Renewable electricity storage using electrolysis

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Electrolysis converts electrical energy into chemical energy by storing electrons in the form of stable chemical bonds. The chemical energy can be used as a fuel or converted back to electricity when needed. Water electrolysis to hydrogen and oxygen is a well-established technology, whereas fundamental advances in CO2 electrolysis are still needed to enable short-term and seasonal energy storage in the form of liquid fuels. This paper discusses the electrolytic reactions that can potentially enable renewable energy storage, including water, CO2, and N2 electrolysis. Recent progress and major obstacles associated with electrocatalysis and mass transfer management at a system level are reviewed. We conclude that knowledge and strategies are transferable between these different electrochemical technologies, although there are also unique complications that arise from the specifics of the reactions involved.

Building sustainable, clean energy systems is one of the most critical problems that the world faces in this century. Population growth and economic development in the coming decades will inevitably result in a substantial increase in global energy consumption (1, 2). Traditional fossil sources of energy are carbon-positive and contribute substantially to climate change. Various alternative sources of carbon-neutral power exist, including nuclear fission, biofuels, and electricity generation from renewable resources such as wind and solar energy (1). It is projected that renewable electricity can provide a dramatic decrease in carbon dioxide intensity, defined as carbon dioxide emissions per unit of energy output, despite the projected increase in overall energy consumption (3).

Electricity from renewable sources such as wind and solar has become economically competitive due to years of cost decline and advances in technology. The globally averaged levelized cost of electricity (LCOE) for utility-scale solar photovoltaic (PV) power has fallen 73% since 2010, while the LCOE from onshore wind has reached $0.03/kWh in some parts of the world (4). The price of renewable electricity from all currently commercial sources is projected to be comparable to or lower than that of fossil fuel-derived electricity by 2020 (4). One of the major contributors to the falling LCOE for solar and wind power electricity comes from the sharp reduction in installation costs. The global capacity weighted average total installation cost of newly commissioned utility-scale PV projects has decreased by 68% to around $1,600/kW since 2010. The construction costs of the new nuclear- and coal-fired power plants are very uncertain and are subject to various factors; however, total costs between $5,500 and $8,100/kW and $3,500/kW, respectively, have been suggested and are expected to increase in the future (5, 6).

Despite the rapid growth of renewable electricity, the current fraction of power generated from renewable sources in the electric energy mix remains low, with a much greater proportion of electricity being produced from gas, oil, and coal. However, based on a reference case prediction, electricity from renewable resources is expected to increase from 18% to about 31% between 2018 and 2050 (3). One of the issues with solar electricity is the intermittent nature of the diurnal solar cycle, which is not well matched with demand and thus requires excess generation capacity at the grid level or backup power on the consumer end. For example, Fig. 1 shows the net electrical load fluctuation as a function of time for a spring day in California. Starting from around 4 PM a supply of an additional 13,000 MW of electricity from nonsolar resources such as natural gas and nuclear within 3 h is needed to replace the electricity shortfall of solar power (7).

The fluctuating power from solar and wind thus requires massive energy storage, both in the short and long terms. There are multiple ways that electrical energy can be stored including physical approaches such as pumped hydroelectric and compressed air energy storage; large-scale batteries such as lead-acid, lithium, sodium sulfur batteries, and flow batteries; and electrolysis, with pumped hydroelectric being the current leading technology in the energy storage sector (8). Most of these methods suffer from being only suitable for short-term storage or are limited by particular geographic requirements. Electrolysis stands out as a means of storing electric energy in the form of stable chemical bonds. The potentially enormous energy capacity, negligible self-discharge rate, existing infrastructure, and low capital cost of containing renewable generated carbon-based fuels make them ideal for seasonal storage, a feature that is highly desirable given the seasonality of renewable energy sources. The need for such a technology will be increasingly acute with the larger anticipated penetration of the low-cost renewable electricity into the power grid, as illustrated in Fig. 1.

While water electrolysis to hydrogen and oxygen is a well-established technology, an efficient and cost-effective means of storing electrical energy in the form of liquid fuels does not yet exist. In order for such a technology to become economically competitive with abundant fossil fuels, one has to start with very cheap electricity. A techno-economic analysis of CO2 electrolysis indicates that a renewable electricity price below $0.04/kWh will be needed for electrolysis-derived fuels to be competitive with fossil-derived fuels (9). This is a target that renewable electricity is well on its way to reaching based on the International Renewable Energy Agency renewable cost database (4).

