Hydrogen Futures

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1. Introduction

“Hydrogen is always labeled the fuel of the future – and always will be.”
- Elon Musk

Sometimes we focus on the obvious. In the short term for most applications lithium ion (LiIon) batteries will be the big winners. This applies to battery energy storage systems (BESS) from residential-scale to utility-scale and most electric-mobility applications. Elon may well be right, but maybe not.

I mentioned fuel-cells briefly in the post linked below (and will not mention them further herein).

https://www.energycentral.com/c/pip/alternatives-alternative-energy

However, I have never delved into hydrogen production methods, nor possible roles for fuel cells that LiIon batteries cannot economically meet. This post will explore current and future methods of hydrogen production and the second post in this series will deal with possible future roles of hydrogen-based mobility and hydrogen energy storage systems.

2. Present Hydrogen Production

Current techniques for hydrogen production are either very energy intensive or produce greenhouse gases (GHGs). There are currently two techniques for producing hydrogen: electrolysis and reforming.

2.1. Electrolysis

Most of the content below comes from the following website:

https://www.energy.gov/eere/fuelcells/hydrogen-production-electrolysis

2.1.1. Polymer Electrolyte Membrane Electrolyzers

In a polymer electrolyte membrane (PEM) electrolyzer the electrolyte membrane is a solid specialty plastic material (see figure below).

- Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons).
- The electrons flow through an external circuit and the hydrogen ions selectively move across the PEM to the cathode.
- At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas.
Anode Reaction: \[ 2\text{H}_2\text{O} \rightarrow 2\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]

Cathode Reaction: \[ 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \]

2.1.2. **Alkaline Electrolyzers**

Alkaline electrolyzers operate via transport of hydroxide ions (OH\(^-\)) through the electrolyte from the cathode to the anode with hydrogen being generated on the cathode side. Electrolyzers using a liquid alkaline solution of sodium or potassium hydroxide as the electrolyte have been commercially available for many years.

2.1.3. **Solid Oxide Electrolyzers**

Solid oxide electrolyzers use a solid ceramic material as the electrolyte. This material selectively conducts negatively charged oxygen ions (O\(_2^-\)) at elevated temperatures. This process generate hydrogen as described below:

- Water at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions.
- The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

Solid oxide electrolyzers must operate at temperatures high enough for the solid oxide membranes to function properly (about 700° to 800°C, compared to PEM electrolyzers, which operate at 70° to 90°C, and commercial alkaline electrolyzers, which operate at 100° to 150°C). The solid oxide electrolyzers can effectively use heat available at these elevated temperatures (from various sources, including concentrated solar) to decrease the amount of electrical energy needed to produce hydrogen from water.

2.2. **Reformers**

Natural gas is methane (CH\(_4\)) that can be used to produce hydrogen with thermal processes, such as steam-methane reformation and partial oxidation. Note that both of
these processes produce CO₂ (a GHG). The following site was used for much of this content:

2.2.1. Steam-Methane Reforming

Most hydrogen produced today in the United States is made via steam-methane reforming, a mature production process in which high-temperature steam (700°C–1,000°C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming is endothermic—that is, heat must be supplied to the process for the reaction to proceed.

Subsequently, in what is called the "water-gas shift reaction," the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. In a final process step called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

Steam-methane reforming reaction
CH₄ + H₂O (+ heat) → CO + 3H₂

Water-gas shift reaction
CO + H₂O → CO₂ + H₂ (+ small amount of heat)

2.2.2. Partial Oxidation

In partial oxidation, the methane (and any other trace hydrocarbons) in natural gas react with a limited amount of oxygen (typically from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of carbon dioxide and other compounds. Subsequently, in a water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and more hydrogen.

Partial oxidation is an exothermic process—it gives off heat. The process is, typically, much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

Partial oxidation of methane reaction
CH₄ + ½O₂ → CO + 2H₂ (+ heat)

Water-gas shift reaction
CO + H₂O → CO₂ + H₂ (+ small amount of heat)
3. Potential Future Techniques being developed

The U.S. Department of Energy is supporting a number of tracks aimed at decreasing the cost of hydrogen production and storage, both in the short-term (incrementally, mainly based on the above techniques, see subsection 3.1 below) and longer term (based on new techniques, subsections 3.2 through 3.4 below). The subsections below briefly examine each of these approaches for hydrogen production. These are drawn from the following web site.

https://www.hydrogen.energy.gov/annual_progress17.html

Note that these are multi-year projects, and each of the reports (drill down from the above linked site) are for 2017 (latest available). These are highly detailed reports, however each contains an overview of the project, which I primarily used for the subsections below.

3.1. Incremental Electrolysis Development

Polymer Electrolyte Membrane (PEM) electrolysis system modeling and optimization: This project seeks to incrementally optimize both the PEM Stack and the balance of plant energy efficiency and production cost over the system lifetime with the following goals:

Stack energy efficiency:
- 43 kWh/kg H₂ (78% lower heating value [LHV]) by 2020

System energy efficiency:
- 44.7 kWh/kg H₂ (75% LHV) by 2020

Hydrogen Levelized Cost:
- $2.00/kg H₂ at plant gate by 2020 (vs. $3.00 /kg in 2015).

