

An Electrifying Chameleon

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1. Introduction

Hydrogen. That is what this post is about. It all started with an article about a new method to produce it that looks really promising. But then we got to the question of what “color” is the hydrogen it produces. I frequently use the terms green hydrogen, gray hydrogen and sometimes blue hydrogen. Green hydrogen is produced via electrolysis using renewable electricity, but what is renewable electricity?

Gray hydrogen is produced by reforming methane (a.k.a. natural gas), and most of the hydrogen currently being used is grey hydrogen. Producing gray hydrogen also produces carbon dioxide (CO₂), the primary greenhouse gas (GHG), and the CO₂ produced in making gray hydrogen is vented to the atmosphere. Which gets us to blue hydrogen, which is made like gray hydrogen, but the CO₂ is captured and sequestered. But at least one source said that only 80% of the CO₂ can be captured. Thankfully, I’m not delving into this matter in this post.

Various parties have invented other colors for hydrogen, but in my mind this is a futile effort. There are a huge number of ways to produce hydrogen. Which of these has the best economics and/or produces the least GHG frequently depends on where the production is performed, where the evaluation is performed, and on the production and evaluation methods. I will just say that hydrogen is a Chameleon, and it can be any color it wants to.

This post will look at green hydrogen, and more specifically, the above question (what is renewable electricity?). Then it will look at the new method to produce hydrogen that I found.

2. Green Hydrogen

Electrolysis splits water (H₂O) into hydrogen and oxygen. Since the hydrogen output from the basic electrolysis process is in a different place than the oxygen output, it is reasonable to assume the output gases are fairly pure. Thus, the simplicity of this process is the best argument for its efficiency in splitting water, and not producing any greenhouse gases. But this assumes it uses electricity that does not produce GHG.

I used “renewable electricity” for GHG-free electricity above, but indeed there are some sources of nearly GHG-free electricity that are not considered renewable, at least where I live. Also, some “renewable electricity” in a simple evaluation does produce GHGs. Thus, the questions that are the titles of the next subsections are really complicated.

2.1. What is Renewable Electricity?

Like I usually do, I will use documents from my home state (California) to address the main question. This is justified because California is generally leading other states in dealing with questions about renewable and carbon-free energy. The document answering the subsection title question is referenced here.¹

¹ Christina Crume, Lynette Green, California Energy Commission, RPS Eligibility Guidebook, 9th Edition, 4/27/17, <https://www.energy.ca.gov/programs-and-topics/programs/renewables-portfolio-standard>

Some methods of producing renewable electricity only require a short sentence to basically say “yes, it’s renewable,” while others take several pages to fully define what processes from that method are and are not renewable. I’ve simplified this through the table below, which will still send you to the above-referenced document for the most complex considerations. I use “yes” or “maybe” for the main question. For fuels, the renewable electricity is generated by using these fuels most efficiently.

Source	Renewable?	Comment
Biodiesel	Maybe	If it generates electricity using biodiesel from biomass feedstock or from an eligible solid waste conversion process using municipal solid waste.
Biomass	Maybe	See Chapter 2, section B in referenced document.
Biomethane	Maybe	See Chapter 2, section C in referenced document.
Fuel Cell using Renewable Fuel	Maybe	See Chapter 2, section D in referenced document.
Geothermal	Yes	Requires certification of facility / process. No supplemental heat source
Hydroelectric	Maybe	See Chapter 2, section F in referenced document. Mostly only small hydro (< 40 MW) is “renewable.”
Municipal Solid Waste	Maybe	See Chapter 2, section G in referenced document.
Ocean-Thermal	Yes	Requires certification of facility / process.
Ocean Wave	Yes	Requires certification of facility / process
Solar	Yes	Requires certification of facility / process
Tidal Current	Yes	Requires certification of facility / process
Wind	Yes	Requires certification of facility / process

Note that most renewable energy that is, and will be available on the California grid is Solar and Wind. These are not only very low-cost, but during periods where they exceed demand plus the ability of utility-scale battery energy storage projects to store, they should be very, very low cost since they would be otherwise be curtailed. These times would be ideal for generating and storing green hydrogen (and oxygen).

2.2. So What Are Carbon-Free Non-Renewables?

Per the document referenced at the end of this paragraph, carbon-free sources include renewables plus large hydropower, and nuclear.²

These sources do indeed produce virtually carbon-free power, and could be used to produce green hydrogen.

