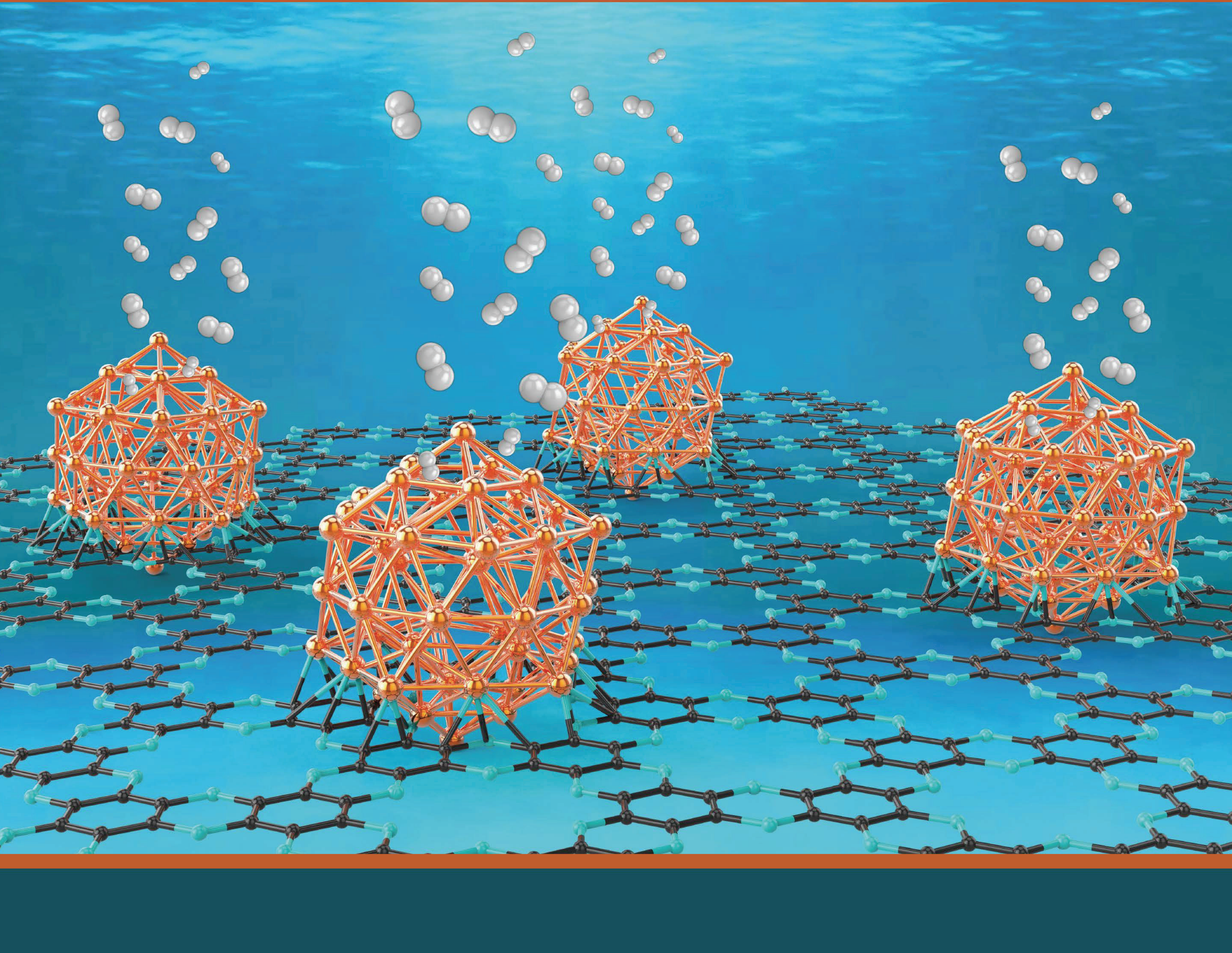
Basic Energy Sciences Roundtable

Foundational Science for Carbon-Neutral Hydrogen Technologies



Report of the Basic Energy Sciences Virtual Roundtable
on August 2-5, 2021

The artwork on the cover illustrates the production of clean hydrogen by water electrolysis.

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Report of the Basic Energy Sciences Roundtable on Foundational Science for Carbon-Neutral Hydrogen Technologies

August 2–5, 2021

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Abbreviations and Acronyms

AEM	alkaline electrolyte membrane
AI	artificial intelligence
AST	accelerated stress test
BES	Basic Energy Sciences
BRN	Basic Research Needs
CT	computed tomography
DFT	density functional theory
DOE	Department of Energy
EERE	Energy Efficiency and Renewable Energy
ESRF	European Synchrotron Radiation Facility
FECM	Fossil Energy and Carbon Management
HER	hydrogen evolution reaction
LA	liquid alkaline
LOHC	liquid organic hydrogen carrier
MD	molecular dynamics
MEA	membrane electrode assembly
ML	machine learning
MOF	metal-organic framework
NE	Nuclear Energy
ORNL	Oak Ridge National Laboratory
PEM	polymer electrolyte membrane or proton exchange membrane
PNNL	Pacific Northwest National Laboratory
PRO	priority research opportunity
SAXS	small-angle X-ray scattering
SOE	solid oxide electrolysis
WAXS	wide-angle X-ray scattering
WE	water electrolysis or water electrolyzer
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction

Executive Summary

The amount of molecular hydrogen used worldwide is enormous; about 70 million metric tons are produced globally every year, with approximately 10 million metric tons produced within the U.S. alone.[1] Hydrogen is used primarily by the industrial sector for oil refining; chemical production, especially for ammonia; steel manufacturing; and transportation fuels. With the recent announcement of the Hydrogen Shot, the first U.S. Department of Energy (DOE) Energy Earthshot, the DOE declared a near-term focus on "accelerating breakthroughs of more abundant, affordable, and reliable clean energy solutions within the decade." Consequently, there is a compelling need for novel approaches to enable hydrogen processes and technologies that do not emit carbon dioxide (i.e., are carbon-neutral). Innovative hydrogen research and development is required to impact how hydrogen is produced, stored, transported, converted, and used. Although progress has been made over the previous two decades, fundamental research can play a critical role in overcoming the technical hurdles that continue to limit implementation of economically viable systems and processes for carbon-neutral hydrogen technologies.

The Office of Basic Energy Sciences (BES)—in coordination with the U.S. DOE technology offices of Energy Efficiency and Renewable Energy, Fossil Energy and Carbon Management, and Nuclear Energy—held a virtual roundtable titled "Foundational Science for Carbon-Neutral Hydrogen Technologies" in August 2021 to discuss the scientific and technical barriers for carbon-neutral hydrogen production, storage, and utilization. The roundtable participants identified four priority research opportunities to address the underlying challenges. These opportunities provide a cogent framework for greatly accelerating the design and development of materials and processes required for carbon-neutral hydrogen systems. Outcomes build upon and go well beyond research opportunities outlined in previous BES workshops and recent DOE reports and identify the most significant avenues for discovering and developing selective, stable, and efficient chemical and materials systems. Such research can create a paradigm shift in the foundational science needed to enable and accelerate progress toward transformative, energy-efficient, carbon-neutral hydrogen technologies.

Innovative scientific breakthroughs are needed in carbon-neutral hydrogen (1) production via water splitting, by catalytic or thermal cracking of methane, from microorganisms under mild biological conditions, or by extraction from biomass, waste and coal through integrated catalytic processes; (2) safe delivery and storage using novel materials- and chemical-based strategies; and (3) utilization across energy-intensive sectors, such as transportation, power generation, and industrial processing. To surpass the boundaries of existing systems, these advances necessitate gaining new mechanistic insights at the molecular level. Breakthroughs can be achieved by integrating novel experimental techniques for materials design, synthesis, and characterization; predictive theory, simulation, and modeling; and analytical data science methods. Such progress can enable innovative chemical and materials synthesis, further our understanding of hydrogen interactions with molecules and materials, facilitate tracking and understanding of the evolution of complex interfaces, and elucidate novel pathways to mitigate critical degradation processes. Research based on the priorities outlined here is expected to greatly influence the production, storage, and utilization of hydrogen-based systems and provide the scientific foundation for clean, future technologies based on the remarkably versatile chemistry of hydrogen.

Priority Research Opportunities for Carbon-Neutral Hydrogen Technologies

Discover and Control Materials and Chemical Processes to Revolutionize Electrolysis Systems

Key question: *How do we codesign multiple components that work together to enable stable, efficient electrolysis for carbon-free production of hydrogen from water?*

Electrolysis requires the coordinated actions of many components under specific operating conditions to achieve high activity and tolerance to impurities in water. To make significant advances, it is critical to achieve a detailed mechanistic understanding of how the material components, systems, and reaction environment work together to produce hydrogen. Understanding multiscale temporal and spatial phenomena is essential for the directed codesign of cost-effective, stable components, including catalysts, membranes, and electrode layers for different operating environments. Toward these goals, the development of in situ and operando characterization techniques and computational and data science tools is needed to capture the evolving complexity of systems under working conditions.

Manipulate Hydrogen Interactions to Harness the Full Potential of Hydrogen as a Fuel

Key question: *What fundamental insights are needed to control and selectively tune hydrogen interactions with molecules and materials?*

Successful carbon-neutral hydrogen technologies require controlling the energetics and mechanisms of hydrogen interactions with molecules and materials. The range of energies that must be controlled spans from weak hydrogen interactions to the strong bond in molecular hydrogen (H_2). Gaining the ability to tune hydrogen interactions for specific binding energies that are stronger than physisorption yet weaker than chemisorption can provide a transformative advance in hydrogen technologies. Mastering this control requires the ability to characterize hydrogen interactions and dynamics for storage and utilization processes at surfaces and interfaces, in molecular species and confined environments, and for integrating these data into predictive models.

Elucidate the Structure, Evolution, and Chemistry of Complex Interfaces for Energy- and Atom-Efficiency

Key question: *How can interacting, evolving interfaces be tailored at multiple length scales and timescales to achieve energy-efficient, selective processes and enable carbon-neutral hydrogen technologies?*

The complexity of the many multicomponent, multiphase interfaces coupled with the reactivity inherent in hydrogen systems presents many challenges. Achieving sustainable processes requires atom-efficient chemical reactions that do not waste atoms or create unwanted by-products. Mapping, understanding, and controlling the spatiotemporal properties and dynamics of complex interfaces involving multiple phases is key to advancing carbon-neutral hydrogen technologies. This major challenge requires the development of integrated, predictive approaches that involve the coupling and parallel application of diverse techniques, including advanced synthesis; ex situ, in situ, and operando characterization; theoretical understanding and modeling from quantum to continuum length scales; data science and machine learning; performance measurements; and multimodal platforms to couple these methods.

Understand and Limit Degradation Processes to Enhance the Durability of Hydrogen Systems

Key question: *How can we identify and understand the complex mechanisms of degradation to obtain foundational knowledge that enables the predictive design of robust hydrogen systems?*

Understanding and mitigating degradation is a formidable challenge in many hydrogen technologies. The lack of mechanistic understanding of multiple degradation phenomena at a molecular or atomic scale is exacerbated by their occurrence over long time periods and the complexity of operating environments. Recognizing the structure–function relationships that govern stability is essential, including performing operando process characterization at interfaces. Such understanding can lead to new design principles and result in more robust, stable materials with significantly enhanced lifetimes, especially when synthesis and performance are coupled with predictive modeling.

1. Introduction

Hydrogen can play a pivotal role in transforming the world's clean energy options and infrastructure, as recognized by the U.S. Department of Energy (DOE) H2@Scale Initiative (**Sidebar 1**).[1] A remaining challenge is the implementation of clean hydrogen solutions that minimize or eliminate carbon dioxide (CO_2) generation. Scientific and technological advances are needed to deploy clean hydrogen technologies across multiple sectors and will require marshalling and coordinating efforts in fundamental research and technological innovations. For a comprehensive clean hydrogen strategy, innovations are needed in *carbon-neutral hydrogen* production, storage, and utilization, where the term carbon-neutral refers specifically to "no net release of CO_2 to the atmosphere." In recognition of the promise of carbon-neutral hydrogen technologies, the DOE announced the first Energy Earthshot, the Hydrogen Shot, in 2021. The Hydrogen Shot sets an ambitious goal of reducing the cost of carbon-neutral hydrogen by 80% to $1 per 1 kg in 1 decade (**Sidebar 2**), highlighting the key role of hydrogen in implementing carbon-neutral solutions.

The versatile chemical reactivity of the hydrogen molecule, H_2, positions it to have a crucial global impact through its use as both an *energy carrier* (i.e., used as a fuel) and a *chemical reactant* (i.e., used in industrial processes). As an energy carrier, the energy in the H_2 bond can be converted to heat by combusting it with oxygen or converted to electricity by splitting H_2 into electrons and protons that react with oxygen to produce water, such as in a fuel cell. H_2 is also an important chemical reducing agent that delivers the electrons in its bond to promote chemical reactions such as the chemical reduction of nitrogen to ammonia. The simplicity of the bond between the two hydrogen atoms belies the complexity of processes required for efficient hydrogen production, storage, and use that are needed to address contemporary global energy challenges.

