Fuel Production from Seawater and Fuel Cells Using Seawater

Shunichi Fukuzumi,*[a, b] Yong-Min Lee,*[a] and Wonwoo Nam*[a]

\[
\begin{align*}
2\text{H}_2\text{O} + \text{O}_2 & \rightleftharpoons 2\text{H}_2\text{O}_2 \\
2\text{H}_2\text{O} & \rightleftharpoons 2\text{H}_2 + \text{O}_2 \\
2\text{H}_2\text{S} & \rightleftharpoons 2\text{H}_2 + \text{S}_2
\end{align*}
\]

97% Sea Water
Seawater is the most abundant resource on our planet and fuel production from seawater has the notable advantage that it would not compete with growing demands for pure water. This Review focuses on the production of fuels from seawater and their direct use in fuel cells. Electrolysis of seawater under appropriate conditions affords hydrogen and dioxygen with 100% faradaic efficiency without oxidation of chloride. Photocatalytic production of hydrogen from seawater provides a promising way to produce hydrogen with low cost and high efficiency. Microbial solar cells (MSCs) that use biofilms produced in seawater can generate electricity from sunlight without additional fuel because the products of photosynthesis can be utilized as electrode reactants, whereas the electrode products can be utilized as photosynthetic reactants. Another important source for hydrogen is hydrogen sulfide, which is abundantly found in Black Sea deep water. Hydrogen produced by electrolysis of Black Sea deep water can also be used in hydrogen fuel cells. Production of a fuel and its direct use in a fuel cell has been made possible for the first time by a combination of photocatalytic production of hydrogen peroxide from seawater and dioxygen in the air and its direct use in one-compartment hydrogen peroxide fuel cells to obtain electric power.

1. Introduction

Although fresh water is essential to maintain human life, the world is facing a global and domestic challenge to reliably supply its population with fresh and safe water, owing to shortages resulting from global population growth,[1–3] climate change,[4–7] contamination of clean water supplies,[8] and public policy.[9,10] Water is also needed to produce hydrogen as a clean and sustainable alternative energy source to fossil fuels by water splitting to prevent global warming stemming from large-scale CO₂ emissions from the combustion of fossil fuels.[11–20] Therefore, water and clean energy are inextricably linked with each other. About 97% of the water on our planet is seawater (3.0–5.0% salts) with 1.0% being brackish ground water (0.05–3.0% salts), indicating that the vast amounts of seawater would provide a nearly unlimited water supply if salinity water could be used directly as a clean and nearly infinite energy source. Microorganisms living in seawater can also be used in sediment microbial fuel cells to generate electric power from various substrates (electron sources) containing in seawater, which reduce dioxygen to water;[21,22] Another important energy source is hydrogen sulfide (H₂S), which is abundant in Black Sea deep water, where the total amount of H₂S is about 4600 Tg.[23]

This Review focuses on production of hydrogen as a clean and sustainable energy source by electrolysis of seawater instead of pure water [Eq. (1)], by hydrolysis of Mg in seawater [Eq. (2)],[24] by decomposition of H₂S in Black Sea deep water [Eq. (3)], and electric power generation by fuel cells using H₂S [Eq. (4)] and also microbial fuel cells using seawater. The solar light-driven production of hydrogen peroxide (H₂O₂) from seawater and dioxygen (O₂) in the air [Eq. (5)] and its use as a liquid fuel in seawater in H₂O₂ fuel cells [the reverse reaction in Eq. (5)][24–26] is demonstrated as a proof of concept for the onsite production and use of renewable and sustainable energy.

\[
\begin{align*}
2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + \text{O}_2 \\
\text{Mg} + 2\text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{Mg(OH)}_2 \\
2\text{H}_2\text{S} & \rightarrow 2\text{H}_2 + 2\text{S} \\
2\text{H}_2\text{S} + 3\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + 2\text{SO}_2 \\
2\text{H}_2\text{O} + \text{O}_2 & \rightarrow 2\text{H}_2\text{O}_2
\end{align*}
\]

