ ions in the absence of ligands while the solution for Fe$^{2+/3+}$-HEDTA was near-neutral pH buffered condition (pH = 5). The onset potential appeared around 0.7 V vs. RHE, which is more positive than that of Fe-HEDTA. This result indicates that the redox potential of Fe$^{2+/3+}$ was successfully tuned by the formation of a metal complex, which helps to reduce the voltage for EC cell to perform the HER and the oxidation of redox ions.

The overpotential for HER to reach 10 mA cm$^{-2}$ is approximately 150 mV on a CrO$_x$/Pt mesh in the present redox solution. This value is larger than that reported for NiMo/Ni-foam (30 mV) in phosphate buffer without redox ions, which is a standard solution for water splitting in near-neutral pH conditions.\textsuperscript{45} HER on Pt is known to be kinetically facile, and the observed overpotential is mainly due to the concentration overpotential from proton donors and hydrogen products.\textsuperscript{45–47} The concentration overpotential is highly dependent on the viscosity of the electrolyte, which alters the diffusion coefficient according to the Stokes-Einstein equation. Diffusion coefficient decreases in viscous solutions, which makes the mass-transport of reactants and products difficult and results in the increase of concentration overpotential. The viscosity of the present dense redox solution is
approximately 3 mPa s, while that of the phosphate buffer solution optimized for HER (0.5 mol L\(^{-1}\) K\(_{1.5}\)H\(_{1.5}\)PO\(_4\)) is 1 mPa s. Since the present measurements were performed in static conditions at room temperature, improving the mass-transport by convection or elevated temperature is also expected to decrease the overpotentials on both the anode and the cathode.

In addition to the overpotential on the anode and cathode, the Ohmic loss needs to be considered. The conductance of the redox solution was 0.075 S cm\(^{-1}\), which led an Ohmic loss of 90 mV at 10 mA cm\(^{-2}\) with a distance of approximately 5 mm between the anode and cathode. The Ohmic loss is comparable to the kinetic losses on the anode and the cathode, so design optimization for the EC cell is required to minimize the distance between the anode and the cathode. Overall, a steady-state operation at 10 mA cm\(^{-2}\)\(_{geo}\) was achieved within 0.8 V to perform HER and the oxidation of redox ions, which is smaller than the voltages of 1.4 V and 1.6 V for water splitting with a polymer electrode membrane and an alkaline electrolyzer, respectively.\(^{24,27}\)

The \(I-V\) curve for a CIGS-PV module that contains 14 PV cells in series was measured under simulated solar conditions (air mass (AM) 1.5G), as shown in Figure 5. 2b. The solar-to-electricity (STE) conversion energy efficiency was 15.5% with a fill factor of 68.3%. The voltage at the maximum power of the CIGS-PV module is 7.6 V, and the EC cell requires 0.8 V to reach 10 mA cm\(^{-2}\)\(_{geo}\). Therefore, nine EC cells in series with 40 cm\(^2\) electrode area in the individual cells are suitable to transfer the power generated from the PV cell effectively.
5.2.2. Solar-Driven Hydrogen Evolution Demonstration Coupled with Oxidation of Fe$^{2+}$-HEDTA

An EC module was designed with six EC cells (Figure 5. 3a) to guarantee operation with the CIGS-PV module. Carbon felt was used as the anode (1.8×22.5 cm$^2$, 3 mm thickness, Figure 5. 3b). Pt was sputtered on SUS mesh (Pt/SUS mesh,1.8×22.5 cm$^2$) (Figure 5. 3c), and six sheets of the Pt/SUS mesh were put together to obtain a sufficient surface area of Pt. The Pt/SUS mesh and carbon felt were connected in series with Teflon-coated copper wires. A spacer with a thickness of about 2 mm was used to prevent a short circuit between the anode and cathodes (Figure 5. 3d). A stand-alone module was assembled as shown in Figure 5. 3e and 2f to produce H$_2$ gas, which was collected in a graduated cylinder. To obtain $I$-$V$ curve of the PV module under natural sunlight, one of the CIGS-PV module was used as a reference and connected to a potentiostat. Although PV-EC modules were placed beside each other to observe the electrochemical reactions in this demonstration, a compact stand-alone module can be fabricated just by placing the PV module on top of the EC module (Figure 5. 3g).
Figure 5.3. Pictures of (a) the electrochemical module with 6 EC cells, (b) with anodes, (c) with cathodes, (d) cross-sectional view of anode and cathode, (e) overall picture of the redox-mediated H\textsubscript{2} production under natural light irradiation, (f) schematic image of Figure 5.3e and (g) the stand alone module.

The light intensity was measured using a Si photodiode as approximately 100 mW cm\textsuperscript{-2}, which was close to the standard intensity of AM 1.5G during a demonstration on December 6, 2018, in Thuwal, Saudi Arabia. The current through the system was monitored using a multi-meter connected in series (Figure 5.4a). During the initial 10 min of experiment, increasing current was observed from 250 to 320 mA. The activation might come from the initial conditioning of electrodes by redox reactions or a slight elevation in the temperature of the electrolyte by solar irradiation. After this induction period, a stable current of approximately 330 mA
was obtained during the demonstration, which corresponds to 8 mA cm$_{\text{geo}}$-2 based on the electrode area (40.5 cm$^2$) in the individual cells.

![Figure 5.4](image)

**Figure 5.4.** (a) Current density based on the geometric area of the electrode in the individual cell (1.8×22.5 cm$^2$) and Faradaic efficiency of H$_2$ during the demonstration. (b) $i$-$V$ curve from CIGS-PV and the voltage measured from the individual EC cells. (Anodes; carbon felts, cathodes; CrO$_x$/Pt/SUS meshes, 6th Dec 2018, Thuwal, Saudi Arabia).

Hydrogen gas bubbles were successfully observed from the cathodes in all EC cells, and the production rate was approximately 15 mL min$^{-1}$ (0.61 mmol min$^{-1}$) from 168 cm$^2$ of PV module. This corresponds to 0.09 mL cm$^{-2}$ min$^{-1}$ (3.7 µmol min$^{-1}$ cm$^{-2}$). Comparing the volume of the hydrogen collected in the cylinder and theoretical one estimated from the measured current, nearly 100% Faradaic efficiency was obtained at the beginning of the measurement (Figure 5.4a). The Faradaic efficiency on the carbon anode is difficult to determine in the device. Potential side reactions on the anode, i.e., oxidation of the malonate buffer and H$_2$, were examined using a glassy carbon rotating disk electrode shown in Figure 5.5. Negligible current was obtained in the absence of Fe$^{2+/3+}$-HEDTA redox ion, and the oxidation of H$_2$ was not observed on the carbon by switching the gas atmosphere
from Ar to H₂, which supports that the anodic current in the stand-alone module comes from the oxidation of Fe²⁺-HEDTA redox ion.