Hydrogen Production: While the most abundant element in the universe is hydrogen (^1H), only a small amount of molecular hydrogen occurs naturally on earth, and this hydrogen is difficult to collect and use. Hydrogen atoms are mostly found bonded to other elements, such as carbon–hydrogen bonds in hydrocarbons, metal-hydrogen bonds in hydrides, or oxygen–hydrogen bonds in water. To make the quantities of H_2 required for industrial and energy applications, it must be generated through chemical reactions to remove the other elements. Today, more than 75% of the H_2 generated worldwide is obtained from steam reforming of methane (the dominant component of natural gas). Two major problems are inherent in this method for producing H_2: the process is energy-intensive and generates large amounts of CO_2. Currently, making the energy required to reach steam-reforming temperatures of 700–1000°C typically produces CO_2. Additional CO_2 is directly produced from the chemical reaction during the steam-reforming process. Although capturing and storing the CO_2 that is generated can reduce carbon emissions, it is also a process that requires additional energy.

Electrolysis of water to produce H_2 primarily uses electricity rather than heat to drive the water splitting reaction, which can decrease energy consumption. Hydrogen generation by the electrolysis of water[2] was discovered more than 200 years ago. The ostensible simplicity of producing H_2 from water (H_2O), generating only oxygen gas (O_2) as the other chemical product, is innately appealing. If the electricity is generated by renewable energy sources such as wind and solar, electrolysis offers an alternative to H_2 generation with low CO_2 emissions. Electrolysis can use intermittent renewable energy sources during times of low energy demand to make H_2 (storing energy in the chemical bonds); this H_2 can be used to regenerate electricity during periods of high demand, a carbon-neutral approach. Energy storage in chemical bonds provides a complementary strategy to batteries, with both approaches providing attractive qualities over different time frames. Although electrolysis is a promising alternative that offers advantages to methodologies in widespread use today, it currently only contributes a small amount to H_2 production. Many more scientific and technological discoveries are required to propel the electrolysis of water into an energy-efficient, cost-effective process capable of operating reliably at the scale needed to supply the enormous amounts of H_2 necessary, as discussed in this report.

Sidebar 1: DOE's H2@Scale Initiative

As defined on the H2@Scale website "H2@Scale is a U.S. Department of Energy initiative that brings together stakeholders to advance affordable hydrogen production, transport, storage, and utilization to enable decarbonization and revenue opportunities across multiple sectors. Ten million tons of H_2 are currently produced in the United States every year. While most of this hydrogen is produced via centralized reforming of natural gas, deployments of clean alternatives, such as electrolysis, are rapidly increasing. Other emerging approaches include thermochemical water splitting, the use of photochemical cells, and biological pathways."[3] The high energy density of H_2, as well as its flexibility as clean energy carrier and chemical feedstock (**Figure S1**), allows H_2 and H_2-based systems to be integrated across the energy landscape. The enormous challenge of achieving carbon-neutral hydrogen technologies is so complex that a cohesive coalition of scientists spanning a wide range of expertise is needed to address the problem. The premise of the H2@Scale Initiative is that significant advances must be made in producing, moving, storing, and using hydrogen to enable affordable, clean energy. DOE-funded research and collaborative efforts of U.S. national laboratories and industry can play a critical role in accelerating early stage research and facilitate demonstration and deployment of new, clean hydrogen technologies. Emerging applications for H_2 may lead to an increase of 10 times the current global demand.[4] Additional information about the full scope of H2@Scale can be found in reference 1.

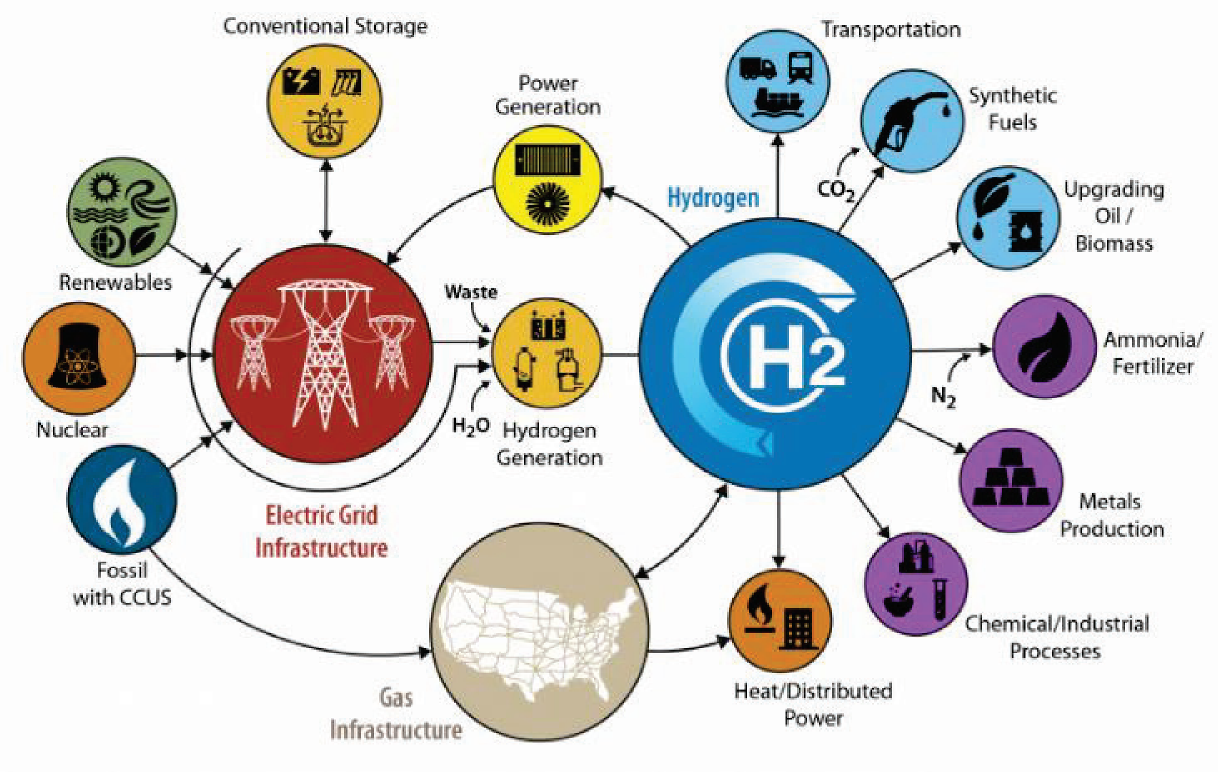


Figure S1. Schematic of the H2@Scale Initiative and the integration of H_2 across energy sectors. Image used with permission of the U.S. DOE.

Sidebar 2: DOE's Energy Earthshots: The Hydrogen Shot

The U.S. DOE announced several new Energy Earthshots to accelerate scientific and technological breakthroughs that will enable clean energy solutions within the next decade. The first of these Earthshots, the Hydrogen Shot, was announced on June 7, 2021, with the "ambitious yet achievable aim of reducing the cost of clean hydrogen by 80% to $1 per 1 kg in 1 decade, e.g., 1-1-1."[5]

Image used with permission of the U.S. DOE.

Innovations realized through the Hydrogen Shot will result in clean hydrogen production and according to Energy Secretary Granholm "will create more clean energy jobs, reduce greenhouse gas emissions, and position America to compete in the clean energy market on a global scale and ensure that environmental protection and benefits for local communities are a priority." The Hydrogen Shot establishes a DOE-wide framework to facilitate and integrate program development and support demonstration projects that will "position the U.S. to compete globally in the clean energy market on a global scale." The first Hydrogen Shot Summit was held virtually August 31–September 1, 2021.[6]

Image used with permission of the U.S. DOE.

Hydrogen Storage: As for most fuels or energy carriers, spatial and temporal mismatches often exist between the locations and time frames of availability compared to when that energy is needed. Thus, hydrogen storage and delivery present many challenges that require further fundamental discoveries. The energy content of H_2 is about three times greater than that of gasoline when evaluated in terms of **mass** (gravimetric energy density). However, because H_2 is a gas at ambient conditions, it has lower **volumetric** energy density by about a factor of four. The energy content of 1 kg H_2 is about the same as that of 1 gallon (3.2 kg) of gasoline. Compressing H_2 for storage to increase the volumetric energy density requires energy. Alternately, converting H_2 to another molecule (chemical storage) or compound can lead to large improvements in volumetric energy density. Advances needed in hydrogen storage include conversion of H_2 into other chemicals for storage (such as ammonia and liquid organic hydrogen carriers) and, equally important, processes that release the H_2 when needed with minimal losses of energy. High atom efficiency is desired so that no chemical by-products are generated.

Hydrogen Use: H_2 is immensely attractive for clean energy because it can be oxidized to produce only water as a by-product. William Grove is credited with the discovery of fuel cells in 1839 that turn hydrogen and oxygen into electricity and water. Thus, hydrogen has long been intimately connected to energy and electricity, and as indicated in **Sidebar 1**, hydrogen has a growing role as an energy carrier in transportation, heating, and power generation.

In addition, **Sidebar 1** identifies diverse industrial processes that use H_2 as a chemical reactant.[1] Hydrogen is envisioned as a pathway to reduce emissions of CO_2 in some industrial sectors where emissions are notoriously difficult to abate. For example, cement production, which accounts for about 8% of all global emissions of CO_2; shipping; aviation; steel production; and long-distance transportation[7] can benefit from technologies that use hydrogen to diminish or eliminate CO_2 emissions.

Although many distinct industries can benefit from carbon-neutral hydrogen, ammonia (NH_3) synthesis and oil refining consume over 85% of the approximately 70 million metric tons of the H_2 currently generated globally. The Haber–Bosch process for ammonia synthesis converts nitrogen (N_2) and H_2 to NH_3 and is considered by many to be a fully optimized chemical process. Most of the CO_2 emissions in the overall process come from the required production of H_2 using steam methane reforming, providing further motivation for carbon-neutral hydrogen production. Moreover, an electrochemical process whereby N_2 is reduced to NH_3 using electrons from renewable energy sources could operate at lower temperatures with reduced energy requirements and much lower CO_2 emissions.[8]

While the focus of this report is on hydrogen, it must be noted that hydrogen chemistry is inextricably connected to the chemistry of oxygen. The oxidation of H_2 at the anode of a fuel cell is balanced by the reduction of oxygen at the cathode, as shown by the reactions below. The reduction of O_2 must be understood and developed further to reach the goal of carbon-neutral hydrogen technologies. The oxidation of H_2 and reduction of O_2 are the two half-reactions used in fuel cells to generate electricity from H_2. The reverse reaction is the electrolysis of water, generating H_2.

$$\begin{array}{c}
H_2 \longrightarrow 2\,H^+ + 2\,e^- \\
{}^{1}\!/_{2}\ O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O \\
\hline
H_2 + {}^{1}\!/_{2}\ O_2 \longrightarrow H_2O
\end{array}$$

Most chemical processes involving H_2 require metal catalysts. The 2017 BES Workshop report "Basic Research Needs for Catalysis Science" describes the fundamental scientific priorities for catalysis to enable clean energy.[9] An overarching problem in catalysis is its reliance on precious metals such as platinum or rhodium, which can cost a thousand times more than earth-abundant metals such as iron.[10] Hydrogen chemistry provides a striking illustration of this conundrum. Platinum is an expensive precious metal used at both the cathode and anode in hydrogen fuel cells, and the high cost and low abundance of platinum deters more widespread use of fuel cells. In contrast, H_2 is generated and used under mild conditions by enzymes in nature exclusively using earth-abundant metals.[11] Hydrogenases are enzymes that accomplish the heterolytic splitting ($H_2 = H^+ + H^-$) using catalysts (mostly iron and iron–nickel) that have evolved over millennia to become extremely efficient. The challenge of emulating the remarkable ability of catalysts in nature by synthetic catalysts has been elusive. Some synthetic catalysts for H_2 production operate at rates even exceeding those in nature, but they fall far short of being as energy-efficient as the hydrogenases and their durability must be enhanced.[12] These observations in H_2 chemistry pose well-defined, but exceedingly difficult problems that challenge the imagination of scientists with expertise in catalyst design, biological function, spectroscopic measurements, electrochemical studies, and complementary computations and modeling. As for the H_2 chemistry described in this report, addressing such monumental problems calls for diverse scientific and technological expertise and for cohesive efforts to address these major issues.

All of these desired technological advances for hydrogen technologies, with their associated consequential environmental and economic benefits, ultimately depend on our ability to understand, and precisely control, the chemistry of H_2, starting at the foundational level of how the H_2 bond is formed and how H_2 reacts with other molecules. This fundamental chemistry must be understood to provide guidance on how to accomplish the technological needs for a secure energy future.