² Liz Gill, Aleecia Gutierrez, Terra Weeks, California Energy Commission, “SB 100 Joint Agency Report: Charting a path to a 100% Clean Energy Future,” page 39, March 15, 2021, <https://www.energy.ca.gov/publications/2021/2021-sb-100-joint-agency-report-achieving-100-percent-clean-electricity>

2.3. What about Zero and Negative Emissions Technology?

These are either undeveloped or very inefficient resulting in some significant GHG emissions. For example, Bio-Power (without GHG capture and sequestration) was modelled in the CEC report linked below and found to have negative GHG emissions only in very limited circumstances.

<https://www.energy.ca.gov/sites/default/files/2021-12/CEC-500-2021-053.pdf>

The good news is that carbon dioxide capture methods continue to improve. California has widely available geologic-sequestration sites. Pilot projects over the next ten years could easily produce cost-effective negative emissions power production technologies. Also see the next section regarding using biogas in a “carbon-negative cycle.”

3. Electrified Membranes

Many of you might be familiar with reverse osmosis desalinization. This process essentially filters the salt out of sea water, brackish water or water otherwise contaminated with soluble salts. This uses a semipermeable membrane with pores small enough to stop a percentage of salt ions from passing through it when a water-pressure gradient across the membrane forces the water molecules through it. By passing water through membranes many times, it eventually reaches an acceptable purity.

A process similar to the above will work for many fluids, including mixed gases. In the case of mixed gases the new process applies a voltage / current across the membrane. This accelerates the target gas (hydrogen) through the membrane, and makes the process much more efficient. I discovered this process in my weekly issue of Science, referenced here.³

The daunting cost of installing a hydrogen infrastructure has been a major driver behind the decision of policy-makers in the United States and elsewhere to put the hydrogen effort on hold. Clark et al. address head-on the hydrogen infrastructure need by exploiting electrochemical membrane reactors to strip hydrogen from more convenient carriers, including ammonia (NH₃), methane (CH₄), and biogas. These fuels could potentially be delivered to a point of need by using an existing infrastructure, where they could then be converted to hydrogen for use in fuel cells.

The concept of using liquid or easily liquefied hydrogen carriers to fulfill hydrogen delivery needs has gained traction in recent years. Ammonia as the carrier is attractive because the cycle is entirely carbon free; whereas methane is attractive because the locally produced carbon dioxide can potentially be sequestered; and biogas is attractive because if deployed alongside sequestration, it results in a carbon-negative cycle. Among the reactor types available for extracting hydrogen from hydrogen-bearing compounds, electrochemical membrane reactors based on proton ceramic electrolytes offer distinct advantages. Such reactors combine thermochemical catalysts that facilitate decomposition of the carrier with electrochemical pumping of hydrogen across a proton-conducting solid-state membrane. Because only protons, which emerge in the form of

³ Arthur J. Shih and Sossina M. Haile (Summary), Daniel Clark et al (Report), Science, “Electrifying membranes to deliver hydrogen” (Summary), “Single-step hydrogen production from NH₃, CH₄, and biogas in stacked proton ceramic reactors” (Report), April 22, 2022, <https://www.science.org/doi/10.1126/science.abo5369> (Summary), <https://www.science.org/doi/abs/10.1126/science.abj3951> (Report), Note that access to the full content of either the summary or the report is limited to members of AAAS.

hydrogen gas upon undergoing oxidation at the hydrogen evolution electrode, can be delivered across the membrane, one can reasonably anticipate that every electron delivered to the membrane will result in the production of hydrogen in a 1:2 ratio. Furthermore, because of the solid-state and gas-impermeable nature of the membrane, one can expect the hydrogen produced to be entirely free of impurities—in particular, of unreacted carrier molecules, species that simply cannot get to the other side of the membrane. Another added benefit is the ability to pressurize the hydrogen by only increasing the current.

Author's comment: See the earlier paper linked below, specifically subsection 4.2 regarding cracking (separating ammonia into nitrogen and hydrogen). Also, the second link below is to reference 3 in the paper linked below. This is a thorough evaluation of the economics of using ammonia as a hydrogen carrier, including a strong focus on using an advanced cracking catalyst (lithium amide-imide). In rereading this paper, it sounds like the cracking system might benefit from electrochemical membrane reactors explored in this section / paper. However, based on the text below, it could be the new technology might completely displace traditional catalytic membrane reactors.