**Figure 5.5.** Cyclic voltammograms using a glassy carbon rotating disk electrode in 1.5 mol kg⁻¹ malonate buffer (a) without and (b) with 1.0 mol kg⁻¹ Fe²⁺/³⁺-HEDTA at 900 rpm. (pH = 5, Ar or H₂ atmosphere).

The I-V results of the reference PV showed 12% STE conversion energy efficiency under natural solar irradiation and was compared with the voltage of individual EC cells measured by a multi-meter connected in parallel (Figure 5.4b). The voltage of individual EC cells was approximately 0.7-0.9 V, which is consistent with the measurement obtained using a 1 × 1-cm² geometry in the laboratory shown in Figure 5.2a, except for the EC cell No. 3, which required 1.3 V. This was later found to be the result of a loose connection between the electrode mesh and copper wire in this EC cell.

The overall voltage for the EC module was 5.1 V. The current at 5.1 V in the reference PV module was 330 mA, which is consistent with the measured current of the stand-alone module. Figure 5.4b clearly shows that the stand-alone device was operated at a voltage below the maximum power of the PV cell ($V_{Pmax} = 6.5$ V), where stable current can be obtained, while the current is expected to drop...
significantly above $V_{p_{\text{max}}}$. However, the Faradaic efficiency gradually kept dropping to 80% after 60 min, which indicates the presence of a side reaction with Fe^{3+}-HEDTA on the cathode (Figure 5.4a). The stability of the CrO$_x$ layer in the presence of redox ions is further discussed in section 5.2.4.

The various efficiency results are summarized in Table 5.1. The efficiency of the PV-to-EC power transfer (the power utilization) was 85% according to the operating point and maximum power of the PV cells. The PV-to-EC power transfer efficiency is expected to be improved further by increasing the number of EC cells based on $V_{p_{\text{max}}}$ of the PV module and the operation voltage of individual EC cells. The STH conversion energy efficiency can be evaluated with a variety of thermodynamic voltages, which depend on the counter half reaction. The counter half reaction is denoted in parentheses to describe the corresponding STH conversion energy efficiency.
Table 5.1. Various efficiencies for the stand-alone device measured at 2:10 pm on December 6, 2018, in Thuwal, Saudi Arabia.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
<th>Efficiency / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar-to-electricity (STE) conversion energy efficiency</td>
<td>( \frac{\text{Power max of PV}}{\text{Input light intensity}} )</td>
<td>12</td>
</tr>
<tr>
<td>PV-to-EC power transfer efficiency</td>
<td>( \frac{\text{Power at operation}}{\text{Power max of PV}} )</td>
<td>85</td>
</tr>
<tr>
<td>Solar-to-hydrogen (STH) conversion energy efficiency ((S^2^-/S))</td>
<td>( \frac{\text{Production rate of } H_2 \times 2 \times 0.14}{\text{Input light intensity}} )</td>
<td>1.4</td>
</tr>
<tr>
<td>Solar-to-hydrogen (STH) conversion energy efficiency ((\text{Red/Ox}))</td>
<td>( \frac{\text{Production rate of } H_2 \times 2 \times 0.43}{\text{Input light intensity}} )</td>
<td>4.4</td>
</tr>
<tr>
<td>Voltage efficiency for the electrochemical system</td>
<td>( \frac{0.43 \times 6}{\text{Operating voltage}} )</td>
<td>51</td>
</tr>
</tbody>
</table>

The STH conversion energy efficiency for H\(_2\)S into H\(_2\) and S uses the thermodynamic voltage of 0.14 V (third row in Table 1). The STH conversion energy efficiency \((S^2^-/S)\) was 1.4%, which represents the net efficiency for the solar-driven H\(_2\) production coupled with sulfide remediation shown in Figure 5.1. The STH conversion energy efficiency \((\text{Red/Ox})\) was 4.4% when introducing the thermodynamics of redox ions, which represents the efficiency of the present stand-alone device only without considering the homogeneous reaction with sulfide. Voltage efficiency discusses the energy loss due to the overpotentials in the electrochemical cells during operation compared with the thermodynamics of the desired reaction. The voltage efficiency for the electrochemical module was 51% from the operating voltage (5.1 V) and the thermodynamically required voltage for
HER and the oxidation of redox ions (0.43 V × 6 EC cells). The voltage efficiency for water splitting is reported to be 70-80% in alkaline electrolyzers and 95% in polymer electrolyte membrane (PEM) electrolyzers, even at high current density (200 mA cm\(^{-2}\)).\(^{48}\) Although the sluggish OER was replaced with the kinetically facile redox reaction, there is a large voltage loss in the present system compared with a water-splitting device. One of the reasons is the thermodynamic voltage. The water splitting thermodynamically requires a large voltage (1.23 V), so the portion of additional losses (Ohmic drop and the overpotentials on anode and cathode) appears to be smaller than in the present reaction, which requires 0.43 V.

Solar-to-hydrogen conversion energy efficiency 10% is often used as a benchmark for solar-driven water splitting, which corresponds to the H\(_2\) production rate 153 μmol cm\(^{-2}\) h\(^{-1}\). Although the efficiency to split H\(_2\)S is low in the present stand-alone module, the H\(_2\) production rate was 222 μmol cm\(^{-2}\) h\(^{-1}\), which exceeds the benchmark value for water splitting. Higher H\(_2\) production rate can be easily obtained because the required voltage for the present reaction is significantly lower than that for the water splitting, which helps to increase the current density and resultant H\(_2\) production rate per unit area.

The STH conversion energy efficiency could be improved further. For instance, the number of EC cells could be optimized according to the generated voltage of the PV, which would improve the PV-to-EC power transfer efficiency. The voltage efficiency could also be improved through fine tuning the electrolyte and elevating its temperature to decrease the additional voltage losses in the electrochemical module, especially the diffusion overpotential and Ohmic loss.
Improvement is also necessary for the Faradaic efficiency of H$_2$, which remained 80% after the gradual degradation of CrO$_x$ nano-membrane layer. The origin of degradation and alternative candidates are discussed in section 5.2.4.