As detailed in this report, essentially all aspects of how hydrogen is currently produced, stored, and utilized must be improved through a synergistic combination of basic scientific approaches to answer fundamental questions. Such changes are recognized to have consequential influences on the myriad industrial sectors that rely on hydrogen (**Sidebar 1**), as scientific research lights the pathway to technological innovations that transform our energy infrastructure. The ultimate goal is a secure energy future that delivers on the long-sought promise of abundant, clean energy.

The Roundtable: The DOE BES Roundtable on “Foundational Science for Carbon-Neutral Hydrogen Technologies” was held August 2–5, 2021, and the roundtable participants were charged with identifying the fundamental research needed to enable carbon-neutral hydrogen technologies. In 2004, one of the first BES Basic Research Needs (BRN) reports, “Hydrogen Production, Storage, and Use - Basic Research Needs for the Hydrogen Economy,” was published.[13] Major scientific and technological advances have been made since the time of that report’s publication, providing a firm foundation for new research opportunities that are described in this report. A crucial difference compared to the previous BRN report is the current emphasis on carbon-neutral hydrogen processes.

The roundtable to establish fundamental scientific research objectives for BES was coordinated with some of the DOE energy technology offices that are part of the DOE Hydrogen Program focusing on more applied topics: Energy Efficiency and Renewable Energy (EERE), Fossil Energy and Carbon Management (FECM), and Nuclear Energy (NE). This synergistic, cohesive, scientific, and technological effort encompassing multiple offices of DOE was needed to achieve the broad, impactful goals for the roundtable. The discussions at the roundtable included the science foundations for the DOE Hydrogen Program Plan[14] and those needed to achieve the goals of the Hydrogen Shot (**Sidebar 2**). Input from multiple DOE offices was critical for the roundtable’s technology status document, a comprehensive summary of state-of-the-art in hydrogen technologies,[15] and to establish a framework to discuss and assess gaps in scientific knowledge. The roundtable participants discussed the fundamental research needed to overcome critical scientific and technological barriers in carbon-neutral hydrogen technologies and identified opportunities for future research directions.

Four priority research opportunities (PROs) were identified that build on foundational studies and define the most compelling opportunities for future research endeavors:

- Discover and control materials and chemical processes to revolutionize electrolysis systems
- Manipulate hydrogen interactions to harness the full potential of hydrogen as a fuel
- Elucidate the structure, evolution, and chemistry of complex interfaces for energy- and atom-efficiency
- Understand and limit degradation processes to enhance the durability of hydrogen systems

It has been more than 250 years since Henry Cavendish discovered hydrogen and called it “inflammable air.”[16] Although today’s scientific progress provides a convincing case for the role of hydrogen for energy technologies, further scientific and technological advances are required to reduce carbon emissions and enable cost effective, carbon-neutral hydrogen technologies. The next section of this report provides in-depth discussion of the four PROs.

2. Priority Research Opportunities (PROs)

PRO 1: Discover and Control Materials and Chemical Processes to Revolutionize Electrolysis Systems

Electrolysis of water to generate hydrogen requires the coordinated actions of many components under specific operating conditions to achieve high activity and tolerance to impurities in water. To make significant advances, it is critical to achieve a detailed mechanistic understanding of how the materials components, systems, and reaction environment work together to produce hydrogen. Understanding multiscale temporal and spatial phenomena is essential for the directed codesign of cost-effective and stable components, including catalysts, membranes, and electrode layers for different operating environments. Toward these goals, the development of in situ and operando characterization techniques and computational and data science tools is needed to capture the evolving complexity of systems under working conditions.

1a. Summary

Electrochemical processes can be used to convert water into hydrogen and oxygen. The energy to drive this endothermic reaction can either be electricity input to an electrolyzer—ideally produced using renewable, carbon-neutral processes—or light coupled directly with a photoelectrochemical cell. Although <0.1% of the hydrogen production worldwide in 2019 was generated by electrolysis, production capacities have increased dramatically over the last decade.[1,17,18] To achieve the very aggressive goals set by the Hydrogen Shot (see **Sidebar 2**), the electrolysis of water can play a huge role in carbon-neutral hydrogen production, especially because a carbon-free pathway for this technology has already been demonstrated at the multimegawatt scale. Water electrolysis (WE) is a likely technology that can be implemented in the near-term, but many fundamental scientific challenges must be addressed to reach the goals set by the Hydrogen Shot.

As described in **Sidebar 3**, an efficient WE cell consists of a series of stacked components creating multiple, complex interfaces (see also **Sidebar 6** in **PRO 3**). In general, both low- and high-temperature cells contain an electrolyte/separator layer with anode and cathode catalyst layers, as well as support layers and flow fields for fluid management. Each cell is separated by a bipolar plate or interconnect. Electrolysis requires the coordinated interactions of many components under specific operating conditions, such as in proton exchange membrane (PEM), alkaline (both liquid alkaline [LA] and alkaline electrolyte membrane [AEM]), and intermediate- and high-temperature (including solid-oxide electrolyte [SOE]) cells. It is critical to achieve a mechanistic understanding of how the multiple components and materials (e.g., catalytic active sites, binders, membranes) and the reaction environment work together to efficiently produce hydrogen. Gaining insight into multiscale temporal and spatial phenomena is essential for the directed codesign of cost-effective, durable, and stable catalyst layer–membrane assemblies under different reaction environments.

Sidebar 3: Stacked Material Components in an Electrolyzer Cell

Electrolyzers are complex devices with individual cells comprised of many different material components stacked together. For example, in the WE cell shown below, the cell comprises (1) an anode side where the oxygen evolution reaction (OER) takes place ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), a Ti mesh flow field, Pt-coated Ti porous transport layer, and an iridium oxide (IrO_2) catalyst layer; (2) a perfluorosulfonic acid proton-conducting membrane; (3) a cathode side where the hydrogen evolution reaction (HER) takes place ($4H^+ + 4e^- \rightarrow 2H_2$), a cathode catalyst layer of carbon-supported Pt nanoparticles, a carbon-based porous gas diffusion layer, and Ti mesh flow field.

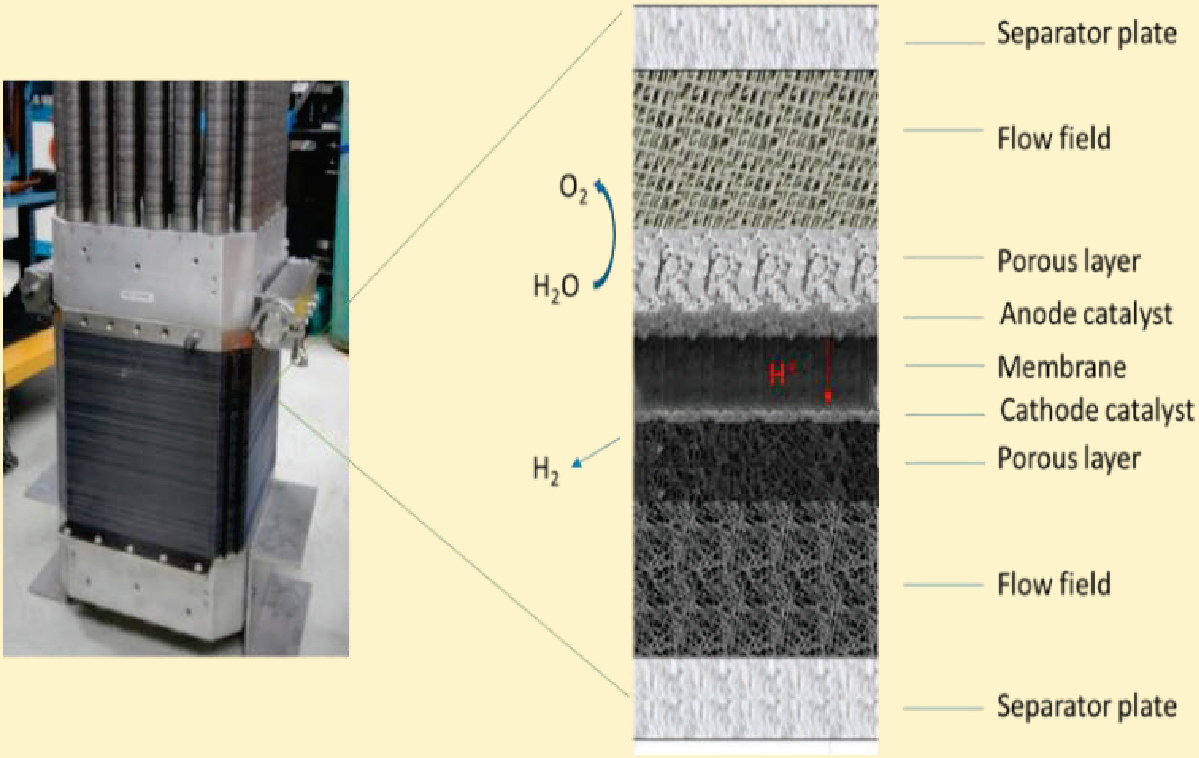


Figure S3. Components of a PEM electrolyzer cell and stack. (Left) Image courtesy of Nel Hydrogen U.S.. (Right) Layered material components forming an electrolyzer stack.[19] Reprinted from A. Villagra and P. Millet, *International Journal of Hydrogen Energy*, **44** 9708–9717 (2019) with permission from Elsevier.

1b. Key Scientific Questions

- How can multiple components be codesigned to work together to enable stable, efficient electrolysis for the carbon-free production of hydrogen from water?

- What are the fundamental differences in reaction mechanisms controlling catalytic activity and stability for the hydrogen evolution reaction (HER) and the OER under different operating conditions, such as acid vs. alkaline environments and low-temperature vs. high-temperature electrolysis?

- What are the fundamental hurdles in developing stable and cost-effective alkaline membranes, and can stable earth-abundant metal catalysts be developed for alkaline HER and OER?

- What in situ approaches are needed to characterize and evaluate changes in membrane and membrane electrode assembly (MEA) properties under relevant operating conditions (aqueous environment, under compression) and understand degradation mechanisms?

- How can the effects of solvent and applied voltage be accurately captured in theoretical modeling of electrolysis?

1c. Scientific Challenges and Research Opportunities

Several research directions must be considered to address the above key scientific questions. As illustrated in **Figure 1-1**, these include the synthesis and characterization of stable and cost-effective MEAs, understanding the reaction mechanisms of the HER and OER as a function of different electrolysis systems and operating environments, developing benchmark materials and procedures for activity and stability evaluation, and advancing in situ/operando and modeling/data science tools. Since WE can occur under different operating environments (e.g., PEM, alkaline, and high-temperature devices), this report identifies and includes research opportunities that are specific for these environments.

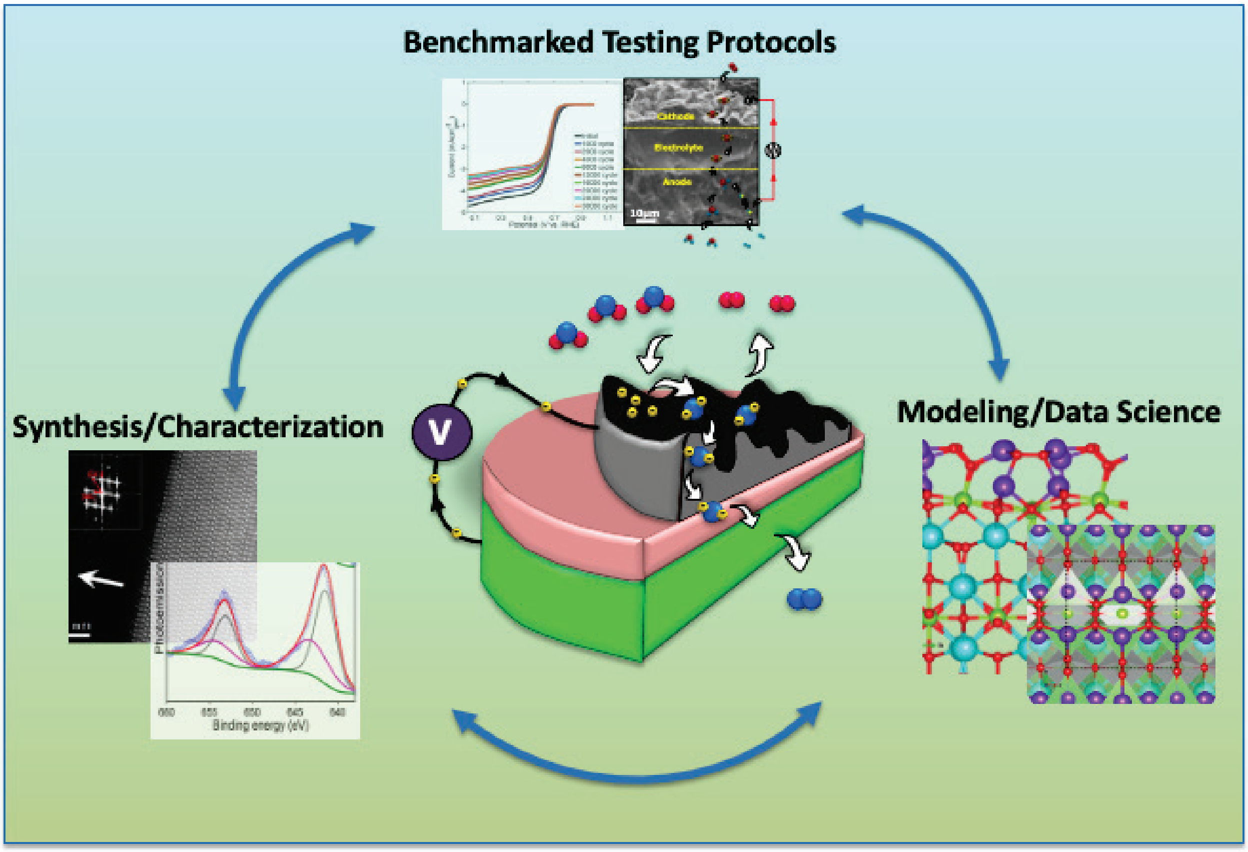


Figure 1-1. Research directions in water electrolysis, including advancements in catalyst synthesis and characterization, membranes and interfaces, development of testing protocols, and innovations in modeling and data science methodologies. Image courtesy of Eranda Nikolla, Wayne State University.