In Fig. 1, we illustrate how a sustainable energy cycle can be achieved by coupling electrolysis with electricity generated from solar and wind, among other renewable sources. Electrolysis can produce both commodity chemicals and hydrogen, mitigating the intermittency of the renewable power. In this scenario, hydrogen-air fuel cells can be used to convert the energy that is stored as hydrogen back to electricity. High-energy-density liquid fuels are the preferred form for seasonal storage and can form a green energy cycle if CO2 in the air can be concentrated to enable efficient...
electrolysis. There is growing research activity on the capture of carbon from the atmosphere (10), and a few companies are working to commercialize carbon capture technology. The electrolysis of CO₂ to CO and hydrogen (syngas) has been achieved with a variety of different electrocatalysts and provides a feedstock for hydrocarbon fuels via the Fischer–Tropsch process. Alternatively, C–C coupled products including ethylene and ethanol can be made directly by electrolysis at copper-containing catalysts, but the efficiency, selectivity, and throughput of those reactions need to be improved. Not shown in the figure is the electrochemical reduction of N₂ to ammonia for the production of fertilizers. In this case electrolysis takes advantage of an unlimited chemical feedstock as Earth’s atmosphere provides the nitrogen and water needed for the reaction. In addition to making fuels and fertilizers by electrolysis, thermochemical catalysis provides an established method for hydrogenating CO₂, CO, and N₂. Two examples are the Fischer–Tropsch and Haber–Bosch processes, which are already well developed at scale for the production of liquid hydrocarbons and ammonia, respectively. It should be noted that nearly 80% of the energy consumed in ammonia synthesis is for hydrogen production via steam reforming and the water–gas shift reaction (11). Water electrolysis provides a potential carbon-neutral alternative for providing hydrogen for these reactions.

An electrolytic process is limited by 3 factors that act effectively as series impedances: electron transfer kinetics at the electrified interface, mass transport of reactants and products, and series resistance, including ion transport. Electron transfer across the electrified interface governs the kinetics of oxidation and reduction, and mass transport controls the availability of the reactant and the rate at which the product can be removed, as shown in Fig. 2A. The electron transfer rate and the mass transport flux are coupled as they both are proportional to the current. Active catalysts are needed to lower the activation barrier by binding and stabilizing certain transition states, Fig. 2B. Increasing the overpotential for one or both electrode processes accelerates the reaction kinetics by effectively lowering the activation barrier, but the extra energy cost lowers the power conversion efficiency, as illustrated in Fig. 2D. When the electron transfer kinetics are sufficiently fast, the highest current density is achieved by accelerating the supply of reactant. In the case of CO₂ electrolysis, this can be accomplished by supplying the reactant and removing the products in the gas phase, taking advantage of the faster diffusion coefficient of gases and avoiding the low solubility of CO₂ in liquid water, as shown in Fig. 2C.

Water Electrolysis

Water electrolysis has a long history, the first published demonstration dating to 1789, and it is now a well-established commercial technology. For example, a large installation of alkaline electrolyzers by Norsk Hydro (1948 to 1990) at a hydroelectric plant was capable of generating about 70,000 kg H₂/d (8). The largest wind-hydrogen plant was installed in Norway in 2004 by Norsk Hydro and Enercon, coupling a 600-kW wind turbine with a 48-kW electrolyzer (12).

There has been increasing interest in water electrolysis over the past 2 decades because of its potential role in a hydrogen-based energy economy involving electrolytic production, storage, transport, and use of hydrogen as fuel (2). Current research focuses on water electrolyzers that can be categorized according to their electrolytes: alkaline electrolytes, proton-exchange membranes (PEM), and solid-state proton or oxide ion conductors. Commercial PEM electrolyzers achieve the best performance (~70% energy efficiency at current densities of 1.7 A/cm², Giner Inc.) (13) but the large overpotential of the anodic water oxidation reaction and the corrosive acidic environment necessitates the use of precious metal catalysts. The membrane electrolyte and manufacture of the bipolar plates also add significantly to cost. Alkaline electrolyzers are the oldest technology with somewhat lower system efficiency (~64% efficiency, at current densities of 1 A/cm², GHW) and lower cost ($800/kW) (13). Alkaline electrolytes enable the use of nonprecious metal catalysts such as Ni and Fe.