### 5.2.3. Homogeneous Reaction Between Fe$^{3+}$-HEDTA and S$^{2-}$

Instead of H$_2$S, 0.02 mol L$^{-1}$ Na$_2$S solution was used as a model sulfide source. A stoichiometric volume of Na$_2$S solution was added to a 0.1 mol kg$^{-1}$ Fe$^{3+}$-HEDTA solution with 1.0 mol kg$^{-1}$ of malonate buffer, which has a red color (Figure 5. 6a), under Ar atmosphere at room temperature. The color of the solution turned to a deeper red immediately after the addition of the Na$_2$S solution and became opaque with the dispersion of particles (Figure 5. 6b-e). After leaving overnight under Ar flow, transparent supernatant and white precipitate were clearly observed (Figure 5. 6f). The following reaction mechanism between the H$_2$S and Fe-complex is suggested with Equation 5. 8 as a rate determining step.

\[
\begin{align*}
H_2S + Fe^{3+}(OH^-)L^{n-} & \leftrightarrow Fe^{3+}(SH^-)L^{n-} + H_2O \quad (5. 8) \\
Fe^{3+}(SH^-)L^{n-} + Fe^{3+}(OH^-)L^{n-} & \leftrightarrow (Fe^{3+}L^{n-})_2S^- + H_2O \quad (5. 9) \\
(Fe^{3+}L^{n-})_2S^- & \rightarrow 2Fe^{2+}L^{n-} + S \downarrow \quad (5. 10)
\end{align*}
\]

The color changed to a deep red color because of the formation of a reaction intermediate in Equation 5. 8, which has a light absorption peak at 490 nm. The reaction took a few minutes to complete at ambient temperature. In commercialized homogeneous processes to oxidize H$_2$S in liquid phase, such as the Lo-cat and Sulferox processes, the reaction temperature is elevated to 40-60 °C, which will
help to increase the homogeneous reaction rate. The form of H$_2$S in the electrolyte depends on the solution pH. The major species is dissolved H$_2$S below pH 7, and it shift to HS$^-$ up to pH 12, finally S$^{2-}$ in alkaline conditions. Accordingly, concentration of dissolved sulfide species increases in alkaline condition. Although the major sulfide species is not clear when alkaline Na$_2$S solution was added to buffered redox solution (pH = 5) at this preliminary stage, homogeneous H$_2$S treatment to solid sulfur with redox ions is demonstrated in a wide pH range from highly acidic to slightly alkaline condition (pH = 9) in previous reports.$^{11,16,18}$ Further study is required to optimize conditions, such as pH and temperature, for overall process including electrochemical systems and homogeneous reactors using H$_2$S gas as a sulfide source to achieve efficient solar conversion and H$_2$S treatment.

Figure 5.6. Photographs of 0.1 mol kg$^{-1}$ Fe$^{3+}$-HEDTA in 1 mol kg$^{-1}$ malonate buffer (a) before adding NaS solution, (b)-(d) during homogeneous reaction with 0.02 mol L$^{-1}$ Na$_2$S solution in the order, (e) after completing reaction, and (f) overnight at static condition under Ar flow.

The precipitation was collected after centrifuging and washing with water. The Raman spectra confirmed that the powder obtained was composed of solid
sulfur (Figure 5. 7a). Characteristic peaks of Na$_2$S at 168 nm and 232 nm were not observed in the precipitate, which shows that sulfide ions reacted with Fe$^{3+}$-HEDTA. The purity of obtained solid sulfur is not studied in this preliminary stage because it highly depends on the washing and separation process. However, commercialized Sulferox process which also applies Fe based redox solution can produce 99.5% purity of sulfur after filtration and melting process. These existing technique will definitely help the present redox-mediated process in the future work.

Figure 5. 7. (a) Raman spectra of precipitate, reference commercial sulfur and Na$_2$S·9H$_2$O measured with 785 nm laser. (b) UV-vis spectra of before and after the homogeneous reaction between Na$_2$S and Fe$^{3+}$-HEDTA buffered solution. Spectra after oxidizing the supernatant in air are also shown. The inset photographs were taken before the dilution for UV-vis measurements.

UV-vis spectra were collected with a series of redox solutions after diluting the concentration of Fe redox ions to 0.2 mmol L$^{-1}$ (Figure 5. 7b). The Fe$^{3+}$-HEDTA redox shows absorption below 450 nm with an absorption peak at around 250 nm, while the blank malonate buffer has absorption below 250 nm. A transparent supernatant was collected after the homogeneous reaction with sulfide and allowing it settle down overnight under Ar atmosphere (bottom inset photograph in Figure 5. 7b). The absorption peak at 250 nm clearly decreased after
reaction with Na₂S, which indicates that Fe³⁺-HEDTA was successfully reduced to Fe²⁺-HEDTA by the oxidation of sulfide ions. The absorption peak still remained, which might have come from unreacted Fe³⁺-HEDTA or the reoxidation of Fe²⁺-HEDTA by air during dilution. Characteristic peak of sulfide solution at 230 nm was not observed in the redox solutions after homogeneous reaction, which indicates that sulfide ions completely reacted with Fe³⁺-HEDTA redox ions. The collected transparent supernatant was subsequently stirred in the presence of air and returned to the original red color (top inset photograph in Figure 5.7b). The UV-vis spectra confirmed that Fe²⁺-HEDTA can be reoxidized to Fe³⁺-HEDTA, which indicates that the Fe²⁺/³⁺-HEDTA redox ions can serve as reversible charge carriers. Examination of cycle stability for Fe²⁺/³⁺-HEDTA redox ion between the electrochemical and homogeneous reaction is required in the future study.

Considering that Fe metal complexes are applied for the commercialized liquid phase H₂S treatment, in which O₂ is introduced as a strong oxidizer (1.23 V vs. RHE) to reoxidize Fe²⁺ species,¹¹,¹² reasonable stability of metal complex, especially ligands, is expected in the present concept using a mild anodic electrochemical potential (0.5 V vs. RHE according to Figure 5.2a).

The presence of buffer ions is essential to minimize the concentration overpotential (pH gradient). The potential-pH diagram of various Fe-redox species shows that the oxidation of Fe-redox species requires an appropriate pH. For example, a dense Na₂S solution (1.0 mol L⁻¹) at highly alkaline pH failed to form solid sulfur as a black precipitation (Figure 5.8), resulting in the formation of Fe₅S. In addition to the potential use of a non-noble metal cathode, near-neutral pH
conditions in the presence of buffer (malonate in this case) offered an environment to make redox cycles achievable with the Fe-HEDTA redox solution.

![Image](image_url)

**Figure 5.8.** Picture of the dispersion of particles after homogeneous reaction between 0.1 mol kg\(^{-1}\) Fe\(^{3+}\)-HEDTA and 1.0 mol L\(^{-1}\) Na\(_2\)S

### 5.2.4. Stability of the Permselective CrO\(_x\) Layer in the Presence of Metal Complex

A decrease in the Faradaic efficiency of H\(_2\) was observed in the stand-alone device (Figure 5.4a). We hypothesized that the degradation of CrO\(_x\) layer came from an electrochemical reduction of solid Cr\(^{3+}\) containing layer to soluble Cr\(^{2+}\) ion during HER in the presence of metal complex. To confirm the hypothesis, electrochemical stability tests were performed with different oxidizers, i.e., O\(_2\), Fe\(^{3+}\)-HEDTA and Fe(CN)\(_6\)\(^{3−}\), and potential-pH diagram was estimated in the presence of metal complexes.