PEM electrolyzers are a commercial technology that can operate under ambient conditions with a quick response rate to generate high-purity hydrogen at high current densities. However, capital cost reductions and efficiency improvements are required to expand into emerging energy markets and reach parity with hydrogen derived from fossil fuel sources. The major contributions to efficiency loss are membrane thickness and the large activation overpotential for the OER on the anodic side.[1,17-20]

Alkaline electrolyzers can be classified into two types: those that use a liquid potassium hydroxide electrolyte at a concentration of 25–30% imbibed into a porous separator and those that use a polymer membrane electrolyte with cationic functional groups, termed an anion exchange membrane (AEM), that selectively conducts hydroxyl ions. LA-WE is an established technology, while AEM-WE technology is still largely in the research and development stage. AEM-WEs have attracted significant recent interest because they can support pressurized operation, transient input power, and notably higher current densities compared to LA-WEs.[21]

Intermediate- and high-temperature solid oxide electrolysis (SOE) cells are divided in two categories: electrolysis cells that contain oxygen ion-conducting oxide membranes and proton-conducting solid oxide electrolyte systems.[22] SOE cells with oxygen ion-conducting electrolytes are the more mature of the two technologies and typically use an yttria-stabilized zirconia (YSZ) electrolyte. Proton-conducting SOE cells largely use Ba–Zr and Ba–Ce doped yttria electrolytes.[23] Proton mobility in proton-conducting cells is more facile than oxygen ion mobility, allowing intermediate cell operating temperatures (400–700°C).[24]

Advancing electrolysis systems requires the scientific knowledge gained from addressing the following challenges:

- Understand catalyst activity, stability, and durability and elucidate elementary reaction steps in HER and OER
- Polymer/membrane degradation, particularly at higher temperatures
- Development of in situ and operando characterization tools to understand dynamical change under realistic operating conditions

Understand catalyst activity, stability, and durability and elucidate elementary reaction steps in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)

Understanding the factors contributing to catalyst chemical and structural stability and size and compositional variability (including in commercial catalysts) are important areas of research to advance WE.[25,26]

Elucidating the interactions between the electrocatalyst and monomers/binders and how this impacts activity and stability is of critical importance. The development of active and stable platinum group metal–free electrocatalysts for water oxidation and the HER is another important research direction. Furthermore, proton transport is a critical factor in water oxidation. Design of second coordination sphere functionalities in molecular complexes can facilitate the understanding of proton removal and how these factors influence reaction kinetics and overall efficiency, which can include hydrogen bond acceptors and modifications of the local proton activity. These effects can then be replicated using the local microenvironment around catalyst active sites in anodic materials.

Questions remain about the formation of the oxygen–oxygen bond in water oxidation that are important for developing improved anodic catalyst materials under all conditions. Two different classes of mechanisms have been proposed (**Figure 1-2**)—nucleophilic attack of a hydroxide ion on an electrophilic metal oxo, or radical oxygen coupling.[27] On surfaces, these two mechanisms are sometimes described by an oxygen–oxygen bond that can be formed either through two absorbed water/hydroxide molecules or through the participation of lattice oxygen. These mechanisms have been investigated computationally and spectroscopically on some heterogeneous catalysts, which indicate the mechanism may change as a function of applied potential and/or restructuring of the catalysts, and likely depend on the solution pH and electrolyte identity.[28] The relative energetics and kinetic limitations of each reaction pathway can be investigated in more detail using molecular catalysts that can tune the radical vs. electrophilic nature of metal-oxo intermediates through the ligand environment and oxidation state. The electronic structures of homogeneous complexes are more easily determined using spectroscopic techniques. Mechanistic studies can also be used to identify the most likely catalytically active species and quantify the relative reactivity of these intermediates with water and hydroxide to determine the kinetic limitations of each pathway. These studies can be translated to heterogeneous materials by modifying the primary environment around active sites[27] and how their electronic structure changes with applied potential. Investigations into how the catalyst interface and electrolyte modify the nucleophilicity of hydroxide can also provide information about achieving optimal catalyst performance depending on the primary reaction mechanism.

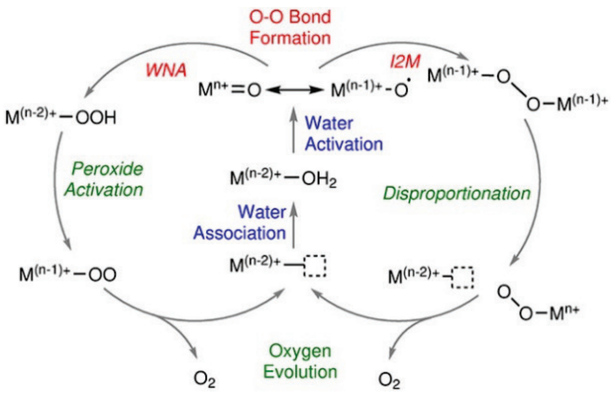


Figure 1-2. Depiction of two major mechanistic pathways for oxygen–oxygen bond formation.[28] Image reprinted from Schilling and Luber, *Front. Chem*. under Creative Commons Attribution 4.0 International (CC by 4.0). Copyright © 2018 Schilling and Luber.

An area for improvement in both efficiency and cost for WEs is the anode catalyst. These catalysts are typically composed of precious metals (iridium or ruthenium) that operate at high overpotentials. Establishing the fundamental chemistry of earth-abundant metals is required to design new catalysts that do not rely on precious metals. In the near term, lowering the catalyst loading and improving electrode processing can provide improvements. To this end, understanding and reducing the costs of catalyst supports can improve activity at lower catalyst loadings.[29] Additionally, developing methods for rapid and precise deposition of material can also improve manufacturing time and costs. For any new catalyst, long-term stability will be critical (see **PRO 4**). Methods for evaluating activity over time, as well as morphological changes under operating conditions, are critical in this regard.

Research should also focus on establishing benchmark catalysts (especially for the OER), protocols, and metrics that extrapolate catalyst performance from well-defined three-electrode systems to electrolyzers and scaled-up operations.[30] Identification of benchmark catalyst properties and compositions and possibly synthesis methods are of interest so that catalyst comparisons can be done across the board and effectively used for development of data science approaches that enable connections/correlations across large reported data sets.

Areas of catalyst research in intermediate- and high-temperature SOEs include understanding stability and potential regeneration of the catalysts under prolonged exposure to elevated temperatures and complex gas atmospheres. Anodic and cathodic atmospheres commonly used in steam electrolysis can accelerate metal corrosion, change oxide defect chemistry, and modify bulk metal microstructures. A critical research area for stable long-term performance of SOEs is to develop a mechanistic understanding of the chemical and morphological degradation of metal and oxide catalysts, and dopant exsolution in multi-cation oxide catalysts under complex WE atmospheres.

Polymer/membrane degradation, particularly at higher temperature

Water management and its impact on the strength and stability of membranes and separators are critical factors for both low- and high-temperature technologies. Polymer membranes (PEM and AEM) absorb significant amounts of water (typically 30–40% by weight) under fully flooded and hydrated conditions.[17] The impact of this swelling on membrane strength (compressive and tensile) is difficult to determine because of a lack of characterization tools to measure membrane swelling in liquid water. However, empirical observation indicates that much thicker membranes are required for electrolyzer operation vs. fuel cell operation, even at lower hydrogen generation pressures. Quantitative understanding of the influence of liquid water absorption on ion exchange membranes, including under compressive loads, would enable the rational design of polymers for electrolyzer cells with clear targets and the ability to predict in-cell performance without requiring tests for tens of thousands of hours. New membrane materials must be compatible with the interface and diffusion kinetics of catalyst preparations.

Proton conductors have been shown to exhibit high degradation in the presence of liquid water;[23,31] however, the mechanisms for this degradation are not well understood. Developing an understanding of water reactivity with ceramic membranes is an important research direction toward the design of stable intermediate temperature proton conducting membranes.

Develop in situ/operando characterization tools to understand dynamical change under realistic operating conditions

The chemical and electrochemical transformations that govern the performance of electrolyzers are dynamic and molecular/atomic in nature. They are induced by chemical, electrical, and mechanical stimuli. To fully understand these processes, new characterization tools are needed that can be employed under conditions that mimic those encountered in practical applications and provide sufficient spatial and temporal resolution to define the underlying molecular phenomena. A critical question for electrolysis is how the properties of the MEAs change under electrochemical conditions. Ideally, in situ/operando measurements should reveal the following properties during reaction: (1) the oxidation state and local coordination environment of the metal catalysts change, (2) structural and chemical stability of the membrane, and (3) reaction intermediates formed and identification of other adsorbates on the surface of the catalysts. One research direction is to perform simultaneous measurements of all these properties using synchrotron-based techniques equipped with in situ cells. For example, in situ cells can provide capabilities for the synchronous measurements of X-ray absorption spectroscopy (XAS) for electronic properties and local structural arrangement, X-ray diffraction (XRD) for long-range order of materials (see **Sidebar 7**), and diffuse reflectance infrared Fourier transform spectroscopy to identify adsorbed species. For liquid phase reactions such as electrolysis, in situ/operando cells can be modified to include Raman spectroscopy to characterize surface intermediates. Multimodal XAS/XRD/Raman capabilities can address complex problems across multiple scales that can allow direct correlation between changes in the electronic/structural properties with the reaction pathways occurring within MEAs and their interfaces under different electrochemical reaction environments.

Advances in computational methods and tools are also needed that more accurately represent the operating environment of components and materials in an electrolyzer, including catalysts and polymers. The synergistic coupling of computational methods with experiment to predict, validate, and understand catalyst/polymer performance requires that the computational approach account for key aspects of operation such as solvation, electric fields, and the electrochemical environment (e.g., pH, cations, and anions). Development of computational and experimental approaches to tackle multiple length scales and demonstrate predictive capabilities for guiding experimental work is a critical research direction. Furthermore, another essential tool is the advancement in data science methods that can be effectively coupled with experimental work to provide missing or new correlations across large data sets, enabling predictive learning to support accelerated experimental findings.

1d. Potential Impacts

Addressing the scientific challenges in this PRO can have significant scientific impact on enhancing the mechanistic understanding of water electrolysis to accelerate innovations enabling carbon-neutral hydrogen production. Below is a summary of potential scientific impacts:

- Demonstrate the design of electrolysis systems with optimized combinations of multiple components, catalysts/membranes/binders, from a bottom-up rational design approach rather than empirical trial and error

- Compare activity, stability, and reaction mechanisms for the HER and OER under different operating environments, such as PEM vs. alkaline (both liquid and membrane) and low-temperature vs. high-temperature electrolysis

- Advance catalyst and membrane understanding that can be applied to other electrocatalytic reactions and electrochemical devices

- Develop characterization and computational/data science tools that can be used for other electrochemical applications

The research opportunities described in this PRO demonstrate how fundamental research can have significant impact on technological approaches to low-cost clean hydrogen production, which is the focus of DOE’s Hydrogen Shot (**Sidebar 2**). Water electrolysis represents a very promising technology for the carbon-neutral production of hydrogen within the next decade. Therefore, addressing the fundamental scientific issues can advance WE to the scale and cost that are compatible with the Hydrogen Shot goals.

