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Perspectives on low temperature electrolysis and potential for renewable hydrogen at scale

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Introduction:

As renewable energy penetration increases on the electrical grid and existing infrastructure ages, new approaches are needed to increase the resilience of the electrical grid. Energy storage solutions are required to accommodate the intermittent nature of most renewable energy sources; to cover not only longer-term outages but to also curtail excess generation. A holistic view across sectors is also needed to optimize energy and fuel usage and minimize harmful impact to the environment. As part of that strategy, approaches that can bridge different infrastructures such as transportation, electricity, and the chemical industry will play an important role in balancing supply and demand.

Hydrogen is one such potential bridge (1). While hydrogen has been promoted many times previously for its potential role in the energy system ('Hydrogen Economy'), the changing energy landscape and recent efforts and advances suggest hydrogen is at a transition point where it will move beyond just *potential* and see dramatically increased involvement in society's energy use. Specifically, advances in fuel cell vehicles (10,000 light duty vehicles worldwide and over 100 fuel stations for public fueling) have demonstrated the viability of hydrogen-powered transportation through zero emission vehicles. There are multiple efforts underway to explore increasing hydrogen's role in the energy system. The US Department of Energy has a recent program entitled "H2@Scale" that has performed analysis exploring the increasing utilization of hydrogen in the energy system (Figure 1). In addition, hydrogen is a major industrial

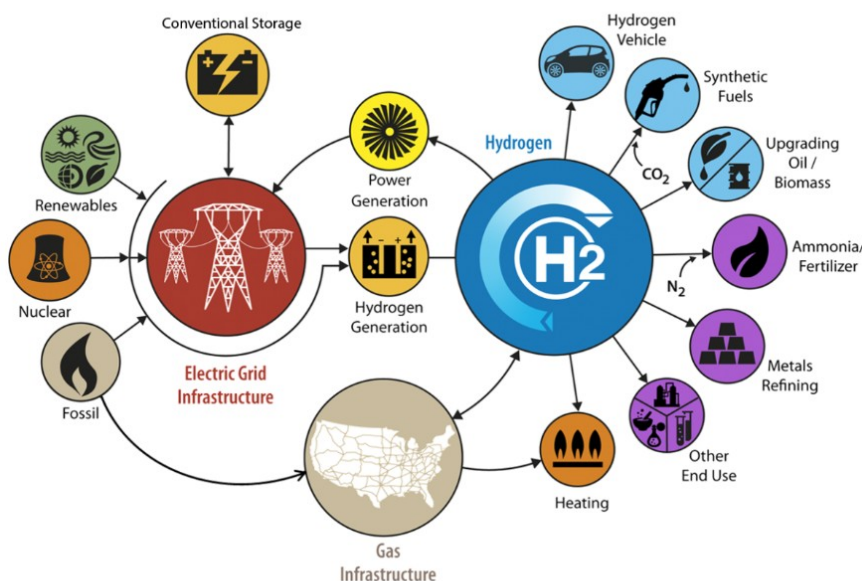


Figure 1: H2@Scale schematic

feedstock today, and industry engagement on the broad use of hydrogen has increased significantly. The Hydrogen Council was founded in January 2017 as a group of industrial leaders with billions of US dollars invested in the H₂ supply chain. Their analysis efforts suggest huge economic impacts of hydrogen including 18% of all energy going through hydrogen by 2050. These are just a few of many efforts in this area.

Renewable sources of hydrogen will be required for many of the initiatives being explored today, such as green production of ammonia and the capture and utilization of waste carbon dioxide. At the same time, the increasing abundance of low cost, renewable electrons is a major factor in enabling the transition to renewable hydrogen. The industrial revolution was based on the cheap and abundant supply of fossil fuels. Society has applied the chemical energy available in these fossil fuels to supply grid electricity, provide heating to buildings, and power transportation and industry. Historically, the stored chemical energy of fossil fuels served as the basis for supplying almost all of our energy needs. In the past decade, renewable generation from solar and wind has dropped dramatically in cost due to technology advances and increases in production volume and scale. The lower cost of renewables as well as policy for increasing renewable energy generation, often legislated through the form of renewable portfolio standards, has led to greatly increased generation from these variable energy sources. Hydrogen, either as a starting point for further chemical processing or as an end use fuel, offers great promise as an energy carrying intermediate to address the many challenges our energy system currently faces, and alongside renewable electricity will usher in the green, decarbonized industrial revolution.

A key technology in enabling hydrogen to couple (electrical) power generation with end use applications is electrolysis. Electrolysis involves the electrochemical splitting of water to hydrogen and oxygen and is generally discussed in terms of high temperature and low temperature processes. Currently, the primary commercial pathway for renewable hydrogen is low temperature electrolysis. Liquid alkaline KOH electrolyzers and proton exchange membrane (PEM) water electrolyzers are the two commercially available technologies and both have been demonstrated at relevant (MW power input, 1000 kg/day) scales (Figure 2). Though 96% of hydrogen produced today is derived from fossil fuels (2), hydrogen from electrolysis is cost competitive and profitable for specific industrial applications, particularly where the delivery infrastructure is lacking. As well as markets which traditionally have not been limited by the operating cost of electrolyzers because they are coupled with inexpensive, often times microgrid electricity (such as hydropower) thus agnostic to traditional grid electricity prices.

Anion exchange membrane (AEM)-based systems, which could leverage advantages of both the liquid KOH and PEM systems, still need development to reach acceptable durability and performance levels. Other technologies, such as high temperature electrolysis, may have applicability in the future but similarly are not currently mature enough to address these markets.