2. Electrolysis of Seawater

2.1. Production of hydrogen and dioxygen from seawater

Direct electrolysis of seawater with robust electrocatalysts results in the cathodic evolution of hydrogen at high current efficiency [Eq. (1)].[27–31] However, large volumes of chlorine and hypochlorite are normally evolved at the anode by the oxidation of Cl⁻ under acidic and basic conditions [Eqs. (6) and (7), respectively] instead of O₂ evolution by the oxidation of water [Eq. (8)], presenting a major environmental problem.[32,33]

\[
\begin{align*}
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2\text{e}^- \quad E^0 = 1.36 \text{ V} \\
\text{Cl}^- + 2\text{OH}^- & \rightarrow \text{OCI}^- + \text{H}_2\text{O} + 2\text{e}^- \quad E^0 (\text{pH } 14) = 0.89 \text{ V} \\
4\text{OH}^- & \rightarrow 2\text{H}_2\text{O} + 4\text{e}^- \quad E^0 (\text{pH } 14) = 0.40 \text{ V}
\end{align*}
\]

Values of $E^0$ in Equations (6)–(8) are given vs. SHE. The relative ratios of Cl₂, HOCl, OCI⁻, and O₂ with hydrogen (H₂) are changed in seawater depending on pH, catalysts, and applied potentials.[34–39]

A Pourbaix diagram of electrochemical OER (oxygen evolution reactions) from an aqueous NaCl solution at room temperature (total mass of chlorine species: 0.5 μm) is shown in Figure 1, where the OER is thermodynamically more favorable.
than the chlorine evolution reaction (ClER), irrespective of pH.\textsuperscript{[40]} However, the ClER, which is a two-electron oxidation reaction with only a single intermediate, proceeds with a much faster evolution rate than the OER and therefore the ClER [Eq. (6)] is the predominant anodic reaction in acidic electrolytes on a variety of metal oxide catalysts.\textsuperscript{[13,14]}

Under basic conditions, formation of hypochlorite also has a kinetic advantage over OER. However, thermodynamics is highly favored for OER over hypochlorite formation.\textsuperscript{[40]} In addition, the standard redox potential of formation of hypochlorite is pH dependent in contrast with ClER, and the pH dependence slope is the same as the OER potential in the Pourbaix diagram (Figure 1).\textsuperscript{[40]} In such a case, the electrode potential difference to OER remained roughly 0.48 V, which is larger than that under acidic conditions. If the electrocatalytic oxidation is performed at an overpotential (η) lower than 0.48 V under alkaline conditions, no hypochlorite is formed and OER occurs exclusively with faster kinetics.\textsuperscript{[40]} In addition, non-noble metal electrocatalysts that may degrade under acidic conditions, can be used under alkaline conditions. Thus, a general design criterion for the selective OER operation at pH > 7.5 in seawater is given by Equation (9):

\[
\eta_{\text{OER}} \leq 0.48 \text{ V at pH > 7.5} 
\]  

Figure 1. Pourbaix diagram for an aqueous NaCl solution with total chlorine concentration \(c_{\text{Cl}} = 0.5 \text{ mol L}^{-1}\), with plots of electrode potentials for OER at an oxygen partial pressure of 0.21 bar (=0.021 MPa) vs. pH. Red squares indicate the operating potentials (vs. SHE) after constant current electrolysis (10 mA cm\(^{-2}\)) for 1 h with an NiFe LDH catalyst in 0.1 m KOH and 0.5 m NaCl (pH 13) or 0.3 m borate buffer and 0.5 m NaCl (pH 9.2). The light blue shaded area shows the proposed general criterion for selective OER according to Equation (9). Reprinted with permission from Ref. [40]. Copyright 2016, Wiley-VCH Verlag GmbH.

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to produce synthesis gas (a mixture of H\(_2\) and CO), which can electrolyze not only H\(_2\)O but also a mixture of H\(_2\)O and CO\(_2\) to produce synthesis gas (a mixture of H\(_2\) and CO), which can be further converted into various types of synthetic fuels.\(^{43-47}\)