PRO 2: Manipulate Hydrogen Interactions to Harness the Full Potential of Hydrogen as a Fuel

Successful carbon-neutral hydrogen technologies require controlling the energetics of hydrogen interactions with molecules and materials. The range of energies that must be controlled spans from weak hydrogen bonding interactions to the strong covalent hydrogen–hydrogen bond of molecular H_2. Interactions in which the hydrogen–hydrogen bond is retained, though often significantly weakened, are crucially important to understand and control. Gaining a fundamental understanding of how hydrogen binds to metals, and how the H–H bond is cleaved in molecular systems or materials, is pivotal to the use of hydrogen as a chemical reactant or as an energy carrier. Interactions of H_2 have a key role in realizing the full potential of carbon-neutral hydrogen technologies, including production, storage, and use. This PRO is primarily focused on the scientific barriers encountered in storage. Attaining the ability to tune hydrogen interactions for specific binding energies that are stronger than physisorption, yet weaker than chemisorption, would offer a transformative advance in hydrogen technologies. Mastering this control requires characterization of hydrogen interactions and dynamics for storage and utilization processes at surfaces and interfaces, in molecular species and in confined environments, and to integrate these data into predictive models.

2a. Summary

Current technologies for the storage and transport of hydrogen include physical and materials-based storage (**Figure 2-1**).[32] Physical storage systems are more extensively developed and have focused on cryogenic or compressed gas systems because of the low volumetric density of hydrogen compared to conventional fossil fuels. These technologies, however, are hampered by compatibility issues of the materials and extremes in operating temperature and pressure. A recent assessment of hydrogen storage strategies[33] suggests that key performance targets for improving storage systems should focus on an operating temperature in the range of −40 to 85°C and a minimum delivery pressure of 5 bar. Cryogenic systems obviously require a much lower temperature, and compressed gas systems operate at pressures as high as 700 bar.

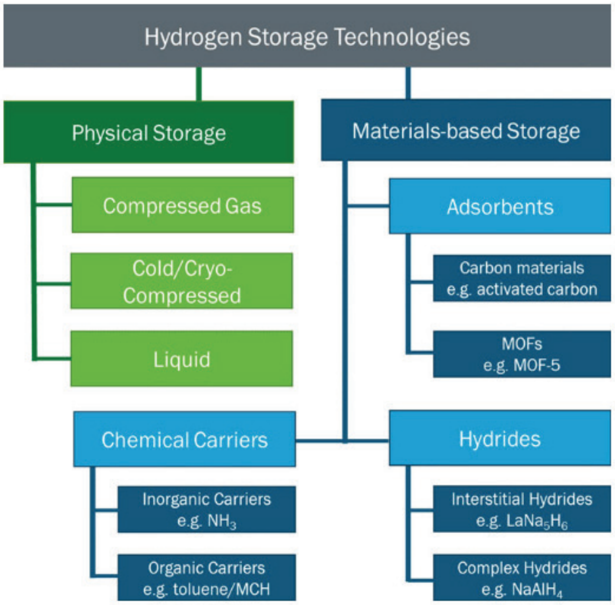


Figure 2-1. Overview of physical and materials-based hydrogen storage technologies (MCH = methylcyclohexane; MOF = metal organic framework).[32] Republished with permission of Springer from M. Wieliczko and N. Stetson, *MRS Energy & Sustainability*, **7** 1-9 (2020); permission conveyed through Copyright Clearance Center. Inc.

Materials-based systems for hydrogen storage present attractive alternatives to the physical storage of H_2 as a liquid or compressed gas, offering the possibility of high-density, large-scale storage of hydrogen for long durations, providing opportunities for decarbonization of both stationary and transportation applications. Strategies for designing materials for hydrogen storage are focused on three classes of materials that encompass the extremes of energies of hydrogen interactions: adsorbents, chemical carriers, and interstitial/complex metal hydrides. Adsorbents interact with hydrogen through weak physisorption with a heat of adsorption typically less than −7 to −10 kJ/mol, so ambient temperature storage of hydrogen at a high capacity is not feasible. At the other extreme of energy, chemical storage systems such as chemical carriers and metal hydrides involve cleavage and regeneration of strong chemical bonds, requiring thermal energy and often catalysts to break the X–H (X = B, C, N, O, or metal) bond to generate and release H_2.[34]

To address challenges in hydrogen storage, a variety of storage modes and their potential pitfalls must be considered. A common scientific challenge across all current storage modes is that hydrogen physisorption is too weak and X–H bonds are too strong for an efficient storage process; a "just right" interaction with hydrogen is needed to bridge this energetic gap (see **Sidebar 4**). Uncovering the fundamental science required to create storage materials with prescribed hydrogen interactions provides a major challenge and a compelling research opportunity in chemical reactivity, materials chemistry, catalysis, and adsorption.

2b. Key Scientific Questions

- What fundamental insights are needed to control and selectively tune hydrogen interactions with molecules and materials?
- Can new insights in hydrogen interactions be exploited to control the kinetics and transport phenomena at surfaces, at interfaces, and in confined environments?
- What experimental and computational methods are needed to determine and understand the energetic landscape of hydrogen interactions with molecules and materials?

2c. Scientific Challenges and Research Opportunities

Systematic methods for tuning hydrogen interactions with materials-based storage systems or chemical carriers are currently limited, and there is little rational basis to guide the selection of materials or molecular features to target for tuning the interactions. To achieve transformational advances in hydrogen storage, new fundamental knowledge is needed to guide the design of materials with prescribed energetics. Whether the goal is to design a porous material for adsorptive storage or a catalyst for the release of hydrogen from liquid or solid phase storage materials, experimental and computational methods must be developed that provide insights on the nature of bonding interactions, the nature of diffusion properties, the role of steric hindrance, and the energetic landscape of the entire system. Key opportunities in hydrogen storage include:

- Designing materials that interact with hydrogen in an energy regime between physisorption and strong X–H bonds
- Elucidating methods for the design of robust, unconventional catalysts for hydrogen uptake and release in storage materials
- Understanding changes in hydrogen interactions and evolution of materials over long timescales

Design materials that interact with hydrogen in an energy regime between physisorption and strong X–H bonds

The ability to tune hydrogen interactions over a range of energies has long been sought. Storing hydrogen at ambient temperature requires adsorption energetics within the range from -15 to -25 kJ/mol.[33] Hydrogen spillover in carbon nanotubes was proposed as a potential weak chemisorption mechanism for enhancing hydrogen adsorption interactions at ambient temperatures.[35] Following adsorption, dissociation of the hydrogen–hydrogen bond of H_2 occurs, followed by surface diffusion of hydrogen atoms on the support. Several features, including defects, functional groups, catalyst dispersion, and catalyst-support interactions, all play a complicated role in the spillover process that is still not well understood. Although hydrogen sorption via a spillover process is of considerable scientific interest,[36,37] some limitations are recognized for application to transportation or stationary applications. An example[33] of tuning hydrogen binding energies in a metal-organic framework (MOF) that adsorbs substantial amounts of hydrogen at ambient temperature is described in **Sidebar 4**.

A fundamental gap in scientific knowledge concerns the nature of bonding interactions and the dynamics of gas–solid interactions in the region between classic physisorption (H_2 binding enthalpy) and chemisorption (enthalpy of hydrogenation). Developing materials that offer an optimal heat of adsorption for hydrogen requires knowledge of the gas sorption properties in this energetic realm. Understanding the mechanisms that control the interactions is especially important to enable the development of reliable strategies to obtain adsorption behavior over a wide range of hydrogen capture and sorption energetics (see **Sidebar 5**).

Specific information about the binding energies, binding sites, role of steric hinderance, and permeation and diffusion properties are of key importance. An equally crucial requirement in meeting this challenge is the development of first principles modeling (e.g., ab initio molecular dynamics) to extrapolate experimental data to enable the prediction of preferential adsorption or materials stability. Novel syntheses, new or repurposed experimental techniques, computational tools, and machine learning (ML) are required to address these challenges.

The approaches described above focus on *strengthening* hydrogen interactions, but materials such as hydrogen-containing solids and liquid carriers require strategies for *weakening* hydrogen interactions. A successful approach for reducing the binding energy (enthalpy of adsorption) of hydrogen in molecular compounds has been demonstrated in bifunctional Lewis acid/base pairs (**Figure 2-2**).[38,39] The B–H and P–H bonds are strong, but when prepared in the same molecule, uptake of molecular H_2 occurs at temperatures significantly lower than in conventional materials.[38]

Understanding how to tune the binding energy of hydrogen in bifunctional molecules could lead to the development of new materials and approaches to store hydrogen. The families of interstitial metal hydrides cover a wide range of energetics (**Figure 2-3**), and an improved fundamental understanding of the nature of the interactions of hydrogen with metals could provide insight into the development of a new class of materials with greater gravimetric hydrogen density to enable envisioned clean energy applications.[40]

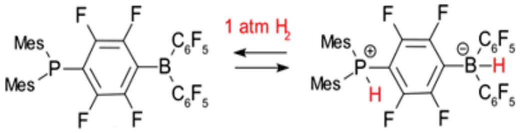


Figure 2-2. The binding energy of hydrogen (enthalpy of hydrogenation) to molecular Lewis acid/base pairs can be tuned over a broad range of energies by manipulating the hydride affinity of the acid and the proton affinity of the base.[38] Image from D. Stephan, "The Broadening Reach of Frustrated Lewis Pair Chemistry," *Science*, **354** aaf7229 (2016). Reprinted with permission from AAAS.

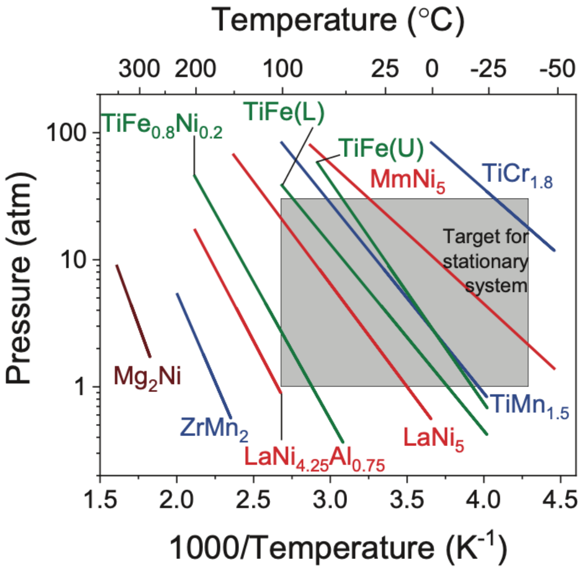
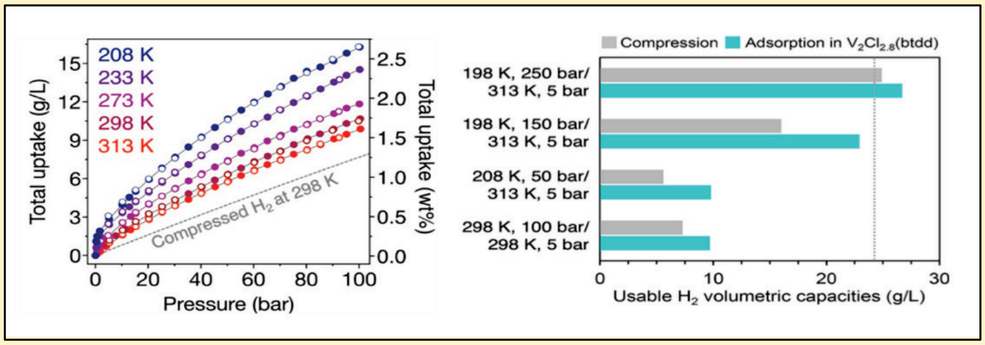


Figure 2-3. van't Hoff plots showing a wide range of hydrogen interaction energies measured in interstitial metal hydrides with estimated targets for stationary applications.[40] Image reprinted from Modi and Aguey-Zinsou, *Front. Energy Res.* under Creative Commons Attribution 4.0 International (CC BY 4.0). Copyright © 2021 Modi and Aguey-Zinsou.

Sidebar 4: Creating Weak Chemisorption Sites for Hydrogen in a Metal Organic Framework

New approaches are needed to increase hydrogen binding strengths and adsorptive storage capacities to exceed capacities that are possible with high compression (350–700 bar). The chemistry of H_2 with metals or complexes where π-basic metal sites and dominant orbital interactions play a critical role in hydrogen binding, provide a framework for creating materials with weak chemisorption (or strong physisorption) sites for hydrogen. Organometallic complexes that bind H_2, a landmark discovery by Kubas and coworkers,[41] bind hydrogen by donation of electron density from π-basic metal sites into the lowest unoccupied orbital of hydrogen. The tungsten complex $W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)$ has a hydrogen binding enthalpy of −80 kJ/mol, which is too strong for hydrogen storage applications, but it provides a model for manipulation of hydrogen binding enthalpies.