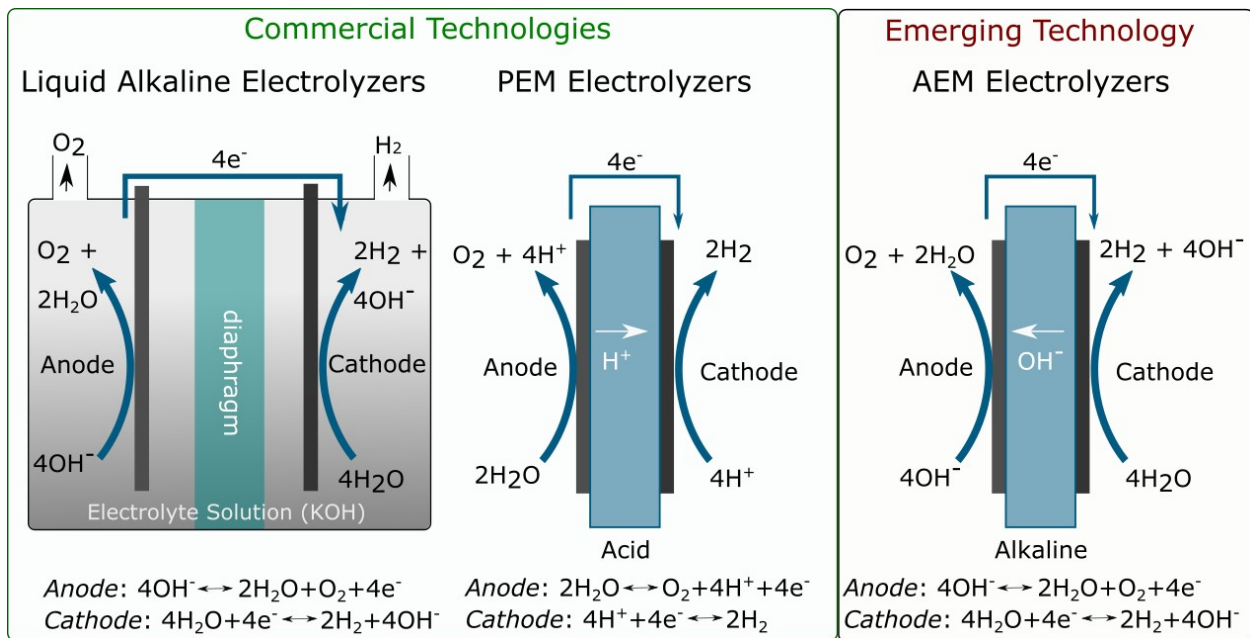


Figure 2: Low temperature electrolysis technologies and reactions, emphasizing major differences: 1) Liquid electrolyte and gapped electrodes in KOH vs PEM or AEM; 2) Water consumption and production in AEM vs PEM which complicates the water balance; 3) KOH electrolyzers use porous diaphragm versus solid polymer membranes in PEM and AEM which complicates gas separation and management.

Technology status and motivation:

General overview of commercial technologies:

Electrolysis of water has been employed for commercial production of hydrogen and oxygen for many decades. KOH electrolyzer systems have existed since the late 1800s with significant development occurring in the 1920s and 1930s to produce electrolyzers at scales of 10,000 Nm³/hr (~50 MW power input) and larger. For example, large electrolyzer installations operated for decades at Aswan Dam in Egypt, Nangal in India, and Ghomfjord in Norway. Many large installations were driven by the need to provide hydrogen for ammonia generation, using low cost electricity from hydroelectric power. KOH electrolyzers recirculate concentrated KOH electrolyte on both sides of a porous diaphragm separator, which is sandwiched between electrodes and bipolar plates made of nickel and stainless steel (Figure 2). The resulting gaps between electrodes result in high ohmic drop which limits operating current density, resulting in very large footprint systems to meet the product H₂ demand (Figure 3). KOH systems operate at balanced pressure due to the low bubble point of the separator between the electrodes. Therefore, many KOH systems operate at atmospheric pressure. Oxygen generation above approximately 10 bar requires significant precautions and special cleaning standards to avoid safety issues (3). Some smaller KOH electrolyzers (up to about 60 Nm³/hr / 0.5 MW) operate at pressures from 10-30 bar. Both pressurized and atmospheric systems have demonstrated high reliability in the applications that they serve.

The first PEM-based electrolyzer systems were developed in 1955 by General Electric, and the technology was sold to Hamilton Sundstrand in 1985 for use in space and submarine applications

for oxygen generation. Key differences from KOH technology include use of pure water as the circulating fluid, a solid polymer electrolyte that enables differential pressure operation, the ability to operate at higher current densities, and more expensive materials of construction due to the limited stability of many metals when exposed to the locally acidic environment of the membrane. PEM systems also have proven reliability, with 50,000 hour lifetimes demonstrated and systems operating in the field for many years. Since the commercialization of PEM electrolyzers, capacities have steadily increased, with systems demonstrated at 100s of Nm³/hr scale. Many systems are fielded at the 50-200 kW scale, with a more limited number of installations at MW scale (Figure 3).



Figure 3: 135 MW KOH electrolyzer plant on left and 1 MW PEM system on right

Low temperature electrolysis technology state of the art:

KOH Electrolyzer Technology Status:

Atmospheric alkaline electrolyzers are similar in scale to the stacks built 50 years ago, with modules in the 300-500 Nm³/hr range. The low material cost enables stack operation at relatively low current density but high efficiency with power consumption as low as 4.4 kWh/Nm³ at full output. Stacks can be integrated into larger systems or containerized with compression and storage. Cost reduction opportunities still exist in the replacement of high cost interconnect materials, component integration, and more efficient catalysts to enable higher current density for similar efficiencies.