An SOEC for simulated seawater electrolysis is shown in Figure 3, where a button cell is sealed with a glass sealant to separate the gas environment between the anode and the cathode.\(^{48}\) The NiO/YSZ electrode (cathode; YSZ = yttria-stabilized zirconia) was obtained by mixing 60 wt% nickel oxide powder and 40 wt% YSZ powder together with a small amount of carbon black.\(^{48}\) The 50:50 w/w La\(_0.8\)Sr\(_{0.2}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-\delta}\) (LSCF)–Ce\(_{0.2}\)Gd\(_{0.8}\)O\(_{2-\delta}\) (GDC) composite anode (oxygen electrode) was obtained by mixing LSCF–GDC50 powder together with an appropriate amount of poly(ethylene glycol).\(^{48}\) The water bath was heated up, providing a high moisture content (70% partial pressure of H\(_2\)O). Dry H\(_2\) was flowed into the water bath while the anode (oxygen electrode) side was exposed to air. The SOEC was left for around 3 h at operating temperature (800 °C) and H\(_2\) was kept flowing to make sure that the nickel oxide was completely reduced prior to the electrochemical measurements. The two electrodes are in contact with two Pt wires, which serve as the voltage and current probes.\(^{48}\)

The energy efficiency (\(\eta_{\text{elec}}\)) of steam electrolysis of simulated seawater is expressed by Equations (10) and (11):

\[
\eta_{\text{elec}} = \frac{\text{H}_2 \text{ production rate} \times \text{LHV of } \text{H}_2}{\text{electrical energy input}} \times 100\% \quad (10)
\]

\[
\eta_{\text{elec}} = \frac{(\Delta H / nFV)}{100\%} = 1.291 \text{ V/V} \quad (11)
\]

where \(\Delta H\) is the enthalpy change of H\(_2\) (124.6 MJ kg\(^{-1}\) at 800 °C) and \(V\) is the applied voltage. The electrical energy efficiency, which is the amount of electrical energy input per unit of H\(_2\) produced, at a current density of 1.0 A cm\(^{-2}\) from seawater was obtained as 109.4%, being nearly the same as that from pure water (110.3%).\(^{48}\) The electrical energy efficiencies of higher than 100% result from the high heat supplied by the furnace, leading to a reduction in electrical energy needed for the high-temperature electrolysis.\(^{48}\) The simulated seawater and pure water electrolysis showed similar degradation rates of about 15% per 1000 h in terms of increases in the operating voltage with constant current.\(^{48}\) The degradation rate in the electrolysis of steam produced from simulated seawater was virtually the same as that from pure water.\(^{48}\)

### 2.2. Extraction of carbon dioxide and hydrogen from seawater

The world’s oceans contain approximately 100 mg L\(^{-1}\) total carbon dioxide, of which 2–3% is dissolved CO\(_2\) gas in the form of carbonic acid (H\(_2\)CO\(_3\)), 1% is carbonate (CO\(_3^{2-}\)), and the remaining 96–97% is bicarbonate (HCO\(_3^-\)).\(^{48}\) When the pH of seawater is decreased to 6 or less, carbonate and bicarbonate in the seawater are re-equilibrated to release CO\(_2\) gas (Eq. (12)).\(^{50}\)

\[
\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2(g) \uparrow \quad (12)
\]

Thus, electrochemical approaches based on continuous electrodeionization (CEDI) principles are being developed to use pH to exploit seawater as a means to recover CO\(_2\) from seawater.\(^{30-34}\) The electrolytic cation exchange module (E-CEM) configuration (Figure 4) is composed of a center compartment and electrode compartments (cathode and anode capable of reversing polarities), and the three compartments are separated by two cation-permeable membranes.\(^{50,54}\) Extruded cation-permeable heterogeneous monolithic polyethylene membranes incorporate gel polystyrene cross-linked with divinylbenzene and functionalized with sulfonic acid groups, which provide discrete channels for cations to migrate through the polymer matrix, whereas blocking the passage of anions.\(^{54}\) Electrons traveled from the cathode to the anode in external circuit. Seawater is passed through the center compartment of the E-CEM (Figure 4), whereas seawater through a reverse osmosis (RO) unit is passed through the anode and cathode.
When direct current is applied to the module, H\textsuperscript{+} ions and \( O_2 \) gas are produced at the anode during the oxidation of the anolyte RO water [Eq. (13)].\textsuperscript{[54]}

\[
2 \text{H}_2\text{O} \rightarrow 4 \text{H}^+ + \text{O}_2 + 4 \text{e}^- \tag{13}
\]