The stability of the CrO\(_x\) layer was further studied on a polycrystalline Pt RDE in the presence of O\(_2\), Fe\(^{2+/3+}\)-HEDTA, or Fe(CN)\(_6\)\(^{4−/3−}\) by switching the
electrode potential between HER (approximately −0.18 V vs. RHE) and 0 V vs. RHE at 1600 rpm.

**Figure 5.9.** (a)-(c) Chronoamperometry using a CrO₅/Pt rotating disk electrode. (d)-(f) Cyclic voltammograms for the CrO₅/Pt electrode before and after the chronoamperometry. Voltammogram measured with a bare Pt electrode is also shown. (1600 rpm, pH = 5, 298 K)

In the presence of O₂, the measured current at 0 V vs. RHE remained close to 0 mA cm⁻² during the stability test in 0.5 mol L⁻¹ of phosphate buffer at pH 5 (Figure 5.9a). The diffusion-limiting current density for the oxygen reduction reaction (ORR) was approximately −5 mA cm⁻² on a bare Pt electrode (Figure 5.9d). The suppression of ORR by the CrO₅ layer is consistent with previous reports and is explained by the unique permselectivity through the layer.³⁵–³⁷ The CrO₅ layer prevents the diffusion of O₂ while allowing the mass-transport of protons and H₂. The cyclic voltammograms measured before and after the stability test remained unchanged (Figure 5.9d), which also indicate the excellent stability of CrO₅ during HER in the presence of O₂.
The stability test was also performed in the redox solution used for the demonstration, which contains 1 mol kg\(^{-1}\) of Fe\(^{2+/3+}\)-HEDTA (50% Fe\(^{2+}\) and 50% Fe\(^{3+}\)). The measured current density at 0 V vs. RHE was close to 0 mA cm\(^{-2}\) at the beginning of the stability test, but it kept decreasing to approximately −4 mA cm\(^{-2}\) at the end of the potential-step stability test (Figure 5. 9b). The increase of cathodic current is ascribed to the reduction of Fe\(^{3+}\)-HEDTA, which has more positive redox potential (0.43 V vs. RHE). This suggests that the role of the permselectivity of CrO\(_x\) layer was not maintained.

In contrast, the current density remained 0 mA cm\(^{-2}\) when the stability test was conducted at a constant potential (0 V vs. RHE), which suggests that the semipermeable function of the CrO\(_x\) layer was gradually lost when applying more negative potential in the potential-step stability test. The cyclic voltammograms measured before and after the stability tests (Figure 5. 9e) are also consistent with the chronoamperometry results. A reduction current was observed above 0 V vs. RHE, which originated from the reduction of Fe\(^{3+}\)-HEDTA after the potential-step stability test, while only HER current below 0 V vs. RHE was measured after applying constant potential (0 V vs. RHE). This loss of semipermeability of the CrO\(_x\) layer was very gradual because the reduction current measured at 0 V vs. RHE (−4 mA cm\(^{-2}\)) was smaller than that measured with a bare Pt electrode (−60 mA cm\(^{-2}\)).

To investigate the impact of a different metal complex, Fe(CN)\(_6^{4-/3-}\) was introduced instead of Fe\(^{2+/3+}\)-HEDTA to perform the stability test. Because of the limited solubility, the total concentration of Fe(CN)\(_6^{4-/3-}\) was 0.5 mol kg\(^{-1}\) (50%
Fe$^{2+}$ and 50% Fe$^{3+}$). There was clearly severe decomposition of the CrO$_x$ layer within 60 min (Figure 5. 9c), although the concentration of redox ions was lower than that of Fe-HEDTA shown in Figure 5. 9b. At the end of the stability test, the current density became close to the diffusion-limiting current density measured on the bare Pt ($-110$ mA cm$^{-2}$) shown in Figure 5. 9f. Cyclic voltammogram of CrO$_x$/Pt after the stability test in Figure 6f shows the cathodic current coming from the reduction of Fe(CN)$_6^{3-}$ above 0 V vs. RHE, which indicates that the functionality of CrO$_x$ layer was lost.

The comparisons in Figure 5. 9a-c imply that just the production of hydrogen gas (approximately $-10$ mA cm$^{-2}$) does not damage the CrO$_x$ layer (Figure 5. 9a) and that the degradation is influenced by the different type of Fe redox species (Figure 5. 9b and c). Most critically, the degradation is highly dependent on the ligand of the redox species present in the electrolyte. The comparison in Figure 5. 9b indicates that applying a negative potential triggers the degradation, which implies that the potential dependent redox process is involved in the loss of the CrO$_x$ layer.

The oxidation state of the CrO$_x$ layer is supposed to be +3 after deposition, so the redox reaction from Cr$^{3+}$ in CrO$_x$ to soluble Cr$^{2+}$ ions seems to be the origin of the degradation. To clarify this hypothesis, the thermodynamics of Cr$^{2+}$/CrO$_x$ was estimated in the presence of the metal complex. Although CrO$_x$ layer is suggested to be mixed oxide and hydroxide CrO$_{(1.5-n)}$(OH)$_{2m}$,H$_2$O,$^{51,52}$ it is assumed that the CrO$_x$ is Cr(OH)$_3$. The activity of the solid phase is unity, and the total activity of Cr$^{2+}$ ions ($a_{Cr^{2+}}$) is assumed to be 1 $\mu$mol L$^{-1}$ to obtain the
equilibrium potential and compare the influence of the metal complex. The redox
potential of Cr\(^{2+}\)/Cr(OH)\(_3\) in the absence of ligand \(E_{\text{Cr}^{2+}/\text{Cr(OH)}_3}\) is described by
Equation 5.11:

\[
E_{\text{Cr}^{2+}/\text{Cr(OH)}_3} = E_{\text{Cr}^{2+}/\text{Cr(OH)}_3}^0 - 0.0591 \times 3 \times \text{pH} - 0.0591 \times \log a_{\text{Cr}^{2+}}. \quad (5.11)
\]

where \(E_{\text{Cr}^{2+}/\text{Cr(OH)}_3}^0\) is the standard potential of Cr\(^{2+}\)/Cr(OH)\(_3\), which is −0.136 V vs.
SHE. The redox potential is −0.7 V vs. SHE (−0.4 V vs. RHE) at pH 5, which is
sufficiently negative to avoid the reduction of Cr(OH)\(_3\) compared with the potential
applied in Figure 5.9a. Therefore, it is difficult to further reduce Cr(OH)\(_3\) to soluble
Cr\(^{2+}\) in the absence of ligand.