Balanced pressure alkaline electrolyzer stacks are typically in the 10-30 Nm³/h range, although larger stack concepts have been developed. Response time to varying power input can typically be faster for pressurized systems vs. atmospheric due to the smaller gas volume changes. However, as discussed above, pressure is often limited to 10 bar due to high pressure oxygen safety concerns. Balanced pressure systems have increased in efficiency over time but typically operate at intermediate efficiencies, near 5 kWh/Nm³. Most development is in scaling to larger cell stacks and increasing efficiency.

Proton Exchange Membrane Technology Status:

Despite recent advancements in PEM systems, the basic cell configurations, materials, and manufacturing methods have been slow to change, particularly for the membrane electrode assembly (MEA). Most private investment has been applied to product scale up and feature development, and relatively low production volumes have limited the need to advance manufacturing to higher speed methods. In addition, the design legacy of these systems in life

support applications for closed environments drove a strong focus on reliability with little consideration for cost and efficiency. However, as discussed later in detail, advanced manufacturing can also significantly reduce the cost of electrolyzer components and provide payback on investment even with underutilized (low capacity factor) equipment.

In the United States, there has been two orders of magnitude less investment in PEM electrolysis compared to PEM fuel cells (PEMFC), which has resulted in PEMFC development that has provided fundamental understanding of membrane, ionomer, and catalyst materials as well as electrode structure, porous transport layers, and how to modify them. Application of these

learnings from PEMFCs to electrolyzers can enable the industry to address the high cost components in PEM electrolyzer cells and advance manufacturing maturity. As a key example of the potential for cost reduction, the bipolar plate, or separator

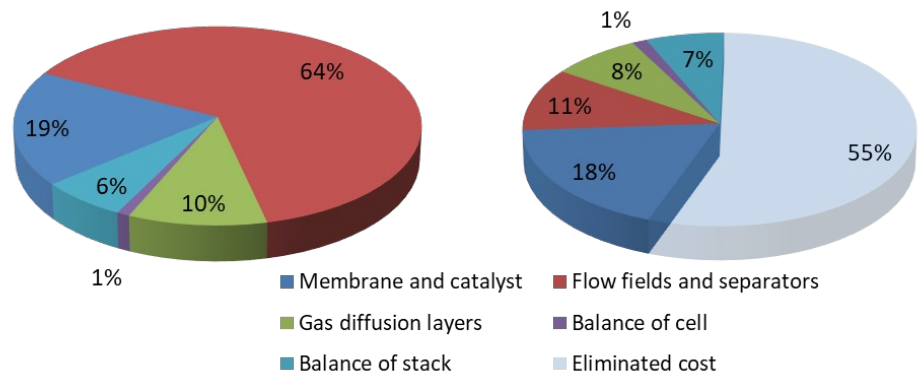
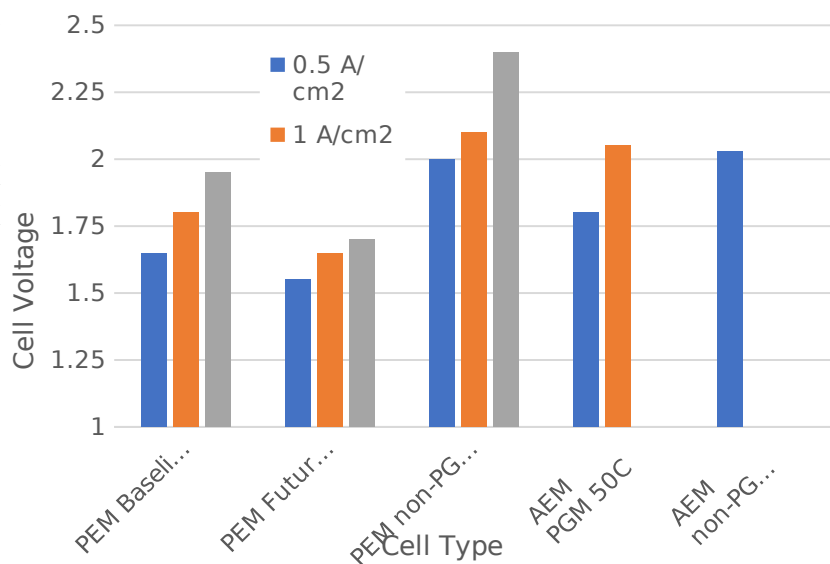


Figure 4: Cost breakdown before and after bipolar plate cost reduction

plate and associated flow fields, was originally the largest cost component of a PEM cell stack (4–6). Leveraging PEMFC knowledge, directed programs reduced the cost of the bipolar plate subassembly by a combination of re-examination of the manufacturing methods, integration of multiple components into a single part, and alternative conductive coatings (7). Reduction in use of titanium, elimination of platinum, improved process yields, and reduction in manual processes led to an 80% reduction in the component cost as a function of hydrogen output (Figure 4).

Anion Exchange Membrane Technology Status:



advantages of KOH and PEM together with the potential ability a non-corrosive liquid phase. g current densities with non-ow field materials but is still at elevated temperature (50°C h more difficult than in PEM 1 (Figure 2), while stability is cell (8). The water required to oy water transport through the ver the maximum achievable for cost savings in AEM cells d to PEM systems, in order to

provide significant benefit reaching 1 A/cm² with stable performance is an important milestone for the AEM technology. Finally, the performance of AEM electrolyzers show significant performance improvements upon addition of free electrolyte (KOH or K₂CO₃ for example) into the water feed, approaching that of PEM systems. The reason for the performance impact is not currently understood and is much different than PEM systems that do not show performance improvements with added electrolyte. Demonstrated performance for several membrane-based cell configurations is summarized in Figure 5.