The \( O_2 \) gas is flushed from the anode compartment with the flow of the anolyte water.\textsuperscript{[54]} The protons are driven from the anode surface, through the cation-permeable membrane, and into the center compartment where protons are replaced by Na\textsuperscript{+} in the flowing seawater, resulting in the effluent seawater, which can be acidified without the need for any additional chemicals.\textsuperscript{[54]} At a seawater pH \( \leq 6 \), the bicarbonate and carbonate in the seawater are re-equilibrated to carbonic acid [Eq. (12)].\textsuperscript{[50, 54]} The \( \text{CO}_2 \) from the carbonic acid in the effluent acidified seawater is vacuum stripped by a gas-permeable membrane contactor [Eq. (14)].\textsuperscript{[54]}

\[
\text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \tag{14}
\]

The Na\textsuperscript{+} ions from seawater in the center compartment are passed through the cation-permeable membrane, which is the closest to the cathode.\textsuperscript{[54]} Water is reduced at the cathode to \( \text{H}_2 \) gas and \( \text{OH}^- \) [Eq. (15)].\textsuperscript{[54]}

\[
2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2 \tag{15}
\]

The Na\textsuperscript{+} ions react with the \( \text{OH}^- \) ions to produce NaOH in the cathode compartment.\textsuperscript{[54]} The NaOH and \( \text{H}_2 \) gases are continuously flushed from the cathode compartment with the flow of the catholyte RO water.\textsuperscript{[54]} The acidified seawater is recombined with the solutions from the cathode and anode compartments and the overall reaction is given by Equation (16).\textsuperscript{[54]}

\[
2 \text{H}_2\text{O} + 2 \text{HCO}_3^- \rightarrow 2 \text{OH}^- + \text{O}_2 + 2 \text{H}_2 + 2 \text{CO}_2 \tag{16}
\]
Seawater containing HCO$_3^-$ (142 ppm, 0.0023 m) and a flow rate of 1900 mL min$^{-1}$ require a theoretical applied minimum current of 7.0 A to lower the pH to less than 6.0 and convert HCO$_3^-$ to H$_2$CO$_3$. The theoretical amount of H$_2$ gas produce at 7.0 A is 0.0022 mol min$^{-1}$. The ultimate goal is to produce CO$_2$ and H$_2$ in quantities needed to make fuel at energy efficiencies similar to commercial electrolysis.

### 2.3. Solar hydrogen production from seawater

Hydrogen is produced photoelectrocatalytically from seawater under solar irradiation at ambient temperature without any externally applied bias potential by using a materially optimized thin-film transparent titania photocatalyst. The overall solar energy conversion efficiency, which is defined as the heat energy of reaction attained by combustion of H$_2$ with O$_2$ per the total solar energy supplied, was determined to be 0.388%. The maximum quantum efficiency of 54% was obtained at the irradiation wavelength of 320 nm. However, the quantum efficiency became zero at irradiation wavelengths longer than 410 nm. A number of photocatalysts, which can absorb visible light (> 400 nm), have been utilized for photocatalytic H$_2$ production from seawater, which, however, required the assistance of an externally applied bias potential.

Electrolysis in seawater is often inhibited by the presence of salts and impurities contained in seawater, which fouled the catalytic systems to decrease the required voltage and electrolysis efficiency. In contrast to liquid seawater, the atmospheric water vapor over the sea is virtually free of contaminants, with high humidity near the ocean surface all year round. Thus, stable solar H$_2$ production has been made possible by using the ambient humidity over the seawater at efficiencies comparable to land-based H$_2$ production by liquid pure water splitting. The near-surface relative humidity over the oceans is fairly constant between 75 and 90% with only minor variation by season or time of day. Marine solar water vapor electrolysis can indirectly split seawater without any water purification process. The electrolyzer consists of two stainless steel grids for the anode and the cathode, two carbon Toray paper sheets as gas-diffusion layers, and one membrane electrode assembly (MEA) with catalyst particles (Pt/C) on either side of a sulfonated polytetrafluoroethylene (Nafion) proton-exchange membrane (Figure 5). The photovoltage required for solar-driven water electrolysis was obtained by employing a commercially available triple-junction amorphous Si (a-Si) photovoltaic from SolarFocus. The solar-to-hydrogen conversion efficiency before and after 50 h of operation was increased from 6.0% to 6.3% by using an ambient seawater humidity feedstock as compared to a drop from 6.6% to 0.5% using liquid seawater feedstock. The solar-driven seawater vapor electrolysis system could create a new market in offshore solar utilities with built-in energy storage to solve the intermittency issue, minimizing land usage and environmental impacts of solar arrays. A recent analysis of a potential solar-driven seawater vapor electrolysis facility estimated that a 1 GW annual average output would require around 180 km$^2$ of land usage.