The standard redox potential is expected to shift due to the formation of a
metal complex between Cr\(^{2+}\) and ligand following the thermochemical cycle
shown in Figure 5.10a. L and \(\beta\) represent the ligand and the formation constant of
the metal complex, respectively. The redox potential in the presence of ligand is
described by Equation 5.12.

\[
E_{\text{Cr}^{2+}L_m/\text{Cr(OH)}_3} = E_{\text{Cr}^{2+}/\text{Cr(OH)}_3}^0 + 0.0591 \times \log \beta - 0.0591 \times 3 \times \text{pH} - 0.0591 \times \log \left( \frac{a_{\text{Cr}^{2+}L_m}}{a_L^m} \right) \\
(5.12)
\]

The first two terms on the right side of the equation are used to obtain the
standard potential of Cr\(^{2+}L_m\)/Cr(OH)\(_3\), and the last two terms are used to
compensate for the activities according to the Nernst equation. The bulk activities
at equilibrium were obtained from the corresponding equilibrium constants listed
in Table A2 using the HySS program in the pH range of 4 to 6, where the Cr(OH)$_3$ does not dissolve and the malonate buffer can be a proton donor for HER. The speciation distribution of Cr$^{2+}$ species is shown in Figure 5. 10b.

![Figure 5. 10.](image)

Figure 5. 10. (a) Thermochemical cycle between Cr(OH)$_3$ and Cr$^{2+}$. (b) Speciation distribution of Cr$^{2+}$ in 1 mol L$^{-1}$ of malonate buffer in the presence of 0.5 mol L$^{-1}$ of Fe(CN)$_6^{4-}/3-$ or 1.0 mol L$^{-1}$ of Fe$^{2+}/3+$-HEDTA obtained by HySS program. The corresponding equilibrium constants are shown in Table A2 in appendices. (b) Estimated potential-pH diagram for Cr$^{2+}$/Cr(OH)$_3$ in the presence of metal complexes.

Since malonate buffer can also form a complex with Cr$^{2+}$, Cr$^{2+}$-malonate and Cr$^{2+}$-(malonate)$_2$ coexist with Cr$^{2+}$-HEDTA or Cr(CN)$_6^{4-}$. Notably, Cr(CN)$_6^{4-}$ is a major species in the presence of cyanide at pH 5, while Cr$^{2+}$-HEDTA remains as a minority. The difference arises from their formation constants (Table A2), where cyanide can form a metal complex more easily than HEDTA. As the pH shifts to more alkaline conditions, deprotonated malonate anions become favorable, which leads to Cr$^{2+}$-(malonate)$_2$ predominating in both solutions.
The redox potential obtained from Equation 5. 12 is shown in Figure 5. 10c. It is clear that the complexation shifts the redox potential to be more positive and closer to the potential of HER, which supports the enhanced degradation in the presence of metal complex shown in Figure 5. 9. Since Cr(CN)$_6^{4-}$ is more favorably formed than Cr$^{2+}$-HEDTA, the redox potential of Cr$^{2+}$L$_m$/Cr(OH)$_3$ in the presence of Fe(CN)$_6^{4-/3-}$ becomes more positive than that in Fe$^{2+/3+}$-HEDTA. This results in a larger driving force to reduce the Cr(OH)$_3$ layer to soluble Cr$^{2+}$ ions during the stability test. The difference of the redox potentials of Cr$^{2+}$L$_m$/Cr(OH)$_3$ in the presence of Fe(CN)$_6$ and Fe-HEDTA becomes similar at pH 6 because Cr$^{2+}$-(malonate)$_2$ becomes predominant in both solutions.

Because Cr-malonate complex can also be present, the stability test was performed to identify the effect of malonate anions with bubbling O$_2$ in a solution of phosphate and malonate buffer at pH 5 (Figure 5. 11).
Figure 5.11. Potential-step chronoamperometry using a CrO₃/Pt rotating disk electrode with bubbling O₂ at 1600 rpm in phosphate and malonate buffer solution at pH 5 and 298 K.

Indeed, the current measured at 0 V vs. RHE gradually kept decreasing after 200 min in the presence of malonate buffer, which indicates that ORR started to take place due to the degradation of the CrO₃ layer, while the current was maintained close to 0 mA cm⁻² in the phosphate buffer solution. The formation constant of the soluble Cr²⁺ phosphate complex has not been reported, so the positive potential shift due to complex formation is not expected in the phosphate solution. The degradation in the malonate buffer solution does not appear to be as severe as in the redox solutions (Figure 5.9b and c). The difference in reaction kinetics between ORR and redox reduction must be mentioned. The redox reaction is a kinetically facile charge transfer process. Without exposing the Pt surface, a certain amount of leaching Cr may trigger the redox reaction by charge tunneling through the remaining layer. The kinetics of Fe(CN)₆⁴⁻/³⁻ is approximately two orders of magnitude faster than that of Fe²⁺/³⁺-HEDTA,²² which could be another reason why the redox reduction current was severely observed in the presence of Fe(CN)₆⁴⁻/³⁻. On the other hand, ORR is a kinetically sluggish electrocatalytic
reaction that requires adsorbed intermediate to form on the Pt surface. Therefore, a sufficient amount of Cr has to be etched before O\textsubscript{2} molecules are able to reach the Pt surface, which may be one of the reasons why it took more than 200 min before the degradation became obvious in Figure 5. 11. A quantitative description of how much Cr must be leached to observe undesired redox reactions and ORR is beyond the scope of the present work.

The stability of the permselective layer is a remaining problem that is caused by the redox reaction forming a soluble metal complex. To overcome this issue, a redox inactive layer could be a promising candidate, such as SiO\textsubscript{x} and TiO\textsubscript{x}.\textsuperscript{38–42,54–56} Optimization of the layers’ thickness and pore size on a desired substrate is required to prevent the diffusion of redox ions while allowing protons and H\textsubscript{2} to go through.

5.3. Summary

This study demonstrated a stand-alone module where 14 CIGS-PV cells and 6 EC cells are directly connected in series to produce hydrogen and oxidize Fe\textsuperscript{2+}-HEDTA redox under natural light irradiation. The module was successfully operated below the voltage of the maximum power of the PV cells with a PV-to-EC transfer efficiency of 85%. The rate of H\textsubscript{2} production was 15 mL min\textsuperscript{−1} with an irradiation area of 168 cm\textsuperscript{2} (222 \(\mu\)mol h\textsuperscript{−1} cm\textsuperscript{−2}), and its STH conversion energy efficiency coupled with sulfide remediation was 1.4%. Due to the unique thermodynamic characteristics of H\textsubscript{2}S, the rate of H\textsubscript{2} production in the present
module exceeds the benchmark value (153 $\mu$mol h$^{-1}$ cm$^{-2}$) for 10% of STH conversion energy efficiency for water splitting.