<https://energycentral.com/c/ec/release-crackers>

[https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/880826/HS420 - Ecuity - Ammonia to Green Hydrogen.pdf](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/880826/HS420_-_Ecuity_-_Ammonia_to_Green_Hydrogen.pdf)

In contrast to their electrochemical counterparts, traditional catalytic membrane reactors use a membrane that is hydrogen-permeable, typically made with palladium (Pd) or a Pd alloy, rather than one that is proton-permeable. Hydrogen is driven across a traditional membrane by mechanical pressure, which creates a chemical potential gradient. In the electrochemical membrane reactor, protons are driven across the membrane by application of a voltage/current, which indirectly drives the flux of hydrogen gas.

Author's comment: the paper linked directly above uses an improved cracking catalyst (lithium amide-imide) in lieu of a palladium catalyst.

The mention of “hydrogen-on-demand” below needs additional discussion. Ammonia is the most efficient carrier of hydrogen. It is also possible to produce “green-ammonia” using the traditional Haber-Bosch process with green hydrogen as an input gas and GHG-free energy to drive the process. The green ammonia is much easier to transport and store than hydrogen. It is also relatively easy to crack the ammonia and thus retrieve the green hydrogen, and do this at a small-scale (see the above-linked post and paper, and the electro-chemical process described in this section). Thus the most efficient process (thus the process with the best economics) might be to make the green hydrogen at a large-scale when and where GHG-free power is the least expensive, ditto green ammonia, transport the green ammonia to large and small hydrogen users, and crack the ammonia to produce green hydrogen on their sites.

Recent advances in electrochemical membrane reactors have spurred the race to implement “hydrogen-on-demand” solutions. In devices scaled up for practical applications, challenges emerge. As noted by Clark et al., managing the temperature profile across the reactor is particularly difficult. The process of pumping hydrogen across an electrochemical membrane leads to an increase in temperature because of the changes in hydrogen concentrations. At the same time, the decomposition reactions are inherently endothermic and drive the temperature down. Consequently, in a reactor

with a simple linear flow, the upstream regime will be much cooler than the downstream regime. Such a temperature gradient introduces efficiency penalties.

Clark et al. meet this challenge by engineering a counter-flow geometry that enables transfer of the heat generated at the downstream portion of the reactor, as a consequence of the electrochemical pumping, to the upstream portion of the reactor, where the carrier decomposition reactions cool the system. Beyond the use of a counter-flow design, thermal gradients are mitigated by formulating an interconnect material that provides excellent heat transfer as well as electrical contact between adjacent cells in the reactor. The interconnect composition is also designed to match the thermal expansion behavior of the electrochemical components of the reactor, contributing to its long-term stability. With these advances in reactor design and material components, the authors achieved an unprecedented combination of carrier gas conversion, hydrogen recovery, system size, and reactor lifetime.

The >99% hydrogen extraction efficacy of the system of Clark et al. exceeds all other values in the literature. Although extraction efficacy is not a commonly discussed metric, it is useful for describing the overall performance of a catalytic membrane reactor and can be calculated by multiplying the carrier conversion fraction by the hydrogen recovery fraction. Another important metric is the pressure difference across the membrane. In traditional catalytic membrane reactors, in which mechanical pumps pressurize the reactant supply, the penetrating gas emerges at a pressure lower than that of the feed. Therefore, additional mechanical pumps are required to pressurize and compact the hydrogen for storage and transport. Clark et al. demonstrated an integrated system in which chemical transformation, purification, and pressurization are all achieved in a single device, an accomplishment that is only possible in an electrochemical membrane reactor. The combination of hydrogen extraction efficacy and exhaust gas pressurization achieved in their system are truly unprecedented. Future efforts will likely be directed toward increasing the hydrogen flux, which remains moderate for their electrochemical system and does not factor into the extraction efficacy or pressurization metrics.

Final author's comments: The improving efficiency of cracking ammonia gives me hope that an ammonia carrier may lead to the most economic process for distributing green hydrogen. I believe that hydrogen will have a strong role to play in our path to a greenhouse-gas-free future.