Pump price for a hydrogen refueling station in California is $15 to $20/kg. Mileage is 50 to 65 m/kg (2018 Honda Clarity Fuel Cell).

PEM High-Performance, Long-Lifetime Catalysts: Hydrogen production for mobility and energy storage from PEM water electrolysis is attractive due to its efficiency, ability to quickly cycle up and down, and delivery of hydrogen with high and differential pressure. However, capital costs are high due to expensive materials, especially the membrane and catalyst. Though membrane costs are predicted to decrease, precious metal catalysts costs will come to dominate capital costs as this technology matures.

Decreasing the precious metal requirement for PEM electrolysis is therefore vital for the widespread use of this technology. The overall objective of this project is to commercialize the low-precious-metal-loading, high-performance catalysts.

PEM High Performance Platinum Group Metal Free Membrane Electrode Assemblies: To date, the only pathway with promise to achieve platinum group metal-free electrode formulations in membrane-based electrolysis cells is utilization of anion exchange membrane (AEM). The basic local environment of the membrane allows a range of stable transition metals and metal oxides to be utilized at high potential for catalysis. AEMs also enable the use of much less expensive flow field materials other than the titanium often used in polymer exchange membrane systems. At the same time,
a solid-state electrolyte eliminates the need for corrosive liquid electrolytes such as concentrated potassium hydroxide and allows leveraging of high-performance membrane electrode assembly technology.

High Temperature Alkaline Water Electrolysis: Hydrogen production from water electrolysis for mobile and energy storage applications is attractive due to its high efficiency, fast ramp rates, and high-pressure capability. However, current hydrogen production from electrolysis comprises only a small fraction of the global hydrogen market due to the high cost associated with expensive stack materials (membrane, catalyst, and bipolar plates) and electricity consumption of the commercially available electrolysis systems. This project aims to develop a high temperature alkaline water electrolyzer that can simultaneously reduce the electrolyzer cost (by adopting inexpensive material) and improve energy efficiency (by enabling high-temperature operation).

Solid Oxide Based Electrolysis and Stack Technology with Ultra-High Electrolysis Current Density: Although current electrolysis systems have the potential to integrate with wind and solar energy sources, the key challenges are low system efficiency and high capital costs. This project aims to address these barriers with an innovative solid oxide-based electrolysis and stack technology with ultra-high steam electrolysis current (>3 A/cm²) for potentially ultra-low-cost, highly efficient hydrogen production from diverse renewable sources.

Other projects: Note that there three other project reports that deal with specific components within the three primary designs. I have not provided descriptions of these, as they seem to delve too deeply into detailed technology. Go through the above link and drill down through "Electrolysis" if you are interested in seeing these.

3.2. High-Temperature Thermochemical

There are two projects for hydrogen production using similar concepts based on concentrated solar-generated thermal energy that supports water-splitting reactions. Both projects are focused on identifying chemical compounds that support the water-splitting (WS) reactions, and developing reactor vessels that can support these processes.

High Efficiency Solar Thermochemical Reactor: This research and development project is focused on the advancement of a technology that produces hydrogen at a cost that is competitive with fossil-based fuels for transportation. A two-step, solar-driven WS thermochemical cycle is theoretically capable of achieving a solar-to-hydrogen conversion ratio that exceeds the DOE target of 26% at a scale large enough to support automated processes. The challenge is to transition this technology from the laboratory to the marketplace and produce hydrogen at a cost that meets or exceeds DOE targets.

Conceptually, heat derived from concentrated solar energy can be used to reduce a metal oxide at high temperature producing oxygen (Step 1). The reduced metal oxide is then taken "off sun" and re-oxidized at lower temperature by exposure to water, thus producing hydrogen (Step 2) and completing the cycle. Commercial success of solar thermochemical hydrogen production is contingent upon developing suitable redox-active materials and incorporating them into an efficient reactor. There are numerous material chemistries that have attributes suitable for inclusion in a thermochemical hydrogen production system. The challenge is to identify an optimally performing material. In addition, the development of redox material and reactor are not mutually
exclusive, but must be conducted in parallel. To maximize the probability of success, this project also addresses the reactor- and system-level challenges related to the design of an efficient particle based reactor concept.

**Flowing Particle Bed Solar-thermal Redox Process:** In order to meet DOE targets for economical and efficient solar-thermal hydrogen production at the commercial scale, advances in active redox materials and reactor fabrication materials are needed. Ideal solar-thermal water splitting materials have high hydrogen production capacity, relatively low thermal reduction temperatures (closer to 1,200°C than 1,500°C), fast reaction kinetics, reduction enthalpies on the order of the water splitting enthalpy, are solid in both oxidized and reduced forms, operate with small ΔT between reduction and operation, and are highly stable over hundreds of thousands of cycles. This team will develop new materials that possess these properties in conjunction with project collaborators. Materials development has focused on spinel structure and perovskite structure materials, which have both shown promise in reaching the targets.