Solid sulfur was obtained by subsequent homogenous reaction between Fe$^{3+}$-HEDTA and S$^{-2}$ in Na$_2$S solution instead of H$_2$S gas, which produced a transparent Fe$^{2+}$-HEDTA solution. This confirmed that the Fe$^{2+/3+}$-HEDTA redox ions serve as a reversible charge carriers. The stability of the permselective CrO$_x$ layer remains as a challenge. A series of experiments and thermodynamic studies revealed that the degradation of the CrO$_x$ layer most likely resulted from the reduction of the Cr$^{3+}$-containing layer into a soluble Cr$^{2+}$-complex in the presence of ligands. A redox-inactive semipermeable layer is necessary for future work to establish a membrane-less stand-alone system for H$_2$ evolution.

5.4. Experimental methods

Materials

All chemicals were purchased with the following purities: KOH (99.99%, Sigma-Aldrich, St. Louis, USA), FeSO$_4$·7H$_2$O (99.0%, Sigma-Aldrich), HEDTA-Na$_3$ (≥ 99%, Fisher Scientific, Pittsburgh, USA), HEDTA-Fe (99%, Phygenera, Langenberg, Germany), K$_3$[Fe(CN)$_6$] (> 99.9%, Sigma-Aldrich), K$_4$[Fe(CN)$_6$] (99.5%, Sigma-Aldrich), KH$_2$PO$_4$ (99.995%, Sigma-Aldrich), K$_2$HPO$_4$ (99.99%, Sigma-Aldrich), K$_2$CrO$_4$ (≥ 99%, Sigma-Aldrich), H$_2$PtCl$_6$·H$_2$O (99.995%, Sigma-Aldrich), Pb(C$_2$H$_3$O$_2$)$_2$·3H$_2$O (99.999%, Sigma-Aldrich), C$_3$H$_4$O$_4$ (99%, Alfa Aesar, Ward Hill, USA), and Na$_2$S·9H$_2$O (98+, Strem Chemicals, Newburyport, USA). The water used in all experiments was obtained from a
Milli-Q Integral system (Millipore, Burlington, USA) with a resistivity of 18.2 MΩ cm. The pH of the electrolyte solutions was adjusted using KOH.

The solution containing Fe$^{2+}$ is sensitive to O$_2$, so Ar (99.999%) was bubbled through the solutions before adding salts containing Fe$^{2+}$, and an Ar atmosphere was maintained. Carbon felt (AvCarb G100 Soft Graphite Battery Felt, thickness 3.2 mm, Fuel Cell Store, College Station, USA) was pretreated in air at 773 K for 5 h to make it hydrophilic.$^{57}$ A Pt black mesh was prepared by chronopotentiometry at 30 mA cm$^{-2}$ for 10 min in a solution containing 72 mmol L$^{-1}$ H$_2$PtCl$_6$ and 0.13 mmol L$^{-1}$ Pb(C$_2$H$_3$O$_2$)$_2$ after cleaning a pristine Pt mesh (99.99%, wire diameter 0.5 mm, Sigma-Aldrich) in aqua regia for 1 min.$^{58}$ CIGS-PV module (14 cells in series, irradiation area 168 cm$^2$) was provided from Solar Frontier K.K. Pt was deposited on the SUS mesh (SST 316, 90 mesh, wire diameter 0.0035 inch, FuelCellStore) by sputtering 20 nm of Ti, followed by 50 nm of Pt (Pt/SUS mesh). The custom-made electrochemical module used for the demonstration was made of acrylic sheet (Sumipex®). The redox solution was circulated between the storage bottle and EC module by a peristaltic liquid pump (323, Watson-Marlow) equipped with a pump head (313, Watson-Marlow) at 3 mL min$^{-1}$.

**Electrochemical measurements**

Electrochemical measurements were performed using a BioLogic VMP3 potentiostat (Seyssinet-Pariset, France). Ag/AgCl (saturated KCl) (ALS CO., Ltd Tokyo, Japan) was used as a reference electrode. The potentials were reported
with \( iR_u \)-correction using an reversible hydrogen electrode (RHE) scale. The uncompensated resistance \( R_u \) was measured by impedance spectroscopy (100 mHz – 10 kHz, 10 mV amplitude). CrO\(_x\) was deposited on Pt in 0.5 mol L\(^{-1}\) K\(_2\)CrO\(_4\) solution by chronopotentiometry at \(-10\) mA cm\(^{-2}\) for the Pt/SUS or \(-100\) mA cm\(^{-2}\) for the Pt black mesh for 10 min under Ar atmosphere (99.9999%).

A rotating disk electrode (RDE, 3 mm diameter, ALS CO., Ltd, Tokyo, Japan) of polycrystalline Pt was first polished with 1-\(\mu\)m diamond and then with 0.05-\(\mu\)m of alumina, followed by electrochemical cleaning in a 1 M HClO\(_4\) solution between \(-0.02\) and 1.8 V vs. SHE (standard hydrogen electrode) with bubbling Ar (99.999%). Pt wire was used as a counter electrode. CrO\(_x\) was deposited on the Pt RDE in 0.5 mol L\(^{-1}\) K\(_2\)CrO\(_4\) solution by applying a constant current density of \(-280\) \(\mu\)A cm\(^{-2}\) for 10 min with bubbling H\(_2\) (99.9999%).

Homogeneous reaction with sulfide ion

Homogeneous reaction was performed with 0.1 mol kg\(^{-1}\) Fe\(^{3+}\)-HEDTA in 1 mol kg\(^{-1}\) malonate buffer solution (pH = 5) by adding a stoichiometric volume of 0.02 mol L\(^{-1}\) Na\(_2\)S solution with mild stirring in Ar atmosphere at room temperature.

Characterization

The kinematic viscosity and density of the electrolyte solutions were obtained using viscometer tubes (cell constants: 0.003259 and 0.009167 mm\(^2\) s\(^{-2}\), Fisher Scientific) and a density meter (DM40, METTLER TOLEDO, Columbus,
OH, USA), respectively. The conductance was measured using a conductivity meter (S230 and InLab 731-ISM, METTLER TOLEDO). UV-vis spectroscopy was performed using a JASCO model V-670 spectrophotometer with a quartz cuvette and an optical path length of 1 cm. The concentration of Fe redox was diluted to 0.2 mmol L\(^{-1}\) before UV-vis measurement. Correspondingly, malonate buffer and Na\(_2\)S reference solutions were diluted to 0.2 and 0.1 mmol L\(^{-1}\), respectively. Raman spectra were obtained using an Olympus BXFMILHS microscope with a 785-nm laser.
5.5. References


6. Conclusion and Outlook

Due to the growing energy demand and environmental concerns, renewable energy sources are expected to play an important role to develop a sustainable society. Because of their intermittent characteristic, which is an inherent disadvantage against the conventional energy sources, energy storage and conversion techniques are essential to balance energy supply and demand. Electrochemical production of H\textsubscript{2} is an attractive option due to its high gravimetric energy density. Energy efficient, cost effective and durable electrochemical systems are highly desired for deep penetration of renewables in our society.