![Figure 5. Electrolysis cell containing matched projected areas of triple-junction amorphous Si (j-j-Si) and MEA. Reprinted with permission from Ref. [61]. Copyright 2016, Royal Society of Chemistry.](image)

### 3. Hydrolysis of Metals in Seawater

Hydrogen production from the hydrolysis of active metals, such as Mg and Al, has attracted much attention because of their abundance and nontoxicity. Although Mg has a low H$_2$ storage density (3.3 wt%) in water compared to that of Al (3.7 wt%), it is capable of generating hydrogen in a neutral aqueous solution instead of the alkaline solution that is required for the hydrolysis of Al. Hydrolysis of Mg in an aqueous solution produces Mg(OH)$_2$ and H$_2$ as shown in Equation (2), where a passive Mg(OH)$_2$ layer is formed on the Mg surface to hamper the further hydrolysis of Mg. However, the Mg(OH)$_2$ layer is readily broken by the penetration of Cl$^-$ ions, which results in pitting corrosion to maintain the continuous hydrolysis of Mg in seawater.

The effects of NH$_4$Cl on the rate of magnesium hydride (MgH$_2$) hydrolysis are shown in Figure 6, where the rate of MgH$_2$ hydrolysis in deionized water is too slow to be used in controlled H$_2$ generation. In contrast, the hydrolysis of MgH$_2$ in a 0.5 wt% NH$_4$Cl solution produces H$_2$ efficiently (501 mL g$^{-1}$ in 5 min and 980 mL g$^{-1}$ H$_2$ in 30 min) at 60 °C (Figure 6b). The 4.5 wt% NH$_4$Cl solution afforded the best hydrolysis performance (Figure 6c), where H$_2$ is produced more efficiently (1310 mL g$^{-1}$ in 5 min and 1660 mL g$^{-1}$ H$_2$ in 30 min). The rate of hydrolysis of MgH$_2$ is enhanced by addition of NH$_4$Cl because Cl$^-$ may effectively decrease the compactness of Mg(OH)$_2$.

Hydrogen was also produced efficiently by the hydrolysis of milled waste magnesium scraps (MWMS) in nickel(II) chloride (NiCl$_2$) solutions (0.5–2.5 M) and by the hydrolysis of NiCl$_2$-added seawater (Aegean Sea and Marmara Sea water). MWMS was prepared by mechanical grinding with use of a planetary type ball-milling apparatus at a speed of 300 rpm for 15 h grinding time at ball-to-powder ratio of 70:1 (Figure 7). The MWMS sample in Marmara Sea Water, which contained approximately 23 wt% NaCl, produced 6.6 mL H$_2$ in 260 s (ca. 70% conversion), whereas 100% conversion was attained in 233 s in Aegean Sea water containing roughly 37 wt%
An increase in the concentration of NaCl in seawater affected its conductivity, resulting in an increase in the rate of H₂ production. Economical and safe Mg alloys have been developed for faster H₂ production from seawater. The Mg-2.7Ni-1Sn alloy afforded an excellent H₂ production rate of 28.71 mL min⁻¹ g⁻¹, which is 1700 times more rapid than that of pure magnesium (Mg), owing to galvanic and intergranular corrosion, as well as pitting corrosion in seawater (Figure 8). As the solution temperature was increased from 30 to 70 °C, the H₂ production rate in hydrolysis by the Mg-2.7Ni-1Sn alloy was dramatically increased from 34 to 257.3 mL min⁻¹ g⁻¹.

4. Microbial Fuel Cells Using Seawater

Sediment microbial fuel cells (SMFCs) generate electric power from the organic matter content of sediments using bacterial metabolism. The anode electrode was embedded within anoxic marine sediments and connected through electronic circuits to a similar electrode in the overlying aerobic seawater (the cathode) to make an SMFC. The SMFC with an unmodified graphite electrode afforded an electric power generation of 0.01 W m⁻², which can power marine-deployed electronic instrumentation. SMFCs with graphite anodes in the anoxic marine sediment and graphite cathodes were also made in overlying aerobic seawater. A specific enrichment of microorganisms of the family Geobacteraceae on graphite anodes allowed these microorganisms to conserve energy, supporting their growth by oxidation of organic compounds with an electrode that serves as the sole electron acceptor.