Efficient flowing particle reactors need active materials that are robust, attrition resistant and not limited by slow heat or mass transfer properties. Therefore, we have developed particle fabrication procedures for particles that are flowable, reactive and robust, and are currently testing their performance in fluidized bed reactors. We are also evaluating reactor containment materials to ensure stability at the high temperatures at which water splitting occurs. In the end, we will produce reactor-ready materials with demonstrated hydrogen productivities to drive the field closer to meeting DOE’s technical targets, as determined from our process model and techno-economic analysis.

### 3.3. Photo-electrochemical

Photo-electrochemical devices are a single (monolithic) device that uses a semiconductor device plus a separate electrode to harvest light and split water into hydrogen and oxygen.

**High-Efficiency Tandem Absorbers:** The catalyzed surface of a semiconductor is the light-harvesting component, as well as one part of the water splitting system, with the balance consisting of a spatially separated counter-electrode. Discovering a semiconductor system that can efficiently and sustainably collect solar energy and direct it toward the water-splitting reaction could provide renewable and economically competitive fuel for the hydrogen economy.

The goal of this work is to develop a semiconductor material-set or device configuration that:

- Splits water into hydrogen and oxygen spontaneously upon illumination without an external bias.
- Has a solar-to-hydrogen efficiency of at least 15%, with a clear pathway to exceed 20%.
- Can ultimately be synthesized via high-volume manufacturing techniques with a final hydrogen production cost below $2/kg.

A promising semiconductor, GaInAsP, has been identified. The team has performed extensive durability and efficiency testing, and has begun optimizing this material's configuration.
**Wide Bandgap Chalcopyrite Photo-electrodes:** The goals of this project are to demonstrate photo-electrochemical hydrogen production with a dual absorber system capable of generating at least three liters of hydrogen in eight hours and to develop a standalone system with solar-to-hydrogen conversion efficiency of 15% and operational life up to 2,000 hours.

The chalcopyrite material class, typically identified by its most popular PV-grade alloy, CuInGaSe$_2$, provides exceptionally good candidates for PEC water splitting. A key asset of this bandgap tunable, direct absorber, thin film semiconductor material is the outstanding photon-to-electron conversion efficiency, as demonstrated with CuInGaSe$_2$-based PV cells.

A solar-to-hydrogen efficiency of 4% was achieved by the team in 2012 using a 1.6 eV bandgap CuGaSe$_2$ photocathode connected in series with three a-Si PV drivers (side-by-side architecture). The use of such coplanar architecture was dictated by the bandgap of CuGaSe$_2$, which was too narrow for a “stacked” multi-junction integration. With wide bandgap chalcopyrites, the team will be able to stack the PEC device over the PV driver and increase the solar-to-hydrogen efficiency.

**Tandem Particle-Slurry Batch Reactors:** Economically, particle slurry reactors are projected to be one of the most promising technologies for clean solar photo-electrochemical hydrogen production via water splitting, according to a 2009 techno-economic analysis commissioned by the DOE and performed by Directed Technologies, Inc. This techno-economic analysis compared four plausible reactor designs: two panel-based reactors, which resembled typical wafer-based solar cells immersed in a liquid electrolyte, and two particle-slurry reactors. On an energy basis, the hydrogen produced from the particle-slurry reactors was projected to be by far the most cost-competitive as compared to fossil fuels, further supporting the viability of the hydrogen economy.

This project describes a new design for a particle-slurry reactor, where the main innovation is the use of a stacked-compartment arrangement, instead of the typical design where the compartments are arranged side-by-side. Stacking the compartments results in much shorter mass transport distances and provides efficiency advantages due to the tandem light absorbers. It is projected that over five times less piping and pumps are required to circulate the electrolyte, which results in a cost that is half that of the least expensive proposed particle-slurry reactors to date.

To date this project has identified materials for the proposed reactor, and demonstrated several small prototypes.

### 3.4. Biological

Hydrogen can be produced through fermentation of biomass. In general the biomass must be first converted to a simple sugar (typically glucose), and then there is a chemical conversion limit of 4 mol hydrogen per mol glucose. Mole is an SI base unit with an abbreviation mol. Another way of stating the chemical formula: $\text{C}_6\text{H}_{12}\text{O}_6 + 2 \text{H}_2\text{O} = 4 \text{H}_2 + 2 \text{CH}_3\text{COOH} + 2 \text{CO}_2$ is: 1 mol glucose plus 2 mol water yields 4 mol hydrogen plus 2 mol acetate plus 2 mol carbon dioxide.

Three projects are identified to improve the conversion ratio and efficiency of the above described biological process. I am not going into details on these because (1) I feel that these are long-shots, and (2) these processes produce carbon dioxide. If readers wish to explore these, go through the above link and drill down to "Biological".
4. **Photo-Electrochemical System Prototype**

At least one private company, HyperSolar, Inc., has developed a photo-electrochemical process.¹ This process is described in the page referenced below.² HyperSolar's prototype system has recently completed 566 hours of continuous hours of operation.³

HyperSolar has been assigned five patents for elements of their system.⁴ They intend to provide a complete solution that converts sunlight to pressurized hydrogen.⁵

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