Based on results from the tungsten complex, it becomes clear that target storage materials should incorporate less reducing, weaker π-basic metal sites, such as divalent first-row metals, to achieve binding enthalpies in the desired range from −15 to −25 kJ/mol. **Figure S4** describes a recent example of a MOF created from weaker π-basic sites through vanadium(II) coordination using a H_2btdd ligand (H_2btdd = bis(1*H*-1,2,3-triazolo[4,5-b],[4′,5′-*i*])dibenzo[1,4]dioxin).[41] Complexation of H_2 to a V^{II} site results in a hydrogen binding energy of −21 kJ/mol. From **Sidebar 5**, the performance of this material is within the optimal energetic range for H_2 storage, although the gravimetric capacities are low. Hydrogen adsorption isotherms over a temperature range of 208–213 K (**Figure S4A**) show the volumetric uptake of hydrogen, which exceeds the volumetric density of compressed hydrogen at 298 K. Comparison of H_2 adsorption in $V_2Cl_{2.8}$(btdd) with compressed storage (**Figure S4B**) illustrates that the volumetric adsorption capacity of H_2 in this MOF is ~30% greater than the capacity of H_2 obtained through compression under the same conditions.



(*A*) (*B*)

Figure S4. (*A*) Hydrogen adsorption isotherms obtained for $V_2Cl_{2.8}$(btdd) compared to volumetric density of compressed hydrogen at 298 K. (*B*) Comparison of usable volumetric H_2 capacities using $V_2Cl_{2.8}$(btdd) and compression at four different conditions for loading/discharge. The dotted gray line represents the usable volumetric capacity for 350 bar H_2 compressed storage at 298 K.[34] Reprinted with permission: D. Jaramillo, et al., *Journal of the American Chemical Society*, 143 6248-6256 (2021). Copyright 2021, American Chemical Society.

Sidebar 5: Defining the Optimal Range of Enthalpies of Reaction (Adsorption or Hydrogenation) in H_2 Storage Materials

The optimal range of enthalpies of reaction (adsorption or hydrogenation) is derived from the Gibbs free energy change (ΔG) of reversible hydrogen uptake. For a pressure swing between 5 and 100 bar at 298 K, the optimal ΔG is ca. 8 kJ/mol, which includes contributions from entropy (ΔS) and enthalpy (ΔH) shown by the blue dashed line in **Figure S5**. Sorbents have a typical ΔS of ca. 65–100 J/K/mol, leading to an optimum ΔH between ca. 15 and 25 kJ/mol H_2, which is two to three times greater than that of conventional adsorption enthalpies and requires subambient temperature operation. The ΔS for complex hydrides, metal hydrides, and liquid organic hydrogen carriers (LOHC) falls in the range of 110–130 J/K/mol. For a temperature range between 298 and 398 K (red dashed line in **Figure S5**), the optimal ΔG spans 8–10 kJ/mol H_2, leading to an optimal ΔH between 25 and 40 kJ/mol H_2. This is significantly lower than the strength of a typical chemical bond, requiring high temperatures to release hydrogen.

Thus, an understanding of how to manipulate and control hydrogen interactions between conventional physisorption and hydrogenation is required to harness the full potential of H_2 as a fuel. This challenge needs to be met without losing sight of kinetics and capacities. For example, $NaAlH_4$ and $V_2Cl_{2.8}$(btdd) are within the optimal range but suffer from slow kinetics and low gravimetric H_2 capacity, respectively.

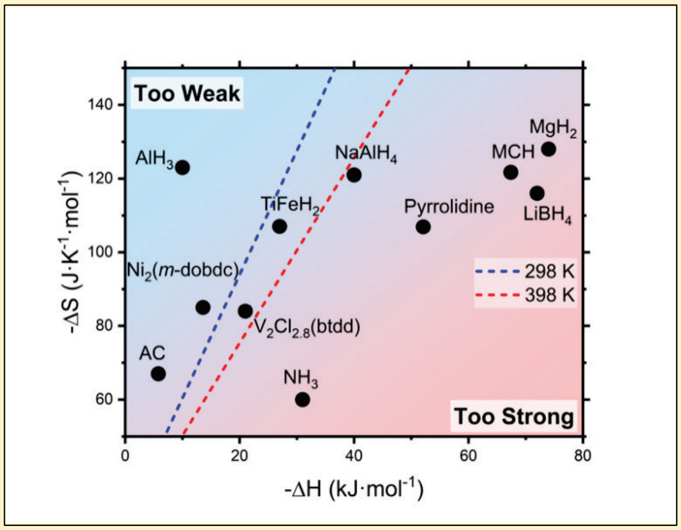


Figure S5. Plot of the range of enthalpy (ΔH) and entropy (ΔS) that can provide the optimum Gibbs free energy (ΔG) for the reversible binding of H_2 to sorbents or chemical storage materials. The blue dashed line represents the optimal ΔG (ca. 8 kJ/mol) at 298 K for a pressure swing between 5 and 100 bar. The red dashed line is the optimal ΔG (ca. 10 kJ/mol) at 398 K for a pressure swing between 5 and 100 bar. (AC is activated carbon). Image used with permission of Mark Bowden and Tom Autrey, Pacific Northwest National Laboratory.

Elucidation of methods for the design of robust, nontraditional catalysts for hydrogen release and uptake in storage materials

Experimental and computational studies to gain insight into the key mechanistic pathways and rate-limiting steps constitute a critical foundation for developing a rational approach to enhance rates, selectivity, and stability of catalytic reactions. New methods are being developed to provide insight into the factors that determine the strength of hydrogen–metal interactions in frameworks, but as described above, there is a need to complement these approaches with the development of new methods to understand the factors that determine the magnitude of hydrogen–metal interactions in the condensed phase (e.g., hydrogen interactions with catalysts in an aqueous or organic solvents).[42] This insight provides a critical understanding to control and tune binding energetics in the condensed phase in a manner that parallels the gas phase. Addressing these challenges can provide an understanding about how the presence of solvents alter the energetics of several reactions, such as the hydrogenation of storage materials.

Additional challenges in catalysis must be addressed related to the release of hydrogen from liquid phase storage materials. For example, heterogeneously catalyzed formation of H_2 gas in the liquid phase presents a three-phase challenge[43] of keeping the surface of the catalyst wetted with the LOHC while gas bubbles are forming.[44] Computational modeling of the release of hydrogen over extended time- and length-scales can provide the insights needed to help address this challenge. Homogeneous catalysts avoid the three-phase problem; if separations are problematic, the catalyst would need to be active for both release and uptake of hydrogen.[45] A homogeneous catalyst would remain in the same phase as the LOHC, creating a challenge for large scale energy storage (megawatts to gigawatts) related to the preparation of highly active catalysts from earth-abundant metals and inexpensive ligands that are stable at high temperatures.

Prominent advantages of LOHCs are their ability to store energy in chemical bonds for long durations and for transport over long distances.[46] Examples include methylcyclohexane (MCH), *N*-ethylcarbazole, and perhydro-dibenzyl toluene. Because of the strength of the interactions of hydrogen with the carrier material (containing a covalent carbon–hydrogen bond), catalysts are needed for both loading and releasing hydrogen efficiently to and from the storage material. Catalyst durability is crucial and understanding the mechanism of the catalyzed reaction pathway is essential. Avoiding catalyst deactivation is also necessary for hydrogen storage applications requiring hundreds or thousands of hydrogenation/dehydrogenation cycles (see **PRO 4**).

Insight about deactivation can guide approaches to design more robust catalysts. An iterative combination of experimental and computational tools can provide the necessary insight for developing approaches to minimize catalyst deactivation. For example, in the catalyzed release of hydrogen from MCH, hydrogen is used as a carrier gas to prevent coking and reduce unwanted side reactions. If the catalyst is deactivated, is facile operando reactivation feasible?

Novel catalytic reactions in the solid state have been one of the most important developments in hydrogen storage during the last 25 years. The seminal discovery of titanium(III) enhancement of hydrogen cycling kinetics in solid sodium alanate ($NaAlH_4$) opened the door to the consideration of complex hydrides as viable hydrogen storage materials.[47,48] Although many hypotheses have been advanced, there is no widely accepted description of the mechanism responsible for the kinetic enhancement of the reversible hydrogenation throughout the bulk solid.[48] Related examples of solid-state catalysis have been observed, but mechanistic understanding remains elusive. Filling this gap in the fundamental understanding of solid-state catalytic effects stands as a frontier research opportunity and is key to the development of complex hydrides for practical hydrogen storage applications. To address these challenges requires new experimental and computational approaches that can provide insight to guide the development of new catalysts and materials.

Understand changes in hydrogen interactions and evolution of materials over long timescales

The ability to use a hydrogen storage material or a catalyst for extended periods is often hampered by unwanted side reactions, the presence of impurities in the hydrogen, or both. Hydrogen adsorption materials have differing forms and phases, each with distinct strengths and weaknesses in terms of stability and evolution over time. Understanding and enhancing stability is particularly important for long timescales that are necessary for large-scale storage in a distributed energy infrastructure. Embrittlement remains a concern for both metal-based hydrogen storage materials (e.g., hydrides) and containers (metals, stainless steel).[49] Understanding the correlation between the alloy–hydrogen structure and the hydrogen adsorption/desorption thermodynamics can facilitate the design of durable phases for high hydrogen content storage and long-term durability. Similarly, containers that have voids, dislocations, grain boundaries, and precipitates can include additional hydrogen trapping sites[49] that may lead to embrittlement of the metals, further inhibiting desorption.

In addition to embrittlement concerns for pipeline materials, storage materials are also susceptible to degradation resulting from other compounds mixed with the hydrogen. Of particular concern are H_2O and O_2 from exposure to air. Chemical reactivity, such as preferential energetics of binding of species other than H_2, may change the local environment at the binding sites. This has been shown for species co-adsorbed with water in hydrophilic MOFs, where initially there is preferential binding of H_2O until a nearly equally energetically favorable gas is co-adsorbed at the metal center, rendering the pore wall hydrophilic and allowing for enhanced physisorption of additional species besides water.[50] These issues may be overcome by using H_2-sized selective porosity in a nanoporous phase (e.g., porous carbons), capture during spillover events using metal catalysts on carbon supports, or a combination of both approaches.[42,51,52] Metal hydrides must also overcome problems arising from impurities, and there is a need to enhance tolerance to impurities that can lead to irreversible reactions with water instead of hydrogen.[51]

In addition to the stability of materials, selectivity is critical for the efficiency of hydrogen adsorption/desorption cycles. Irreversible side reactions can rapidly degrade hydrogen storage materials, illustrating the need for highly selective catalysts for the release of hydrogen to make products that can be readily hydrogenated to regenerate the hydrogen storage material. For example, a reaction that is only 99% selective is not sufficiently stable for 100 cycles, even if only 1% of the reaction is irreversible. Thus, it is imperative to develop and design catalysts with extremely high selectivity for the release and uptake of hydrogen. Additives have been reported to enhance the selectivity in a range of hydrogen storage materials, including alanates, nitrides, and borohydrides.[53] Approaches such as “nanoscaling” have been proposed to bypass intermediates formed in bulk reactions, enabling more selective control over the reaction pathways.[54,55] Chemical additives, such as Lewis bases, have been observed to change the selectivity and reaction pathways for the release of hydrogen from borohydrides. However, little is known about how additives, nanoscaling, or chemical additives change the reaction pathways. More research is needed to provide a clear understanding for predicting a priori how additives enhance reactivity and selectivity.

Capabilities

A combination of experimental and computational approaches working in concert is needed to provide the insight required to develop predictive models of hydrogen interactions. Techniques that probe both the energetics and the dynamics of hydrogen interactions in a wide range of materials (solids, liquids, and gases) over extended length and timescales are essential (**Figure 2-4**).

Operando studies facilitate the elucidation of reaction kinetics, associated structural dynamic changes occurring in gas–solid interactions, or both. For example, neutron and X-ray scattering, from ultrasmall angle X-ray scattering to small-angle X-ray scattering (SAXS) to wide angle X-ray scattering (WAXS) offer the ability to measure length scales ranging from atomic- to micrometer-length scales as well as providing diffraction/crystallographic information (see **Sidebar 7**).[56–58] Coupling vastly different instrumental configurations such as high pressure neutron scattering with nuclear magnetic resonance spectroscopy is a key opportunity for obtaining the in-depth understanding necessary for the development of comprehensive, multiscale models of gas sorption processes.

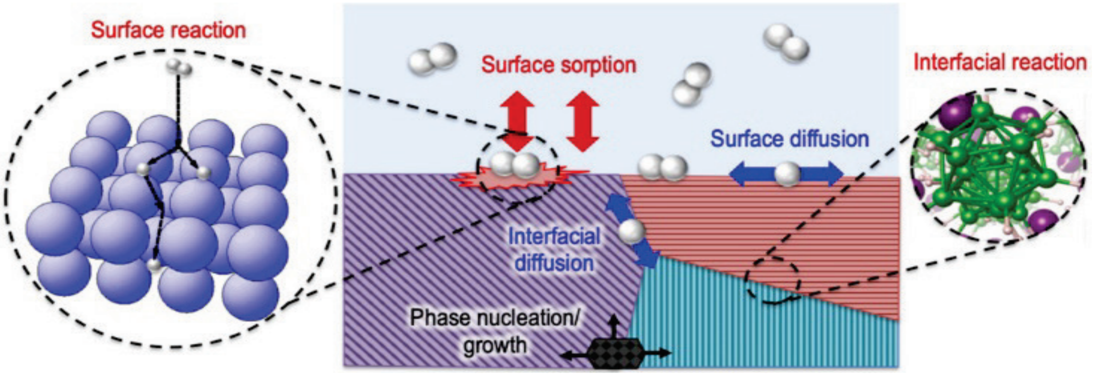


Figure 2-4. Illustration of some of the key surface and interface processes taking place during cycling of a typical nanoscale metal hydride material.[59] Reprinted with permission: B. Wood, et al., *Industrial & Engineering Chemistry Research,* **59** 5786-5796 (2020). Copyright 2020, American Chemical Society.