SMFCs with carbon fabric cathodes were acclimated with sediment and seawater from San Diego Bay, whereas anodes were buried in a flat orientation, which is placed about 7.6 cm below the sediment-water interface and about 7.6 cm above the bottom of the tank as shown in Figure 9, where seawater is introduced up to a height of 50.8 cm. Figure 10A shows the average power generation of two identical sediment microbial fuel cells (SMFC-1 and SMFC-2) operating in the same seawater tank, where the power increased to about 1.8 mW within roughly 40 days. The long time power generation resulted in the power decrease to around 1 mW after
The corresponding electrode potentials during the operation of SMFC-1 are shown in Figure 10 B, where both the cathode and the anode potentials are initially around 75 mV vs. Ag/AgCl (black arrow), the cathode potential increased to around 375 mV vs. Ag/AgCl within a few days, and then slowly increased to 395 mV vs. Ag/AgCl while the anode potential decreased initially to about –400 mV vs. Ag/AgCl and then increased slowly to a value slightly below 0 mV vs. Ag/AgCl. The acclimated cathodes of SMGCs have distinct performance advantages as compared to unacclimated cathodes with possible implications for cathode scaling and size.

5. Hydrogen from Black Sea Deep Water

Hydrogen sulfide (H$_2$S) is found naturally in many gas wells and also in gas hydrates and gas-saturated sediments especially at the bottom of the Black Sea, where 90% of the sea water is anaerobic. The total H$_2$ energy potential is estimated to be about 270 million tons, produced from 4.587 billion tons of H$_2$S in Black Sea deep water. This amount of H$_2$ can provide 38.3 million TJo of thermal energy or 8.97 million GWh of electrical energy. Moreover, the total H$_2$ potential in Black Sea deep water corresponds to 808 million tons of gasoline, 766 million tons of natural gas, 841 million tons of fuel oil or 851 million tons of petroleum. These values suggest that H$_2$ production from H$_2$S in Black Sea deep water may play an important role in satisfying the energy demands of the Black Sea's surrounding countries.

The simplest and direct method that can be applied to utilize Black Sea deep water is catalytic or non-catalytic thermal decomposition of H$_2$S [Eq. (3)], which requires high temperature to break down H$_2$S into H$_2$ and S$_2$. This reaction is largely endothermic, becoming more favorable at higher temperatures. The pyrolysis of H$_2$S occurs in a perfectly stirred reactor for residence times of 0.4–1.6 s at 1073–1373 K under 1 bar pressure. Figure 11 shows the H$_2$S conversion and yields of H$_2$ and S$_2$ with a feed stream composed of 5 mol% H$_2$S and 95 mol% Ar under 1 bar pressure at different temperatures, which are fitted by the computed time profiles based on the proposed mechanisms. Because higher temperatures (above 1200 °C) are required to obtain an H$_2$ yield above 30%, La$_2$SrO$_x$ was used as an effective catalyst to decrease the temperature to 950 °C to obtain the highest conversion of 35.7% for the decomposition of H$_2$S. The results from the laboratory-scale extraction pilot plant unit for the separation of H$_2$S from Black Sea deep water enabled the building of an industrial extraction pilot plant to concentrate H$_2$S from 10 ppm to above 10000 ppm. The processing of $10^9$ m$^3$ of water containing 10 ppm H$_2$S would produce only 0.833 tons of H$_2$. Thus, a new technology for extraction and concentration of H$_2$S is essential for the practical application.

The feasibility of H$_2$ production from H$_2$S contained in Black Sea deep water has been examined by employing a microstructured electrochemical membrane reactor, which is assembled with optimized cell materials, to produce H$_2$ in the electrolyzer mode and to generate electrical energy in the fuel cell mode. Any process developed for H$_2$S decomposition to produce H$_2$ in Black Sea deep water, which is energy intensive, will have substantial equipment and operating costs, heavily depending on technology and the commercial price of energy. The cost of H$_2$ from H$_2$S in Black Sea deep water may gradually shift closer to that of H$_2$ from solar-driven water electrolysis in the long term.
6. Production of Hydrogen Peroxide from Seawater and Its Direct Use in Fuel Cells

Hydrogen peroxide (H$_2$O$_2$) is a clean and sustainable energy source, because the decomposition products are only water and oxygen, and H$_2$O$_2$ is produced from water and dioxygen using solar energy. H$_2$O$_2$ is superior to H$_2$ or natural gas, owing to its safe storage and convenient transportation in liquid form. Furthermore, a one-compartment configuration is possible for H$_2$O$_2$ fuel cells, which is structurally much simpler and cheaper than two-compartment hydrogen fuel cells with expensive membranes.