There has been recent interest in developing better catalysts to lower the cost and increase the efficiency of water electrolysis. In acidic PEM electrolyzers, a volcano plot correlates the rate of the cathodic hydrogen evolution reaction (HER) with metal–hydrogen bond strength on various metal catalysts (Fig. 3A) (14). A simple explanation for the volcano shape is that metals that bind hydrogen too weakly cannot stabilize the M–H intermediate, whereas those that make very strong M–H bonds fill most of the binding sites, leaving little room for a new adsorption event. While the M–H bond strength is a good descriptor for most catalysts, some metals with particular facets, such as Pt (111), exhibit 20 to 200 times higher HER exchange current density in acid than in base, even though the H-binding energy is similar. Mechanistic

Fig. 2. Schematics of electrolysis. (A) Reactants transport to the surface of an electrode where a cathodic reaction occurs. (B) Comparison of the reaction pathways for the HER with and without catalyst. The catalyst stabilizes the intermediate and lowers the activation energy. (C) Electrolyzers in a gas-fed configuration. Gas-fed electrolysis exploits the fast diffusion of gaseous molecules, enabling high current density. Membrane electrolytes are usually required for ion management and gas separation. (D) Kinetics of the electrochemical HER. Transition state energy decreases as overpotential increases.
followed by a deprotonation step. Oxygen gas is formed either from a surface hydroperoxy intermediate, M–OOH, or by bi-molecular recombination of M–O. For oxide-based OER catalysts with rocksalt, rutile, spinel, and perovskite structures, volcano plots have been developed from theoretical considerations (22). An ideal OER with optimal binding energies has a free energy difference between M–OOH and M–OH (ΔGOH – ΔGOOH) of 2.46 eV, requiring an onset potential of 1.23 V (Fig. 3B). Onset potentials of real catalysts, however, are significantly higher because (ΔGOH – ΔGOOH) deviates from the ideal case and is proposed to be regulated by the free energy of M–O bond. A universal average (ΔGOH – ΔGOOH) value of 3.2 eV is consistent with several groups of catalysts because the binding strength of OH scales linearly with that of OOH (22). Although the scaling relation is a useful concept in understanding catalytic activity, experimental quantification is complicated by the fact that the properties of catalyst surfaces may change during electrochemical operation, particularly under anodic conditions. Metal oxidation states, for example, vary with the applied potential, and this effect can lead to dramatic changes in catalytic activity, conductivity, and stability. The transition from Ni²⁺ to Ni³⁺ is typically a prerequisite for high OER activity in alkaline nickel-based catalysts as the former is insulating. Pretreatment of the catalyst surface before testing is important for meaningful evaluation and comparisons. Metal oxides with high solubility at higher oxidation states are often unstable in acid media and a trade-off between the stability and activity of Pt, Pd, Au, and Ru has been observed (23). Currently, iridium oxide is the only known stable catalyst for oxygen evolution in acidic media, and it is used only in pure form in the catalyst layer.

Conductive supports can be used to reduce the precious metal loadings, leading to lower costs and a better utilization of catalysts. However, while carbon can be used as a conductive support for both half-reactions in a fuel cell, it can only be used on the hydrogen side in a PEM electrolyzer; on the oxygen side it quickly corrodes. Oxide supports such as mesoporous tin oxide doped with indium have shown high conductivity (0.3 S/cm) and promising electrochemical stability at anodic potentials (24). Two of the key research topics for acid electrolysis are thus finding a more abundant, lower-cost alternative catalyst to iridium oxide for oxygen evolution and/or discovering a conductive support that also has long-term stability under oxygen evolution conditions in acidic media.

**CO₂ Electrolysis**

Electrochemical reduction of CO₂ to liquid fuel and value-added chemicals represents a possible solution for carbon-neutral seasonal storage of renewable electricity. CO₂ can be reduced to various C₁ products including carbon monoxide (CO), formate, methane, methanol, and C₂+ products including ethylene and ethanol (25). CO₂ reduction with high selectivity to CO and formate has already been realized since these reactions are a 2-electron transfer process (26). It is more challenging to obtain a C₂+ product with high selectivity as the process requires transferring more than 2 electrons and multiple protons, thus requiring multiple reaction intermediates, some of which are shared with different possible products. The high overpotential required for most CO₂ reduction catalysts also implies a low energy conversion efficiency, ≤50% (compared to the 60 to 70% for water electrolyzers) (9).