R&D potential:

KOH:

While liquid alkaline electrolyzer technology is fairly mature in design, cost reduction opportunities still exist in the replacement of high cost interconnect materials, component integration, and advanced cell designs to enable higher current density operation while maintaining similar efficiencies (4). Efficiency can be improved by minimizing the diaphragm thickness, improving gas and water management within the cell via optimization of the electrode porosity and additives to improve wetting, and utilizing higher activity catalysts for both anode and cathode. Improved long-term catalyst stability would also have significant cost impact through fewer cell replacements and at longer intervals over the design life of the system. Electrode and component cost reduction is also a priority through both increasing production volumes and developing high volume manufacturing methods for bottleneck processes. Higher efficiency, lower cost manufacturing processes should be feasible based on advances in coating and assembly processes, such as greater control of deposition parameters and increased automation versus designs of several decades ago. At the systems level, cost reduction is being pursued through scale up and integration into larger balance of plant, with multiple stacks manifolded into one fluids loop for hydrogen and oxygen management.

For pressurized alkaline electrolysis, most development is in scaling to larger cell stacks than are currently commercially available and increasing cell efficiency and reducing manufacturing cost via similar pathways to those above. Pressurized systems have not currently reached output scales as large as the atmospheric systems and have more complex balance of plant due to management of pressurized oxygen but should have a smaller footprint for equal capacity. There are also novel system concepts being explored for pressurized alkaline systems, such as rotation of the stack for improved gas separation and lower material usage due to decreased stack size.

Liquid alkaline electrolyzer technology can also benefit from advancements in AEM materials; catalyst advancements for higher efficiency can be applicable to both systems, while stable membranes could enable some level of differential pressure in liquid alkaline cells if the separator is replaced or integrated with a membrane film or ion-solvating membranes (9, 10). Catalyst and membrane research are described in detail in the AEM section.

PEM:

Membrane:

Membranes used for PEM electrolysis are still extremely thick (~100-250 μm) compared to PEM fuel cells (<25 μm), which is a result of three primary factors. First, PEM electrolyzers typically operate at 30 bar (430 psi) differential pressure versus fuel cells that operate at balanced

pressures up to maximum of 3.5 bar (50 psi). This higher pressure puts more mechanical strain on the membrane and also results in significant back diffusion of hydrogen across the membrane which must be mitigated, especially at low current density when less oxygen is generated for dilution. Second, the manufacturing methods for electrolysis MEAs are much less mature than for fuel cells which results in lower process capability and ability to handle thin membranes. Finally, no commercial membranes to date have been specifically designed for electrolyzers. Membranes have instead been adapted from fuel cell materials which are optimized for some properties that are irrelevant to electrolyzers, such as high conductivity at low relative humidity, and deprioritize parameters of high relevance to electrolyzers, such as water uptake and polymer swelling under flooded liquid conditions or mechanical strength under high loads when fully hydrated.

Good understanding exists around perfluorinated sulfonic acid (PFSA) membrane properties such as water transport, chemical and mechanical durability, conductivity, and dimensional change, as detailed in a recent comprehensive review by Kusoglu and Weber (11). Use of reinforcements, changes in polymer structure, and synthesis method can impact the membrane parameters important for electrolysis systems. Hydrocarbon membranes have also been explored for electrolysis with limited progress. While hydrocarbon membranes have been fabricated with reasonable proton conductivity and mechanical strength, they tend to swell in liquid water (12). In addition, hydrocarbon materials are typically more brittle than fluorinated polymers, which can cause cracking under high mechanical loads such as the seal areas of an electrolyzer cell. Still, some success has been demonstrated with reinforced materials, such as sulfonated Radel materials fabricated by the Hickner group at Penn State and cast with reinforcement by a commercial membrane supplier (13). The reinforced material performed quite well, surviving several hundred hours of operation without failure. Focused programs for PEM membrane and ionomer development for electrolysis in close collaboration with device manufacturers should lead to reductions of factors of 2-3 compared to membranes used in existing PEM systems.

Hydrogen Evolution Reaction (HER):

The hydrogen evolution reaction (HER) in acid is one of the most facile electrochemical reactions, with platinum being the most active material (14). Historically, Pt black catalysts were used in PEM electrolysis since they fit into the legacy electrode manufacturing techniques similar to early PEMFCs.

One of the recent major research topics for HER catalysts in PEM applications is the reduction in the PGM loading. To reduce the loading, the switch from Pt black to Pt supported on carbon (Vulcan or Ketjen black) catalysts is a tremendous cost and material reduction. Pt/C can be obtained in a range of wt%, the carbon ensures good conductivity, and it improves the distribution of the Pt through the catalyst layer. Adopting modern manufacturing techniques from state of the art PEMFCs would also enable loading reductions. Studies have shown that because of the facile nature and fast kinetics of the HER, a Pt catalyst loading of 0.05 mg/cm² using conventional Pt/C catalyst is adequate to sustain current densities of 2 A/cm² (15). Further PGM reduction strategies include alloying Pt or structuring the catalyst using core-shell type approaches to further reduce the PGM content. Examples of the alloying strategy include Pt-Ru

(16, 17), Pt-Cu (18) Pt-Pd (18) and other Pt-x transition metals, with approaches of changing form factor (Pt-Ni), core shell (Pt-Ru) and other configurations.

Another recent strategy for HER catalysis is the use of non-PGM materials. Compared to PGM materials, kinetics on transition metals and compounds seem to be much more sluggish, resulting in at least 100 mV greater overpotential at equivalent current densities. However, non-PGM catalysts offer promise of low capital cost due to PGM elimination. MoS₂-based catalysts have had the longest and most prominent history (19–21), while Mo and Co based selenides and chalcogenides have recently emerged as viable alternatives (22, 23). More recently, CoP catalysts have emerged as higher activity catalysts with considerable durability under PEM electrolysis environments (24, 25).