Efficient photocatalytic production of H$_2$O$_2$ from seawater and O$_2$ in the air was performed in a two-compartment photoelectrochemical cell, composed of mesoporous WO$_3$ supported on a fluorine doped tin oxide (FTO) glass substrate (m-WO$_3$/FTO) as a photocatalyst for H$_2$O oxidation and a cobalt chlorin complex supported on a carbon paper ([Co$_3$(Ch)]/CP) as an electrocatalyst for the selective two-electron reduction of O$_2$. The photoirradiation of m-WO$_3$/FTO with a solar simulator (1 sun = AM 1.5G) in the anode resulted in formation of H$_2$O$_2$ in the cathode cell of the two-compartment photoelectrochemical configuration with no external bias potential being applied. The time courses of the photocatalytic formation of H$_2$O$_2$ are shown in Figure 13. It was confirmed that no H$_2$O$_2$ was produced without [Co$_3$(Ch)] on the carbon paper electrode. [Co$_3$(Ch)] was reported to catalyze the selective two-electron/two-proton reduction of O$_2$ to yield H$_2$O$_2$ efficiently. After illumination for 24 h, the concentration of H$_2$O$_2$ produced in seawater was 48 mM (blue circles in Figure 13), which is high enough to operate an H$_2$O$_2$ fuel cell (see below). However, the production of H$_2$O$_2$ is much decelerated when pure water was used instead of seawater for the photocatalytic H$_2$O$_2$ production (Figure 13).

The similar enhancement of the photocatalytic H$_2$O$_2$ production is observed when seawater is replaced by an NaCl solution with the same concentration as that of seawater (blue squares in Figure 13). The effects of Cl$^-$ on photocatalytic H$_2$O oxidation with m-WO$_3$/FTO and the two-electron reduction of O$_2$ with [Co$_3$(Ch)]/CP were studied by using a photoelectrochemical cell with a three-electrode configuration (see below).

The current-potential curves of m-WO$_3$/FTO under simulated solar illumination (1 sun – AM 1.5G) are compared to those in dark in Figure 14a, where the onset of photocurrent for the H$_2$O oxidation is observed at 0.2 V vs. SCE at pH 1.3 in pure water, which corresponds to the 110 mV overpotential with re-
Upon photoexcitation of WO_3^+

\[2\text{Cl}^- + 2\text{h}^+ \overset{hv}{\rightarrow} \text{Cl}_2\]  (17)

Thus, the enhancement of photocatalytic production of H_2O_2 in seawater (Figure 13) results from the Cl^- catalyzed photooxidation of water.\[116\]

A solar energy conversion efficiency of 0.55% has been reported for the photocatalytic production of H_2O_2 in seawater under simulated solar illumination with a solar simulator (1 sun = AM 1.5G).\[116\] A higher solar energy conversion efficiency of 0.94% was attained under the simulated solar illumination,\[116\] being significantly higher than that of switchgrass (0.2%) producing biofuel.\[120\]

When the WO_3 photoanode was replaced by surface modified BiVO_4 with iron(III) oxyhydroxide [FeO(OH)], the highest solar energy conversion efficiency of H_2O_2 production in pure water was achieved as 6.6% with a decreased simulated solar light intensity (0.05 sun) after 1 h photocatalytic reaction, whereas the efficiency was decreased to 0.89% under 1 sun illumination.\[121\] In this case, however, seawater deactivated the photocatalyst, owing to the instability of BiVO_4 which started to dissolve in the presence of Cl^- under solar illumination.\[121\]