As discussed for the OER, the efficiency of CO₂ reduction on metallic catalysts is limited by linear scaling relations. For example, Fig. 4A plots a correlation of the free energy (calculated by density functional theory, DFT) of 2 intermediates in the reduction of CO₂ to CO, E(COOH), and E(CO). A lower free energy and more stable M–COOH bond is desired, whereas weaker binding to CO is necessary to optimize desorption of the product (27). This is challenging for a single metal catalyst if the intermediates bind to the same site because the M–C bond strengths scale linearly. Multimetallic catalysts take inspiration from the active site of the

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**Fig. 3.** Water electrolysis. (A) HER volcano plot for catalytic elements. Data from ref. 14. (B) Free energy diagram for the OER. The black curve refers to an ideal OER catalyst whereas the red curve represents a real catalyst (22). (C) Comparison between a low-temperature PEM electrolyzer and a higher-temperature SOEC. Data from ref. 43. (D) Electrolyzer and fuel cell mode performance of an SOEC using a proton conductor at intermediate temperatures. Increasing the temperature by 150 °C dramatically improved the cell current density. Data from ref. 44.
CO dehydrogenase enzyme CODH, in which cooperative binding to 2 metal atoms stabilizes a CO$_2$ transition state (28, 29). Cu is a unique CO$_2$ reduction catalyst because it favors C$^+$ products, including some like ethanol that are ideal for seasonal storage. Cu makes a moderately strong bond to CO but not so strong as to poison the surface, allowing sufficient coverage for C–C coupling or protonation steps (30, 31). The catalytic pathways leading to hydrocarbons or oxygenates on Cu are complicated and highly coupled, as evidenced by the relatively low Faradaic efficiency (FE) for producing ethylene and ethanol (Fig. 4B). Alloying Cu with other metals (29, 32–34) and building nanostructures that modulate the chemical environment of the CO binding site (35–37) are interesting strategies for steering the C$_2$ product distribution. Given the complexity of this problem, there is a need for better spectroscopic probes and microscopies that can characterize the structure of the electrocatalytic sites. Systematic high-throughput screening guided by computation and machine learning are also emerging as effective means of attacking electrocatalytic problems of this nature (38).

There are also acute system-level problems for CO$_2$ electrolysis. The low solubility of CO$_2$ in water under acidic conditions creates a mass transfer limitation, and at high overpotentials the HER reaction becomes dominant. Strategies for concentrating CO$_2$ at the electrode surface can mitigate this problem to a certain extent (Fig. 4C) (39) and mass transfer is dramatically improved when CO$_2$ is supplied in the gas phase. In this case, construction of a high-surface-area triple-phase boundary (TPB) where catalyst, electrolyte, and gaseous reactant meet is essential. Fig. 4D shows a TPB made by sputtering a Cu catalyst layer onto a polytetrafluoroethylene (PTFE) substrate that prevents system flooding, on top of which is deposited a carbon conductive layer. Gaseous CO$_2$ diffuses through the porous PTFE layer and the HER is suppressed by using an alkaline electrolyte (40). Lessons from biological systems such as the C4 plants (plants with alternative photosynthetic pathway incorporating CO$_2$ into a C4 intermediate, oxaloacetate) may inspire other strategies for concentrating CO$_2$ in a TPB configuration. Photosynthetic organisms have evolved the ability to channel CO$_2$ to ribulose-1,5-bisphosphate as carbon source for the Calvin cycle. C4 plants acquire extra concentration by trapping CO$_2$ in a 4-carbon compound and passing it to bundle sheath cells for decarboxylation, resulting in a local supply of CO$_2$ for fixation (41). Analogous CO$_2$ storage and delivery would be addressing a major problem of gas-fed CO$_2$ electrolyzers, because the single-pass conversion rate in current electrolyzers is low. One can imagine equipping the diffusion layer in an electrolyzer with gradient-localized “bundle sheath cells” that salvage the unreacted CO$_2$ gas from the TPB and pass it down to reactive sites, achieving higher conversion rates.