Developing a multiscale modeling framework for probing the adsorption, diffusion, and reactions of hydrogen species at bulk, surface, and interfacial regions requires bringing diverse modeling expertise to find strategies and formalisms to combine electron-scale (e.g., density functional theory [DFT]), atomistic-scale (e.g., classical molecular dynamics [MD]), and mesoscale methods (e.g., kinetic Monte Carlo and beyond), into models that yield atomically resolved insights of hydrogen behavior (and potential accompanying material changes) that can explain and predict experimentally measured properties. Model-building strategies could involve sequential parametrization, potentially aided by ML. For example, DFT yields activation energies that can be used as inputs to transition state theory approaches to yield rate constants. These rate constants are then used in a kinetic Monte Carlo model to yield system evolution at the atomic level). Such methods establish real-time communication between models (e.g., how grand canonical Monte Carlo simulations model H_2 adsorption on a porous structure that can be periodically updated via MD-calculated free energies and thermodynamic models). Examples of phenomena these models could target include how atomic hydrogen diffuses from the bulk of a hydride to the interface with a catalyst where it combines into H_2 before desorbing or how H_2 dissociates on the surface of a metal membrane before diffusing as H into the bulk via vacancies and grain boundaries to embrittle the material (**Figure 2-4**).[59]

Data science approaches can be established to describe hydrogen-related properties and predict high-performing storage materials. Analogous to the manner that advances in artificial intelligence (AI) and ML have sped up the analysis of images, implementations of AI/ML techniques can accelerate the way experimental data is collected, processed, and analyzed to yield insights about the behavior of hydrogen and hydrogen materials. AI can assist in the quality control of process conditions and parameters as well as understanding operando structural changes. Multivariable effects, which impact materials performance (either at the processing stage or at the stage of desorption/uptake cycling), could be understood with implementation of AI/ML. ML coupled with MD could also expand the time and length scales that phenomena such as where hydrogen changes states (H_2, H•, H^+) and where quantum effects are relevant. ML predictions of hydrogen properties could rapidly generate comprehensive structure–property maps, revealing hydrogen-related property boundaries and structure–property relationships. AI methods to represent and generate materials could accelerate the realization and design of materials with desirable chemical traits. Strategies to dramatically increase the speed these AI/ML tools can be trained in the face of data scarcity are needed. Approaches can range from training methods (e.g., transfer learning) to data sharing methods (centralized databases). Crucial to these efforts are the sharing of "negative results," particularly conditions that lead to degradation or unsuccessful synthesis.

2d. Potential Impacts

Detailed insight into the properties controlling hydrogen interactions with materials and catalysts can enable hydrogen storage to be substantially improved for carbon-neutral processes, which can have an impact on the ability to decarbonize energy-intensive industries. Reduction of iron ore in making steel is responsible for greater than 30% of CO_2 emissions from industrial processes, so alternative approaches to production, storage, and transport of clean hydrogen can provide opportunities to reduce carbon emissions from industrial processes.[60] Decarbonization of the electric grid using renewable energy from solar and wind can further benefit from the ability to produce, store, and utilize large quantities of energy as clean hydrogen[61,62] providing new opportunities for long duration energy storage. Clean hydrogen also enables safer and lighter energy storage for sectors that are difficult to electrify, including long haul trucks, marine transportation, and underground mining. National and international shipping can be enabled from locations with abundant renewable resources to locations with limited energy resources.

Development of unique experimental and computational methods, coupled with greater understanding of the factors that control the interactions of hydrogen with catalysts and materials, can have a wide-ranging scientific impact beyond carbon-neutral energy storage. Predictive models of gas sorption energetics can enable the design and production of advanced sorbent materials that are key to the transformative advancement of a vast array of new energy storage and gas purification technologies. An attractive avenue is the exploration of “barely porous” materials,[52] which have been shown to be selective for hydrogen, and furthermore, are able to selectively separate hydrogen isotopes of H_2 and deuterium (D_2) through functionalization of the material. Systematic studies of functionalization vs. hydrogen binding preferences, coupled with manipulation of the effective pore sizes and openings, can enable exploration of kinetic quantum sieving vs. chemical affinity quantum sieving on hydrogen adsorption/desorption and storage. This new understanding can assist the development of storage materials with the high selectivity and stability required for multiple storage cycles without substantial loss of capacity or the production of undesirable side-products. Insight into the interfacial dynamics of hydrogen gas formation and dissociation at catalyst interfaces can benefit from improvements into the production of hydrogen by electrolyzers (see **PRO 1**).

Understanding the environmental influences on the nature of hydrogen at metal surfaces is another prominent goal. For instance, the origins of the pH-dependent kinetics of hydrogen evolution and oxidation reactions on platinum is an unsolved question that has persisted for over half a century. A greater understanding of hydrogen interactions on metal surfaces in aqueous media provides a critical connection that can influence hydrogen production, storage, and utilization.

PRO 3: Elucidate the Structure, Evolution, and Chemistry of Complex Interfaces for Energy- and Atom-Efficiency

Many challenges are presented by the complexity of multicomponent, multiphase interfaces coupled with the inherent reactivity of hydrogen systems. Achieving sustainable processes requires atom-efficient chemical reactions that do not create unwanted by-products. Mapping, understanding, and controlling the spatiotemporal properties and dynamics of complex interfaces involving multiple phases is key to advancing carbon-neutral hydrogen technologies. This monumental challenge requires the development of integrated, predictive approaches that involve the coupling and parallel application of the following diverse techniques: advanced synthesis; ex situ, in situ, and operando characterization; theoretical understanding and modeling from quantum to continuum length scales; data science and ML; performance measurements; and multimodal platforms to couple these methods.

3a. Summary

Complex interfaces in multicomponent systems have resulted in numerous scientific challenges for understanding and controlling the properties that govern desired and undesired reactions. Interrogating, interpreting, and controlling the spatiotemporal properties and dynamics of complex interfaces between materials and fluids in hydrogen systems and processes are key to advancing carbon-neutral hydrogen technologies. The development of energy-efficient technologies for hydrogen production, storage, and utilization requires identification of design principles and predictive models for integrating different materials (semiconductors, insulators, electrocatalysts, electrolytes, and membranes) in functional, reactive, and durable systems. Materials and interfaces important for hydrogen technologies are shown in **Table 3-1** (also see **Sidebar 6**).

Table 3-1. Key materials, interfaces, and processes associated with hydrogen technologies.

Inorganic materials with varying electronic properties with nanoscale and microscale features and molecular surface/interphase chemistries that are key to catalytic or transport functionality
Electrolytes that may be soluble or solid ionomers with hydrophilic and hydrophobic domains, absorbed onto or intertwined with inorganic phases leading to key processes occurring in confined nanoscale regions
Solid–gas, solid-liquid and solid–solid interfaces that facilitate fast electron, ion, and/or heat transfer with minimal losses in free energy driving force
Vapor phases that contact both liquids and solids at triple-phase boundaries, where activity is often localized, including bubble formation and multiphase flow
Microphase separated polymers/ionomers whose structure is dependent on electrolyte and ionomer charge type, density, and distribution
Liquid–liquid interfaces, such as those between ionic liquids or nonaqueous electrolytes and aqueous phases

Experimental studies of interface structure and dynamics, and their evolution across length scales combined with molecularly accurate computational models, can provide both a mechanistic understanding and predictive capabilities for improvement. This challenge requires multiscale modeling—quantum mechanical models to understand electronic properties, interface energies, and reaction trajectories; MD models to understand local interfacial effects such as nanoconfinement; and finite element numerical simulations to understand gradients in species concentration, electric potential, temperature, and mechanical forces, and how such evolve with time. New approaches that account for the dynamical nature of soft matter are needed for tracking interface evolution during operation, including under the strong reducing/oxidizing conditions for hydrogen–oxygen transformations.

To elucidate and control interfacial phenomena with the fidelity needed to enhance carbon-neutral hydrogen technologies requires development of new experimental and computational techniques, as well as coupling of existing techniques in new ways. These approaches are intended to enable probing interfaces at multiple length scales, yielding both molecular-scale spatiotemporal resolution of interfacial phenomena, and the relationship of these data to phenomena at continuum and device levels. Both static and dynamic characterization methods can provide molecular-scale maps of thermodynamic driving forces for interfacial processes, including local structural features, electric potentials, concentration and pH gradients, temperature and pressure distributions, and charge density maps. These techniques can facilitate understanding and control over catalytic transformations and the physical processes occurring near interfaces, with applications to hydrogen chemistry and beyond.

3b. Key Scientific Questions

- How can interacting, evolving interfaces be tailored at multiple length- and timescales to achieve energy-efficient, selective processes and enable carbon-neutral hydrogen technologies?

- What approaches are needed to probe and map complex functional and structurally evolving interfaces across material classes (e.g., solid–liquid, solid–solid, solid–gas) and their microenvironments?

- What are the requirements for robust, predictive frameworks to understand interfaces by coupling diverse, complementary scientific methods that accurately describe multiple parallel phenomena, including activity, selectivity, stability, degradation, evolution, dynamics, transport, and electron/ion transfer, through deconvolution of the underlying kinetic, thermodynamic, and transport phenomena at play?

3c. Scientific Challenges and Research Opportunities

Many of the central challenges toward enabling carbon-neutral technologies for the effective generation, storage, and use of hydrogen are influenced by complex interfaces where the governing chemical, physical, and mechanical phenomena are not well understood. These interfaces are composed of many materials with different structures, phases, and geometric and chemical compositions, all under the influence of varying driving forces, leading to both desired and undesired reactions. It is essential that the role of each component of the systems be understood and that the interfaces between these components be designed such that transport and reaction rates are tailored for enhanced performance, spanning length scales from angstroms to hundreds of micrometers, with a special emphasis on interfacial evolution under operating conditions. Addressing these challenges requires integrated approaches that couple advanced synthesis, in situ spectroscopies, modeling from quantum to MD to continuum scales, data science, ML, characterization, and performance measurements. Key opportunities for advancing our understanding of interfaces are to

- probe and map functional and evolving complex interfaces across material classes within their microenvironments;

- develop robust predictive frameworks to understand interfaces; and

- tailor, control, and design interfaces to achieve enhanced performance.

Probe and map functional and evolving complex interfaces across material classes within their microenvironments

Technologies for hydrogen production, storage, and utilization all involve interfacial phenomena (**Sidebar 6**) and share common challenges. Under operating conditions, each interface dynamically adapts and adjusts to local driving forces (e.g., thermal, chemical, electrical, and mechanical) and evolves into chemically and mechanically stable or metastable states. It is difficult to acquire structural and performance information about these interfaces because they are typically not exposed directly to the external environment and are they not accessible for direct analysis. Some current techniques allow probing specific interfacial phenomena, but others need further development.

Research opportunities are recognized in the development and application of complementary experimental and computational methods that can interrogate and simulate the physical structure, chemistry, and performance of interfaces, preferably under operating conditions, leading to correlations between structure, properties, and characteristics of specific interfaces. Characterization methods are needed for model systems to functional devices, with information covering subnanometer to millimeter length scales, and timescales spanning those of elementary chemical reactions (ps) to long-term degradation processes (years). The wide-ranging scientific challenges associated with operando interface characterization include the lack of surface sensitivity and chemical specificity of spectroscopic and scattering techniques, making it difficult to separate the spectroscopic signals associated with the interface with those of interest in the bulk (e.g., intermediate species present at or in the vicinity of the interfaces). There are notable opportunities in correlative characterization combined with modeling, especially of processes that are difficult to access experimentally, as well as ML approaches, where information from a suite of disparate methods is brought together to elucidate the connection between performance and a particular structural motif. ML methods can be made physics aware, such that the underlying experimentally determined thermodynamic factors and physical properties provide descriptors.