In the short and medium-term, Pt/C is not likely to be displaced as the HER catalyst of choice for PEM electrolysis applications. This is because of the potential to reduce the loading of Pt down to at least 0.05 mg/cm² without impacting steady state performance. Long-term, there may be non-PGM options that start to approach the performance of Pt if their durability can meet and exceed the requirements of the PEM systems. The stability of all Pt based, alloyed, and non-PGM HER catalysts and supports materials to electrolysis startup and shutdown conditions should be evaluated.

Oxygen Evolution Reaction (OER):

The oxygen evolution reaction (OER) is the rate-limiting step in PEM electrolysis due to the sluggish 4 electron reaction. Furthermore, the aggressive environment combining low pH and high potentials in PEM systems cause durability problems and has focused catalyst research on PGM oxides. The reaction occurs exclusively on oxide or oxidized surfaces, which introduces non-metallic or semiconducting properties at the interface (26, 27). OER activity decreases going from Os, Ru, Ir, Pt, to Au, following the metal oxophilicity (28, 29). Both stability and conductivity have been correlated with catalyst activity (28, 30). There is a strong case that under acid conditions, OER activity requires defect sites which are created through a dissolution mechanism at the surface. Thus, the more active the metal oxide, the less stable it is. OER is also strongly dependent on the inherent conductivity of the catalyst, support, and interfacial oxide species, the effects of which are magnified across the interfaces that are developed within the anode catalyst layer (Figure 6) (31). For example poor electronic conductivity within the catalyst layer will result in poor lateral conductivity across the catalyst layer, thus catalyst not directly in the vicinity of the PTL interface is not utilized (32).

Ir loading reduction at the electrode level is a primary focus area. The goal is to decrease the catalyst loading to sustainable levels (~0.4 mg/cm²) compared to the current state of the art (1-3 mg/cm²). Historically in PEM systems, unrefined Ir blacks were used for the OER at high loadings > 1 mg/cm² (6, 33). Recently, however, pure metal, oxide, and hydroxide Ir catalysts have been made commercially available. Of significant note is that there is no equivalent to carbon supports for the anode electrode, as carbon readily oxidizes electrochemically above 1.0V. Most other support materials such as reduced and doped titania, various tin-based metal oxides, and metal carbides, nitrides and phosphides are either not conductive enough, or are not stable enough to maintain conductivity over time. One exception is a commercially available TiO₂

supported IrO₂ catalyst; however, the structure is more akin to a core shell catalyst as the Ir loading of 75 wt% coats the entire outer surface of the support in order to ensure an electrical pathway (33, 34).

The lack of catalyst supports combined with lack of microporous layers for commercially available porous transport layers typically lead to poor interfacial contact using conventional MEA approaches (35, 36). However, nanostructured thin film (NSTF) based catalyst layers and MEAs developed by 3M have exceeded 2 A/cm² current density at loadings as low as 0.4 mg/cm² (15, 37). Reactive spray deposition technology (RDST), which synthesizes the catalyst during deposition in a reactive flame spray, has also achieved performance equivalent to conventional PEM electrolyzers at ultralow Ir loadings (38). In both the NSTF and RDST cases, durability has been demonstrated to 5,000 hrs of operation. In the short and medium-term, Ir will not be displaced as the OER catalyst of choice for PEM applications, but there is a lot of room for improvement in terms of both production of better Ir catalysts, stable supports, and new manufacturing techniques that result in well dispersed catalyst layer structures at low catalyst loadings which appears to be the key.

The complete elimination of PGMs under acidic conditions is most likely impossible as there does not seem to be a reasonable oxide or other compound that does not dissolve, oxidize or insulate under OER conditions. Substitution and reduction of Ir through alloying is a more likely approach. However, even among the PGM materials, Ru, which is more active than Ir, has unacceptable durability issues by itself. Many studies have focused on alloying Ir with either Ru to increase the activity and allow for a reduction in total PGM loading, or with transition metal compounds such as Ni, Co, and Fe to reduce the PGM content (39–44). Recent studies have indicated that for any approach in which a less stable metal is added to Ir, the less noble component dissolves over time, and the activity enhancement is largely accomplished through increase in electrochemically active surface area through the dissolution process. Alternatively, some studies have focused on alloying or co-synthesizing Ir with more stable Ti, Sn, Sr oxides or nitrides directly with successful outcomes (33, 45–48). The structure and morphology of the Ir itself can also be altered (48–51). A few recent studies showed the effect of cycling on the reduction in ECSA due to dissolution and redistribution of the Ir on pure Ir-based catalysts (33, 52). Studies of the MEA after cycling and steady state holds show that the Ir dissolves and redeposits in the membrane by the same mechanism that exists in PEMFCs (53). Thus, in terms of long-term strategies, the fundamental dissolution behavior must be managed. We emphasize two points, as in the case of HER materials, steady state, transient and startup/shutdown effects on durability must not be overlooked; and secondly purely electrochemical determination of durability must be supported with dissolution data.

Porous Transport Layers (PTL):

Porous transport layers (PTLs) are key components of the delivery and homogenous distribution of water and electrons over the entire electrode/catalyst area, while continually and efficiently removing the gases and heat produced. The highly corrosive conditions in PEM electrolyzers hinder the choice of materials for anode PTLs resulting in titanium being currently used for lack of cheaper stable alternatives. It is fabricated in the form of porous sintered elements ranging from 0.5 to 2 mm thick, with 20-70% porosity, and a questionable or unknown degree of electron

conductivity. On the cathode side, more forgiving electrochemical conditions permit the use of less expensive and more robust carbon-based PTLs or gas diffusion layers (GDLs).