A number of lessons learned from water electrolyzers can be applied to the CO$_2$ electrolysis problem, although some problems are CO$_2$-specific. pH gradients developed across the membrane electrolyte cost energy in water electrolyzers that operate in neutral or near-neutral solution, and for this reason all water electrolyzers operate under strongly acidic or strongly basic conditions. The use of buffered solutions in CO$_2$ electrolysis creates pH gradients and proton management problems at high current density. For water electrolyzers, a bipolar membrane (BPM) addresses this problem by operating the cathode and anode in acid and base, respectively. This arrangement minimizes the membrane polarization loss because water autodissociation in the BPM provides H$^+$ and OH$^-$ ions to the cathode and anode, respectively. This strategy can be applied to CO$_2$ electrolysis, but with some modification since CO$_2$ reduction requires a different optimal pH from the HER. The use of BPM also mitigates the cross-over problem of both anionic and neutral products (42).

**Solid-State Electrolytes**

Because chemical reaction rates rise exponentially with temperature, intermediate- and high-temperature electrolyzers are
effective in lowering electrode overpotentials for both the anode and cathode reactions. Fig. 3C compares the polarization curves of PEM cell at 60 °C with a solid oxide electrolysis cell (SOEC) at 800 °C (43), and Fig. 3D shows data from a cell containing a solid-state proton conducting electrolyte (44). The electrode reactions in intermediate- (250 to 500 °C) and high-temperature (600 to 800 °C) electrolyzers are slightly different from those in polymer electrolyzers depending on the type of electrolyte used. For example, in an SOEC, water vapor or CO₂ is reacted at the cathode to produce H₂ or CO₂ respectively, and O²⁻ in a 2-electron process. At the anode, O²⁻ ions combine to form O₂ gas.

(Cs₂(HSO₄)(H₂PO₄) have shown high proton conductivity as well as low-temperature operation (<120 °C) compared to typical SOEC anode electrolytes, which have instability at high temperatures (55). Research on solid-state ion-conducting electrolytes such as La₃Sr₂MnO₆⁺δ has shown conductivities at temperatures as low as 120 to 300 °C but are limited by their brittle mechanical properties (56). Future research should focus on improving the electrolyte and catalyst interface to minimize degradation. Another interesting development has been to use solid acids that can conduct both protons and oxide ions. One group made a hybrid SOEC, using BaZrO₃, CeO₂, Y₂O₃, and MgO as the cathode, that could produce 3.16 A/cm² at 1.3 V and 750 °C (57). This performance is much better than that reported for single-ion-conducting electrolytes (55).

Outlook

The growth in renewable energy capacity from solar, wind, and other carbon-neutral sources is limited by the lack of adequate solutions for short- and long-term energy storage. Electrochemical liquid fuels are ideal for long-term energy storage because of their high energy density and the well-developed infrastructure for their transport, storage, and use. Electrolyzers provide a key link between electrical energy and liquid fuel, either by direct electrocatalysis or by water electrolysis from CO₂ and water or through the generation of feedstocks for fuel synthesis, such as hydrogen and syngas. The latter electrolytic processes, which involve 2-electron, 2-proton cathode reactions, are already well-developed from the scientific and technological point of view. Water electrolysis using alkaline electrolytes has been commercialized in parts of the world where hydroelectric power is cheap and abundant. Technology demonstrations for the production of CO and syngas have been successful with both low-temperature polymer electrolyte-based systems and high-temperature solid-state electrolyzers.

The direct electrolytic production of liquid fuels such as ethanol or ammonia requires us to master electrocatalytic reaction cascades beyond simple one-electron intermediates. While the reduction of CO₂ to C–C coupled products on copper-containing catalysts has been known since the 1980s, the detailed mechanism has only recently been understood by combining electronic structure theory with experimental electrochemical and spectroscopic experiments. Encouraging progress has been made in the search for catalysts and electrolytes that enable the selective production of C₂ products such as ethylene and ethanol, but high cathode and anode overpotentials limit the efficiency of these processes. In addition to the study of catalysis, strategies for improving the transport of reactants, products, and ions are also important for the development of efficient electrolyzers for CO₂ and N₂.

Our understanding of well-developed technologies such as water electrolysis provides a useful guide for other problems in electrochemical energy conversion. The principles of catalysis in multi-electron reactions, for example linear scaling relations, are transferable from one reaction to another. Lessons at the system level are also common to different electrolytic systems. For example, proton management using BPMs addresses system-level issues for both water and CO₂ electrolysis. The lowering of electrode overpotentials...
at elevated temperatures is effective for water and CO2 electrolysis to produce H2 and CO and might in the future be applied to reactions that directly produce liquid fuel. Natural enzymatic systems also provide inspiration to develop new electrocatalysts and improve both the selectivity and efficiency of electrocatalysts for the production of liquid fuels.

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