In Chapter 2, a novel approach was developed to improve the stability of oxygen evolution electrocatalysts, namely coating with a permselective CeO\textsubscript{x} layer. A bare NiFeO\textsubscript{x} electrode, a model OER catalyst in alkaline conditions, had an overpotential increase by more than 60 mV during a 100 h stability test at 20 mA cm\textsuperscript{-2} due to the leaching of active Fe sites under OER conditions, whereas only a 10 mV overpotential increase was observed in the presence of CeO\textsubscript{x} layer on NiFeO\textsubscript{x}. Tafel analysis confirmed that intrinsic catalytic active sites and reaction mechanism for OER are retained, i.e., the durability was improved without sacrificing the catalytic activity. The CeO\textsubscript{x} layer formed on NiFeO\textsubscript{x} catalyst had a thickness of 100-200 nm, which is composed of aggregates of nanoparticles (5 nm). To identify the functionality of the CeO\textsubscript{x} layer, systematic measurements were performed by introducing probe molecules, which revealed that negatively charged ions are inhibited to reach the catalyst underneath the
layer while hydroxide ion and oxygen could diffuse through the layer. The improvement of stability during OER by CeO$_x$ coating can be ascribed to the unique permselectivity while preventing the dissolution of Fe species to the electrolyte. The universality of the CeO$_x$ layer to improve durability was also successfully demonstrated using CoO$_x$ as an OER electrocatalyst. Therefore, the present finding is expected to contribute to the development of a variety of OER catalysts.

Although the stability of OER catalysts was significantly improved by the CeO$_x$ layer coating, the overpotential still remains more than 200 mV to reach 10 mA cm$^{-2}$ using state of the art NiFeO$_x$ electrocatalyst. The oxidation of soluble redox ion was proposed as an alternative anodic reaction to the kinetically sluggish OER shown in Chapter 3. The redox ion after the anodic reaction was targeted to oxidize sulfide to solid sulfur to achieve redox-mediated H$_2$S splitting in this dissertation. Broad tunability of redox potential of Fe complexes was predicted based on their equilibrium constants. Estimated Pourbaix (potential-pH) diagrams helped to select suitable redox candidates from a thermodynamic perspective. Besides the thermodynamics, concentration overpotential plays a major role in the observed overpotential because these electrochemical redox reactions are kinetically facile. In such a case, diffusion limitation must be improved to minimize the concentration overpotential. Strategy was guided by Fick’s law (see Equation 3.16, Chapter 3), which determines the diffusion limitation by bulk concentration and diffusion coefficient. Fe$^{2+/3+}$-HEDTA was identified as a promising candidate due to its remarkably high solubility (>1 mol
kg$^{-1}$) and appropriate redox potential (0.43 V vs. RHE at pH 5). Diffusion coefficient of Fe$^{2+/3+}$-HEDTA was further optimized by the choice of supporting buffer and operating temperature.

The above mentioned redox oxidation reaction was designed for near-neutral pH condition (pH 5), therefore, its counter reaction was studied to maximize HER performance by tuning the electrolyte. Since the proton is easily depleted during HER in neutral pH condition, supporting buffer is essential to provide proton. Furthermore, because diffusion coefficients of buffer ions are one order of magnitude lower than free proton, diffusion of proton donating buffer plays an important role, which results in concentration overpotential caused by pH gradient between the bulk solution and the electrode surface. Besides the buffer ions, product hydrogen accumulated on the electrode surface, which can push the backward reaction during HER, has to be taken into account for highly active electrocatalysts, such as Pt. In acidic condition, the overpotential during HER on a Pt electrode is governed by diffusion of produced H$_2$ while electrode kinetics and mass transport of proton are fast enough. In near-neutral pH buffered condition, there is an additional loss due to the mass transport of proton donating buffer ions. A mass transport model which covers buffer ions and hydrogen was developed to figure out the conditions to maximize the HER performance. The concentration overpotential from pH gradient highly depends on the bulk pH against p$K_a$ of buffer ions. Close to the p$K_a$, the concentration overpotential is effectively suppressed above 0.5 mol L$^{-1}$ while in bulk pH far from the p$K_a$, it remains as a major contributor in the observed overpotential even in dense buffered condition.
(1.5 mol L\(^{-1}\)). When the pH gradient is minimized, concentration overpotential from \(\text{H}_2\) becomes predominant. The contribution from accumulated \(\text{H}_2\) increases with increasing molarity of the buffer due to the decreased diffusion coefficient in dense viscous solutions. The present modeling successfully justified why a overpotential minima was observed in 0.5 mol L\(^{-1}\) K\(_{1.5}\)H\(_{1.5}\)PO\(_4\) among the phosphate buffer solutions studied.

Finally, a stand-alone module was fabricated for solar-driven redox-mediated \(\text{H}_2\text{S}\) splitting using CIGS PV module (170 cm\(^2\)) as a light absorber in Chapter 4. Ubiquitous carbon anode and CrO\(_x\) nano-membrane coated Pt cathode was employed in electrochemical cells. The present electrochemical cell can produce \(\text{H}_2\) at 10 mA cm\(^{-2}\) within 0.8 V, which is a significantly lower energy input than water electrolysis. The stand-alone module produced 3.7 \(\mu\)mol cm\(^{-2}\) min\(^{-1}\) of \(\text{H}_2\) under natural light irradiation without any external bias. The corresponding solar-to-hydrogen energy conversion efficiency reached 13% based on the heating value of \(\text{H}_2\). Oxidation of sulfide to solid sulfur was successfully demonstrated by the succeeding homogeneous reaction with Fe\(^{3+}\)-HEDTA, which confirmed the complete cycle of redox-mediated \(\text{H}_2\text{S}\) splitting. The major problem was decreasing Faradaic efficiency of \(\text{H}_2\) during the demonstration, which came from the loss of CrO\(_x\) nano-membrane layer resulting in a side reaction with Fe\(^{3+}\)-HEDTA on the cathode. Control measurements and estimation of redox potential revealed that the redox potential to reduce Cr\(^{3+}\) containing layer to soluble Cr\(^{2+}\) ion was positively shifted close to the potential of HER/HOR in
the presence of metal complex. Therefore, CrO$_x$ nano-membrane layer can be easily lost during HER which leads to the side reaction with Fe$^{3+}$ metal complex.