Under electrolysis potentials, titanium metal would undergo corrosion to form a thin passive film on the metal surface which reduces the surface conductivity (54, 55). To mitigate this effect, titanium PTLs are generally coated with PGMs which adds cost (56–59). However, this seems to be the only solution to guaranteeing stack durability. In addition, PEM electrolyzers can produce hydrogen at significant differential pressures vs the oxygen side, ranging from 15 to 100 bar (60, 61), with even higher pressures (up to 350 bar) having been tested (62). Under these conditions, the titanium PTL on the anode side is subjected to major mechanical stresses (63). A second challenge is to guarantee proper and homogeneously-distributed contact pressure over the catalyst layer. Titanium meshes or expanded sheets generally introduce large mechanical stress to the electrode, causing membrane failure (64, 65). Additionally, rough substrates will not be able to provide proper electrical contact to the catalyst layer leading to increased ohmic and mass transport losses. These phenomena and their effects on resistance are depicted and overexaggerated in Figure 6. Therefore, the choice of materials and optimization of PTL porosity and thickness are important.

Compared to substantial R&D on gas diffusion layers (GDLs) for fuel cells, little attention has been paid by the scientific community to PTLs for water electrolyzers (66). Only a handful of manuscripts are to be found, and there is no current R&D pathway to properly characterize, understand the key properties of, and further develop these components. A few publications exist that study the corrosion/passivation effect on titanium PTLs, different methods of accessing the chemical, electrochemical and mechanical properties, investigate the use of protective layers or micro-porous layers (MPLs), and study possible degradation phenomena (67–74). One important aspect that is still missing is R&D on more advanced and cost-effective methodologies to fabricate the PTLs. Raw titanium is generally expensive, but most PTL costs arise from the manufacturing process. Manufacturing alternatives to provide cost-effective PTLs with large cell areas ($> 0.5 \text{ m}^2$) will be of high importance for large-scale, multi-MW market penetration for energy storage (75–77).

Interfaces:

Proper assembly of highly differentiated components is important so that any additional losses can be avoided. One critical interface is between the PTL and catalyst layer. Poor contact between these components will hinder electron transport and therefore increase ohmic losses. On the other hand, too much pressure will compress the available pores for the water to flow and isolate the active sites, leading to an increase in mass transport losses and a decrease in catalyst utilization. Figure 6 depicts each phenomenon than can occur at the interface between the electrode and PTL.

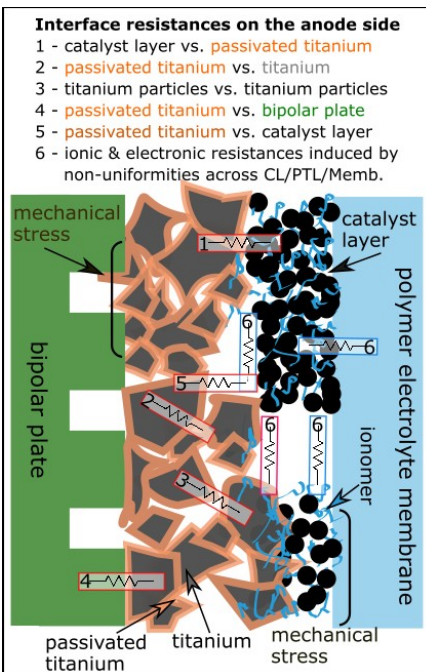


Figure 6: Schematic of the PEMWE anode-side showing worst case interface and heterogeneity induced resistances

Integration of all three cell elements (membrane, electrode and PTL) into a single component should minimize interface resistance issues and facilitate stack fabrication (78–80). Either coating the PTL with the electrode (which may increase electrode/membrane interface resistance) or coating the CCM electrode with a new PTL architecture could accomplish this goal if the electrode is evenly distributed across the catalyst layer thus avoiding the interfacial resistances in Figure 6 (35, 68). An MPL on the PTL can also create a particle size gradient from the PTL to the catalyst layer, smoothing out the transition between the layers and minimizing interfacial resistance (68). New MPLs also need to be stable under electrolysis operating conditions across thousands of hours. Alternatives to fabricating PGM layers on the titanium PTL for oxidation protection and conductivity improvement are also needed to guarantee PTL longevity at reduced stack cost (57, 59). We point out here that the discussion on PTLs, interfaces and MPLs is relevant to AEMWE as well, where a greater degree of freedom of material selection exists.

PEM Development at Scale:

As stack technology grows larger, supply chain maturity is becoming an issue. Electrolyzer cells are now exceeding typical fuel cell active areas for many applications. Therefore, some materials are currently constrained by the available manufacturing width, such as coating widths for catalyst layers. PTLs, especially in titanium, are also not as available in larger form factors. To address applications such as ammonia generation, refining, and vehicle fueling, components have to be made in larger volumes than present. Similar to fuel cells, the industry is not currently prepared for volumes beyond several thousand parts/year (81). Manufacturing

development to scale components is therefore essential to enable continued cost reduction and production capacity increases.

Independent analyses with input from multiple commercial companies as well as technical experts predict near-term capital costs for PEM electrolyzer systems of \$400/kW (82). Both top-down and bottom-up analysis assessments have also predicted ultimate costs of \$250-300/kW, with investment in manufacturing development, electrolysis specific materials, and scale (83–86). These savings are based on a combination of technical advancements which have shown feasibility in long-term bench tests, advanced manufacturing methods including equipment investment, and standard engineering scale up models for balance of plant calculations. Improved current-voltage matching of power electronics with the stack can also substantially decrease the power supply cost in ¢/W .