The chemical energy of H_2O_2 produced in the photocatalytic oxidation of seawater by O_2 in air can be converted into electrical energy by using a one-compartment H_2O_2 fuel cell, composed of a carbon cloth cathode modified with Fe^3+/[Co^6(CN)_6]_2^- and a nickel mesh anode.\[116\] A seawater solution containing H_2O_2 (48 mM) produced by photocatalytic reduction of O_2 was transferred to a hydrogen peroxide (H_2O_2) fuel cell. The H_2O_2 fuel cell exhibited an open circuit voltage (OCV) of 0.78 V and a maximum power density (MPD) of 1.6 mWcm^{-2} (Figure 15).\[116\] The energy conversion efficiency of the H_2O_2 fuel cell was evaluated as roughly 50% by measurement of the output energy as electrical energy vs. consumed chemical energy of H_2O_2, which is comparable to the efficiency of an H_2 fuel cell.\[116\]

A direct H_2S/H_2O_2 fuel cell was constructed with artificial Black Sea deep water containing H_2S as a fuel and H_2O_2 as an oxidant instead of O_2.\[122-124\] The anode, cathode and overall reactions are given by Equations (21), (22), and (23), respectively.\[24,112\]
An increase in the solution pH resulted in an increase in $\text{HS}^-$ concentration of the anolyte, leading to generation of the higher cell power.\(^{(24)}\) The $\text{H}_2\text{O}_2$ concentration has a greater impact on the maximum power density as shown in Figure 16.\(^{(24)}\) The $\text{HS}/\text{H}_2\text{O}_2$ fuel cell yielded a power density of 23 mW cm\(^{-2}\) at a cell voltage of 300 mV and current density of 75 mA cm\(^{-2}\) (Figure 16), which are much higher than those in a direct $\text{H}_2\text{O}_2$ fuel cell (Figure 15).\(^{(24)}\)

**7. Conclusions**

Direct electrolysis of seawater to evolve $\text{H}_2$ and $\text{O}_2$ selectively without formation of chlorine or hypochlorite has been made possible by a general design criterion at pH $> 7.5$ in seawater with an overpotential ($\eta$) $< 0.48$ V. The electrical energy efficiency, that is the amount of electrical energy input per unit of hydrogen produced, was obtained as 109.4% for a high-temperature solid oxide electrolyzer cell with the NiO/YSZ electrode, which exhibited a slow degradation rate of 15% in 1000 h under steam produced from simulated seawater. Seawater is also utilized for photosynthesis principles to recover $\text{CO}_2$ from seawater, accompanied by production of $\text{H}_2$. $\text{H}_2$ can also be produced from seawater under solar illumination at ambient temperature without the assistance of externally applied bias potential by using a material optimized thin film transparent titania photocatalyst. Economical and safe Mg alloys have been developed for faster hydrogen production from seawater. Anoxic marine sediments were used for sediment microbial fuel cells (SMFCs) for electric power generation sufficient to power marine-deployed electronic instrumentation.

Hydrogen sulfide contained in Black Sea deep water has been used for $\text{H}_2$ production by pyrolysis of $\text{H}_2\text{S}$. A direct $\text{H}_2\text{S}/\text{H}_2\text{O}_2$ fuel cell was developed and exhibited high cell performance compared with $\text{H}_2\text{O}_2$ fuel cells. $\text{H}_2\text{O}_2$ can be produced efficiently from seawater and air by using a two-compartment photocatalytic electrochemical cell, composed of mesoporous $\text{WO}_3$ supported on a FTO glass substrate ($m$-$\text{WO}_3$/FTO) for the photocatalytic seawater oxidation and a cobalt chlorin complex adsorbed on a carbon paper ([Co(CH)]/CP) for the selective two-electron reduction of $\text{O}_2$ (Figure 12). The chloride anion contained in seawater acts as a catalyst to accelerate seawater oxidation. $\text{H}_2\text{O}_2$ produced from seawater and air by using solar energy has been used directly as a fuel in an $\text{H}_2\text{O}_2$ fuel cell. Thus, $\text{H}_2\text{O}_2$ can be an alternative sustainable and green fuel for portable electronic items, because oxygen, seawater, and sunlight are abundant resources, and power generation is possible with a fuel cell with a simple one-compartment structure. Further improvement of the photocatalytic activity for production of $\text{H}_2\text{O}_2$ from Black Sea deep water, together with more efficient one-compartment $\text{HS}/\text{H}_2\text{O}_2$ fuel cells without membranes may enable portable sustainable energy conversion systems in the future.

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Conflict of interest

The authors declare no conflict of interest.

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