For future research, overpotential of OER catalysts still remains as a major energy loss in water electrolysis. Extensive compositional screening, such as ion doping, trinary and quaternary metal oxides electrocatalysts is under progress. The permselective layer coating discovered in this dissertation will contribute to stabilizing highly active OER that are susceptible to metal leaching. Other approaches on improving OER activity are nano-structuring of electrocatalysts and deposition on high surface area substrates, like Ni and Fe foams, to increase the number of catalytic sites. Uniform coating technique for the permselective layer is essential for these three dimensional structures.

Faradaic efficiency of H$_2$ during the solar-driven H$_2$S splitting must be improved. Redox inactive nano-membrane layers, like SiO$_x$ and TiO$_x$, are promising alternative layers. Tuning the diffusion of redox ion and proton through the layers is required to control Faradaic efficiency. Alternatively, to avoid side reaction on the cathode, commercially available ion exchange membrane can be applied as a separator between the catholyte and the anolyte containing redox ions. But, resistance of ion exchange membrane in near-neutral pH may result in large Ohmic loss in this configuration.

In addition to water and H$_2$S splitting, the approach to control redox potential and diffusion of redox ions can be applied for a variety of homogeneous reactions, for example, organic synthesis or oxidative upgrading of biomass feedstocks, to produce valuable chemicals.
APPENDICES

Table A 1. Equilibrium constants for (a) Fe-HEDTA, (b) Fe-EDTA, (c) Fe$_{aq}$ and (d) HEDTA and EDTA.

(a)

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(d)

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Table A 2. Equilibrium constants for (a) metal-HEDTA complex, (b) metal-cyanide complex, (c) metal-malonate complex, (d) dissociation of HEDTA and malonate.

(a) metal-HEDTA

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$^a)$ The equilibrium constant for Cr-HEDTA has not been reported. Because close to linear relationship of the equilibrium constant was reported between Fe-EDTA and Fe-HEDTA, the equilibrium constant for Cr-HEDTA was estimated from that of Cr-EDTA$^8$ using following equation.

$$\frac{\beta_{Cr-HEDTA}}{\beta_{Cr-EDTA}} = \frac{\beta_{Fe-HEDTA}}{\beta_{Fe-EDTA}}$$
(b) metal-cyanide

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<td>Fe$^{3+}$</td>
<td>FeL$^{2+}$</td>
<td>[FeL$^{2+}$]/[Fe$^{3+}$][L$^-$]</td>
<td>8.5</td>
<td>5</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>FeL$_6^{4-}$</td>
<td>[FeL$_6^{4-}$]/[Fe$^{2+}$][L$^-$]$^6$</td>
<td>37.2</td>
<td>9,10</td>
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<tr>
<td>Cr$^{2+}$</td>
<td>CrL$_6^{4-}$</td>
<td>[CrL$_6^{4-}$]/[Cr$^{2+}$][L$^-$]$^6$</td>
<td>17.3</td>
<td>Estimated$^{a)}$</td>
</tr>
</tbody>
</table>

$^{a)}$ The equilibrium constant for Cr(CN)$_6^{4-}$ was not reported. The equilibrium constant at 298 K was estimated from $\Delta H$ for Cr(CN)$_6^{4-}$ and $\Delta S$ for Fe(CN)$_6^{4-}$. 9–11

(c) metal-malonate

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Metal chelate</th>
<th>Formulation</th>
<th>Log $\beta$</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>FeL$^+$</td>
<td>[FeL$^+$]/[Fe$^{3+}$][L$^-$]</td>
<td>7.50</td>
<td>12</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>FeL$_2$</td>
<td>[FeL$_2$]/[Fe$^{3+}$][L$^-$]$^2$</td>
<td>13.0</td>
<td>12</td>
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<tr>
<td>Fe$^{3+}$</td>
<td>FeL$_3$L$^{3-}$</td>
<td>[FeL$_3$L$^{3-}$]/[Fe$^{3+}$][L$^-$]$^3$</td>
<td>16.6</td>
<td>12</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>FeL$^2-$</td>
<td>[FeL$^2-$]/[Fe$^{2+}$][L$^-$]</td>
<td>2.17</td>
<td>12</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>FeL$_2$</td>
<td>[FeL$_2$]/[Fe$^{2+}$][L$^-$]$^2$</td>
<td>3.21</td>
<td>12</td>
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<tr>
<td>Cr$^{2+}$</td>
<td>CrL$^-$</td>
<td>[CrL$^-$]/[Cr$^{2+}$][L$^-$]</td>
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<tr>
<td>CrL$_2$</td>
<td>CrL$_2$</td>
<td>[CrL$_2$]/[Cr$^{2+}$][L$^-$]$^2$</td>
<td>7.13</td>
<td>13</td>
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</table>
(d) dissociation of buffer

<table>
<thead>
<tr>
<th>Ligand = L</th>
<th>Protonated ligand</th>
<th>Formulation</th>
<th>Log β</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{2}O\textsubscript{4}\textsuperscript{2−}</td>
<td>H\textsubscript{2}L</td>
<td>[H\textsubscript{2}L]/[L\textsuperscript{2−}][H\textsuperscript{+}]\textsuperscript{2}</td>
<td>8.55</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>HL\textsuperscript{−}</td>
<td>[HL\textsuperscript{−}]/[L\textsuperscript{2−}][H\textsuperscript{+}]</td>
<td>5.70</td>
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<tr>
<td>HEDTA\textsuperscript{3−}</td>
<td>H\textsubscript{3}L</td>
<td>[H\textsubscript{3}L]/[L\textsuperscript{3−}][H\textsuperscript{+}]\textsuperscript{3}</td>
<td>17.7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}L\textsuperscript{−}</td>
<td>[H\textsubscript{2}L\textsuperscript{−}]/[L\textsuperscript{3−}][H\textsuperscript{+}]\textsuperscript{2}</td>
<td>15.1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>HL\textsuperscript{2−}</td>
<td>[HL\textsuperscript{2−}]/[L\textsuperscript{3−}][H\textsuperscript{+}]</td>
<td>9.7</td>
<td>3</td>
</tr>
</tbody>
</table>
References


(Submitted) “A Stand-Alone Module for Solar-Driven H\textsubscript{2} Production Coupled with Redox-Mediated Sulfide Remediation”

K. Obata, Y. Shinohara, S. Tanabe, I. Waki, K. Kotsovos, K. Ohkawa, K. Takanabe

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(2) “Electrochemical oxidation of a highly soluble redox mediator in aqueous solution for energy conversion”


(1) “A permselective CeO\textsubscript{x} coating to improve the stability of oxygen evolution electrocatalysts”