For the system, power electronics which are robust to fluctuations and interruptions are needed to manage intermittent renewable energy input, as well as controls systems which can manage the impact to the system. While in theory, electrolyzer cells should also be robust to on-off cycling and current fluctuations, transient behavior could cause issues with PGM migration or other effects due to momentary cell reversal. These phenomena are not as well understood for electrolysis and require development of accelerated cycling tests and characterization over time. Capital cost and efficiency also must be balanced within the system, optimizing current density as an example. Even at low electricity cost, the electricity cost impact on total cost of ownership is significant. At the same time, lower capacity factors increase the impact of capital cost.

AEM:

Membrane:

AEM electrolyzers have significant R&D needs as they are much less mature than liquid alkaline or PEM technology. While a number of these R&D areas overlap for liquid alkaline systems (particularly in catalysis and materials compatibility) and also for PEM (issues of gas permeability, water uptake/swelling, stability, mechanical properties, interfaces), several are much more severe in the AEM case. Specifically, chemical durability, tradeoffs between conductivity and mechanical properties, and water management concerns are greater in AEMs than in PEM systems, while issues of catalyst/electrolyte interactions and durability are much greater concerns for AEMs than traditional alkaline systems.

Alkaline membranes have seen significant advances in performance and durability when employed in fuel cells (AEMFC). In the past few years, AEMFCs have demonstrated current densities above 5 A/cm^2 , power densities of $\sim 2 \text{ W/cm}^2$, and reasonably stable lifetimes (on the order of 1000 hours) (87, 88). These performance levels would not have been imagined only a few years ago and have been possible through the development of improved AEMs and improved electrode performance based on water management and catalyst/ionomer interactions. Membranes with high conductivity that are hydroxide stable at elevated temperatures have now been demonstrated, and a few different ionomer/electrode fabrication routes have shown the ability to achieve high performance and durability. The current gap between alkaline membrane fuel cells and PEM fuel cells is close, as long as exposure to CO_2 is avoided (even ambient air

levels of 400 ppm). This weakness of fuel cell operation can be more easily avoided in electrolysis operation.

While AEMs developed for fuel cells may have relevance in electrolysis, some specific properties may be a concern. For example, AEMs tend to have lower conductivity than PEM systems (in part due to the decreased mobility of hydroxide compared to protons by $\sim 1/2$). Therefore, AEMs often employ polymers with higher ion exchange capacity that typically take up more water and have reduced mechanical robustness. In membrane-based electrolysis, the ability to perform electrochemical compression at differential pressure in the stack is an advantage over separator-based systems, which is lost with poor membrane strength. The large water uptake of these materials also often increases both water and gas transport rates, which are usually advantageous for water but always disadvantageous for gas. These membrane properties have not yet been optimized specifically for electrolysis application and remain a need.

Ionomer:

Ionomers and electrode fabrication also remain major areas of concern where R&D is required. Currently, the best AEM electrolyzer performance relies on the addition of free electrolyte in the water feed and removal of this free electrolyte leads to the loss of hundreds of mV in performance. The underlying reasons for this are not yet understood but are presumably due to catalyst-ionomer interactions that can be influenced by free ions in solution. The addition of free electrolyte has allowed for improved performance and durability; however, performance is still inferior to PEM technology, and durability has not come close to the level demonstrated for either PEM or traditional alkaline technologies. These are some of the most critical areas for determining the ultimate potential of AEMs and will likely see significant effort in the coming years. Unfortunately, a number of the advances made in AEMFCs do not easily translate over to electrolyzers, as water management issues between electrolyzers and fuel cells are quite different.

Electrocatalysts for Alkaline HER and OER:

Fundamental electrocatalysis research efforts for AEM electrolysis has focused on testing in liquid alkaline electrolytes due to the low technology readiness level of AEMs and ionomers. Recent studies have pointed out two issues with R&D in alkaline solutions. First, alkaline electrolytes are inherently contaminated with transition metals, even in the purest solutions (89, 90). These impurities obfuscate the results of many studies in the field, and when acknowledged have spawned new catalysts themselves (91, 92). The second issue is the use of counter electrodes, such as Pt, which dissolve into solution and redeposit on the working electrode (93). While the latter issue is limited to aqueous R&D studies and is not an issue in MEAs, the former is present in both cases and must be monitored.

HER:

To date, reaction mechanism and materials discovery dominate HER catalyst research in alkaline solutions. The HER in alkaline conditions is not as favorable as in acid due to a change in the reaction mechanism. In order to obtain protons for H₂ production, they must be obtained from water, which necessitates a two-step reaction process (94). While high pH allows for use of non-

PGM materials without significant durability issues, the PGM metals are still more active for the HER, with Ir being slightly more active than Pt (we note that there is a strong dependence on the surface state of the Ir used), followed by Ru and transition metals (14, 95). Two prevailing theories are: 1) a bifunctional reaction mechanism dominates the HER under alkaline conditions (92, 96) or 2) promotion of HER activity is due to electronic factors of the compounds used (97). According to the former theory, two sites are required for the reaction, with one site used to split the water and the second to recombine protons to form H₂. The former type of site is dominant on oxide or hydroxide surfaces while the latter type is dominant on metal surfaces. Fully oxidized or fully metallic surfaces under reaction conditions should therefore not be optimal. Ir is most active because it has a mixture of metal and oxide sites while Pt is fully metallic (14). New catalysts are being designed by combining metals and hydroxides in order to promote the HER, such as Pt-Ru and Pt-Ni(OH)₂ (39, 92, 98–100).

Non-PGM materials typically have poor kinetics compared to PGM catalysts, but higher surface area and loading can offset the performance difference while still providing a cost benefit. KOH electrolyzers use Raney Ni and Ni alloy electrodes, due to the low cost of Ni and the ability to create high surface area electrodes in a sheet or mesh format. Because of the highly conductive electrolyte and porous electrode structure, all of the electrode surface is accessible for reaction (101, 102). On the other hand, AEM electrolyzers do not have the capacity to utilize copious amounts of catalytic material due to the limitations of mass transport in MEA-based devices, and therefore require new, innovative catalysts. Development of non-PGM HER catalysts has focused on Ni-based alloys and compounds, but has primarily been performed in aqueous electrolytes. Recently, however, carbon supports have been utilized to make supported electrocatalysts which incorporate well into MEAs. Supported catalysts disperse well in inks and can be distributed into catalyst layers more evenly while creating the necessary porosity and more efficient conducting pathways, while reducing the total amount of electrocatalyst material in the catalyst layer. The most successful examples of non-PGM HER catalyst appear to be those that use a combination of electronic effects and bifunctional mechanisms, including Ni(NiOH)₂, Ni-N, Ni-Cr-Mo (98, 103, 104). The end results in MEA applications have demonstrated that non-PGM catalysts can bring the HER activity within 100mV of PGM catalysts at equivalent current densities (105–107), which may justify their use in applied systems depending on the balance between operating and capital cost.

OER:

As in the acid case, the OER is still the rate-determining reaction for alkaline applications. Generally, the overpotentials required in acid and base solutions for OER reveal that the energetics of the reaction appear to be unchanged (108, 109). This result is surprising since in acid, the oxygen atom for OER comes from splitting of water, while in alkaline solutions, the oxygen atom comes directly from the hydroxide ion. The OER should be a faster and easier reaction in alkaline solution than in acid. Similar to the HER in liquid KOH systems, Raney Ni or similar materials are typically used as the OER catalyst immersed in highly concentrated KOH. At high Ni catalyst loadings in KOH electrolysis, the electrodes are stable for over 50,000 hr. Similar to Ir in PEM electrolyzers, high loadings can mask degradation such that it is unclear

what penalties variable loads and startup/shutdown will have when low catalyst loadings are used in AEM cells.

R&D work for AEM catalysts is divided into mixed metal oxides and transition metals based on Ni. Pyrochlores such as lead ruthenate blends have shown low overpotentials in AEM-based cells owing to the Ru content (110). For non-PGM materials, Ni-based and complex oxides appear to have OER activities that are very similar to Ir, as measured by polarization curves or in MEAs (111). Conductivity losses most likely related to NiO_x formation (passivation) has been demonstrated to be an important factor in alkaline OER as well, with some researchers using Raney Ni as a support to provide conducting pathways which result in activity enhancements compared to unsupported electrocatalysts (112). The most successful examples of non-PGM OER catalysts appear to be those that utilize conductive supports or bulk conductive electrocatalysts, such as Ni-Mo, LiCoO₂, Ni-Fe, La and Pr perovskites (113–121). While use of carbon-based supports is published in some work, it is highly discouraged due to the fact that the carbon readily oxidizes under these OER conditions (122). As in acid OER, a viable conductive and stable support analogous to carbon for the HER is important for alkaline OER.

AEM Integration and Development at Scale:

To reach the target current densities of 1 A/cm² or greater for AEM cells, elements of membrane stability, catalyst activity, and cell design must be integrated. Membrane conductivity and water transport need to be improved to enable higher currents while maintaining reasonable cell efficiency. Stability at higher temperatures would significantly increase the limiting current based on water transport through the membrane. Tuning the hydrophobicity/hydrophilicity of the PTLs can also aid in promoting water transport to the MEA surface where it is needed and preventing the membrane from drying out.

While AEM technology has made significant progress and has the potential to provide benefits over existing technology, the timeline for getting to scale is significant. If and when stable ionomer materials are developed, the qualification time from bench testing through initial commercial cell introduction is at least 3 years, based on the need to scale material production and verify repeatability at reasonable production quantities, as well as obtain sufficient cell testing to demonstrate durability. Product introduction would very likely be at the smallest cell scales, to manage technical risk and get early field data.

Once successfully transitioned to commercial product, the technology still has to be qualified at each production scale. AEM has a large advantage over many other advanced water splitting technologies in that the stack and system designs for PEM systems should be transferable to AEM technology. The MEA materials have to be scaled and tested, which requires at least 12-18 months per transition. At rough scaling factors of an order of magnitude in output per generation, it would take 5 years for AEM technology to get to MW scale from laboratory scale hydrogen generators.

Conclusions:

Interest in large scale electrolysis is growing rapidly and the technology has the potential to be economical compared to fossil fuel derived hydrogen due to the availability of low-cost

renewable electricity sources as well as material and manufacturing advancements which have shown early feasibility. For low temperature electrolysis, there are well-defined strategies for significant cost and performance improvements over the next few years which require investment to accomplish. While new advanced water splitting technologies could eventually displace existing options, KOH and PEM will represent the capacity base for the next 10 years. AEM technology will take several years, even in the most optimistic scenarios, to reach significant deployment and market penetration at MW scale, while other technologies will take even longer, based on the need to design devices and systems as well as integrate new materials. Therefore, research and development should include a mix of technology pathways to integrate advanced components into existing commercial technologies as well as exploring new ideas. Through the development of electrolysis systems, renewable sources of hydrogen have the potential to impact the energy landscape through multiple industries from the industrial synthesis of ammonia and other chemicals to production of renewable fuels.

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