Develop robust predictive frameworks to understand interfaces

Many phenomena are strongly influenced by specific interfaces, including catalytic activity, selectivity, and stability, coupled with dissolution, degradation, structural evolution, heat transfer, and mass transport. Further influences by the transfer of electrons, protons, and ions have profound consequences for processes that are important for hydrogen production and utilization. Characterization methods coupled with computational modeling and high-throughput experiments have provided insights into these phenomena, leading to, for example, the prediction of adsorption reactivity trends and to improved electrocatalysts for hydrogen-relevant reactions, including the oxygen reduction reaction, OER, and HER.[63,64] However, given the highly disparate length and timescales combined with the diverse nature of the interfaces involved (**Sidebar 6**), such analyses are inevitably based on incomplete data and significant approximations, and they seldom fully describe or predict properties. For example, computational models based on DFT calculations have successfully predicted trends in the activity of platinum-based electrocatalysts for the oxygen reduction reaction, but corresponding predictions of the stability and lifetime of these catalysts remain elusive.[65] **Figure 3-1** shows key examples of electrocatalyst interfacial dynamics and structures critical to water electrolysis that remain difficult to model.[66,67]

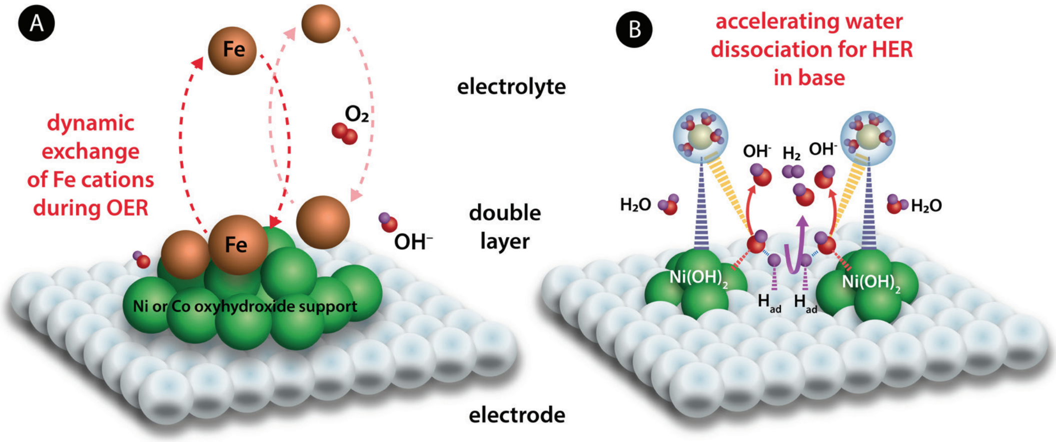


Figure 3-1. Dynamics and multifunctionality at electrocatalytic interfaces. (*A*) In the OER, the high activity of Ni- and Co-based oxyhydroxide relies on Fe species that are under a dynamic equilibrium of adsorbed and soluble Fe species that are essential to the active site. Understanding and tuning these dynamic interfaces are important for creating high-performance alkaline and alkaline membrane electrolyzers. One challenge is maintaining enhanced activity for water oxidation at the anode (over years) while preventing soluble Fe or other species from plating at the cathode and degrading HER performance (Adapted from reference 66. Reprinted with permission: D. Chung, et al., *Nature Energy*, **5** 222–230 (2020) Copyright 2020.) (*B*) In alkaline conditions water is the proton source for H_2 production, which is thought to explain the slow the kinetics of HER relative to the catalyst in acidic conditions. The HER activity of many precious and nonprecious metal catalysts in alkaline conditions can be increased dramatically by modifying the surface with hydroxides/oxides that catalyze water dissociation by increasing the binding strength of the hydroxide and accelerating the formation of metal hydride surface intermediates (Adapted from Reference 67: R. Subbaraman, et al., *Science*, **334** 1256-1280 (2011). Reprinted with permission from AAAS).

To bridge these gaps in scientific knowledge and to minimize the number of experiments that must be performed to fully elucidate the nature of interfaces of interest, models with predictive power are required. For predictability, modeling approaches are required that incorporate experimental data acquired from efforts that can integrate multiple chemical and physical interactions across different time and length scales. These models should capture the relationships between interfacial catalytic properties, interfacial stability, dynamics, and transport processes while providing insights into the fundamental physicochemical processes that control interfacial behavior. Understanding that goes far beyond simple correlations can allow for transferability between disparate systems and processes and ultimately enable control and design of interfaces with desired properties. A classic example of a predictive analytical model that provides fundamental insight into interfacial electronic structure is d-band theory, which has been widely and effectively used to describe adsorption and reactivity trends on the surfaces of metals. However, interfacial systems, including surfaces with highly heterogeneous structural features and nonmetallic catalysts, are not as well described by this theory and have illustrated inherent limitations of the model.[68,69] In recent years, an increase in the number of studies incorporating descriptors has been observed; descriptors are well-defined computational or experimental properties of a material, such as adsorption energies of reaction intermediates or transition states to describe interfacial properties across a series of catalytic surfaces, but these often only illustrate broad trends and fail to predict behavior of complex multicomponent catalysts.[70] Statistical and data-based methods have also emerged to predict adsorption energies on metal surfaces.[71,72] Many such studies have been useful in validating and interpreting behavior and performance characteristics of electrocatalysts and have been successful in predicting new systems while only analyzing one or two descriptors. The inability of existing approaches to capture a priori the spatiotemporal evolution of a system offers a tremendous opportunity.

Sidebar 6: Understanding Interface Complexity Between/Within Electrolyzer Materials

Electrolyzers are complex devices with many heterogeneous interfaces between components. Gradients in electric potential, temperature, activity (concentration) of water and ionic species, and pressure within and across electrolyzer components drive key interfacial phenomena. Simultaneous efforts are needed to control the interface structure at the molecular level (and its time evolution and dynamics), connect it with performance and durability, and design it for improved performance.

Figure S6 shows key driving forces in operating electrolyzers; gradients in electrostatic potential exist in the ionomer and catalyst phases within anode and cathode reaction zones, such as $\nabla\varphi_{\mathrm{ionomer}}$ and $\nabla\varphi_{\mathrm{solid}}$; gradients in the activity of water, a_{H2O}, and hydroxide, $a_{\mathrm{OH-}}$ (i.e., for an AEM electrolyzer here); and gradients in pressure, P. Inset panels illustrate specific key interfacial phenomena: (A) Interface between ionomer/catalyst layer and porous transport layer, which is the electrical interconnection between the conductive, microporous metal support (surface is often oxidized) and the catalyst/ionomer mixture. Ideal interfaces optimize catalyst utilization by minimizing resistances as well as minimizing physical stress that could lead to mechanical degradation. (B) Complex interfaces inherent to catalyst/ionomer within anode and cathode catalyst layers. Key scientific opportunities for research include (1) understanding and controlling chemical interactions between the ionomer and catalyst that can lead to mechanical and chemical stability; (2) tuning the electrical connection between catalyst and support; (3) understanding structural evolution in the active layer driven by potential or other forces; and (4) controlling the length scale of the interactions to optimize electrical, ionic, and mass transport. (C) Schematic of an alkaline ionomer that selectively conducts hydroxide. A PEM electrolyzer would have opposite polarity fixed charge on the polymer backbone. Key issues for alkaline ionomers are related to hydration, ion conductivity, nanophase separation, and (electro)chemical stability. Challenges related to durability include understanding deleterious ionomer oxidation kinetics and mechanisms and developing strategies to prevent ionomer degradation under alkaline conditions. (D) Porous transport layer used to electrically contact the catalyst layers and facilitate liquid and gas transport. Key issues include (1) chemical stability (e.g., formation of electrically resistive interfacial oxides); (2) structure control with multiple pore sizes that optimize interfaces and bulk transport; and (3) cost of raw materials (e.g., Ti) and their scalable processing into hierarchical structures. The porous transport layer shown here includes porosity controlled at two length scales—the microporous region electrically connects to the catalyst, and larger pores facilitate mass transport of liquid and gas.[73] An overarching challenge is the codesign of all these interfaces, along with component domain properties to minimize transport and reaction losses, using earth-abundant materials and scalable approaches for synthesis and fabrication based on the underlying fundamental understanding.

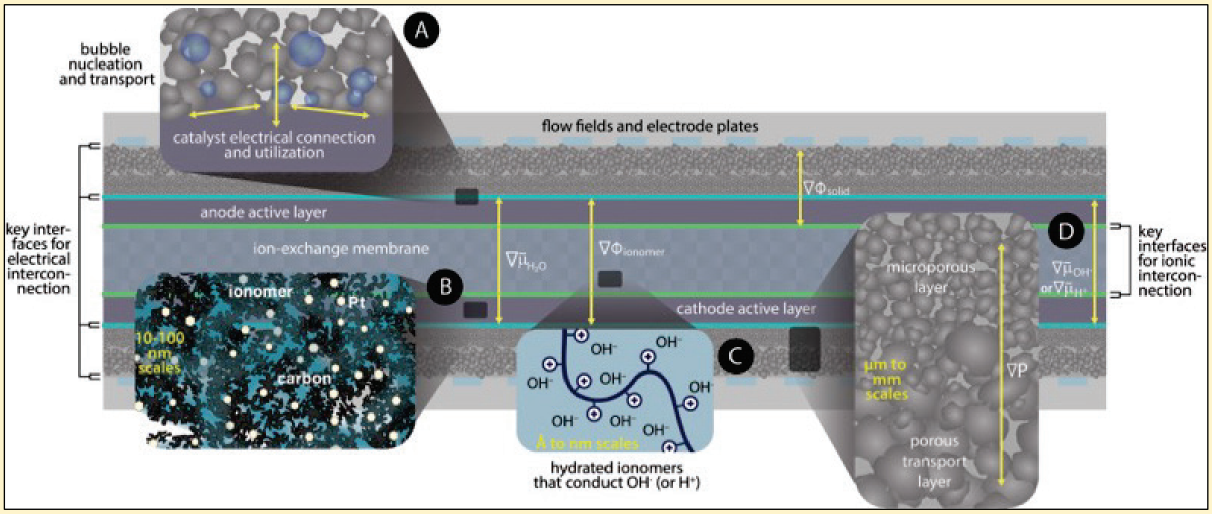


Figure S6. Schematic illustration of critical component materials, 3D architectures, and interfaces in a PEM electrolyzer. Key driving forces leading to bulk and interface reactions and transport processes are shown in each panel (A–D) and discussed above. Image used with permission from Shannon Boettcher, University of Oregon.

New models are needed that can describe multiple reactions, processes, and phenomena by simultaneously spanning quantum mechanical to classical theories. As an example, models that predict both activity and durability of electrocatalytic systems are needed. The longstanding problem of achieving a multiscale model framework across broad time and length scales remains of interest in this context, but it is not the only approach. Models are needed to provide a deep physical insight, which can be accomplished using simplified frameworks with analytical or semi-analytical formats but must also capture sufficient phenomena to achieve the descriptive power mentioned above. For example, approaches that combine existing physical theories with data science–based methods, such as "gray box" models (i.e., combining theory and data),[74] could balance interpretability and physics with predictive power. Frameworks are envisioned that identify what data are lacking and inform measurements to target specific, guided experiments. This approach can be elaborated to implement self-driving laboratories that might combine AI/ML with experimental robotic platforms to automate discovery of new materials.[75] In all these efforts, however, sufficiently detailed experimental feedback of the actual active interfacial structures and chemistries are essential, as is robust theory and computation to provide mechanistic insight.

Tailor, control, and design interfaces to achieve enhanced performance

Developing the fundamental scientific understanding to achieve the Hydrogen Shot goals (see **Sidebar 3**) requires producing optimal hydrogen processes and systems with scalable, inexpensive, fast, and precise techniques. The best structures at different length scales can be revealed through iterative multimodal characterization and modeling, as well as understanding the chemical, electronic, and physical driving forces. A science-based approach is needed to extend control over structure from the individual material components to the assembly of components into desired configurations, particularly control over the interfaces between them.[75] For MEAs in an electrolyzer or fuel cell, the critical catalyst/ionomer active layers have typically been optimized using Edisonian approaches and are often deposited via doctor blade/decal transfer, painting, air spraying, ultrasonic spraying, and ink jet printing with little explicit attention devoted to controlling the interfaces.[76] In PEM fuel cell or electrolyzers, the catalyst nanoparticles are often supported on an electrically conductive material that creates a percolating network within the electrode layers to move electrical charges with a low ohmic drop from porous transport layers to the catalysts. Interspersed at the molecular and nanometer scales with the catalyst is an ionomer that creates a percolative network for ionic (e.g., OH^- or H^+) conduction between active sites and the ionomer membrane and sets the local pH conditions, as well as a void space where reactants/products are transported often via two-phase gas/liquid flow. The design of such layers is a significant challenge because of the competing demands to lower catalyst loading (especially for precious metals) while maximizing activity and mass transport at increasingly large current densities (to lower capital expenses).

A key need in hydrogen technologies is to understand and leverage precision synthesis of the different components (e.g., catalyst, support, ionomers, and membranes) designed with ranges of size and shape, along with chemical self-assembly to generate customizable libraries of inks that can be applied in high-speed manufacturing (e.g., 3D printing or roll-to-roll processes) to provide durable structures with optimal transport of electrons and ions.[77] The chemical and physical interactions that govern the characteristics of the interfaces between deposited layers (e.g., ionomer/catalyst layer and membrane) as well as the interfaces internal to each layer at the subnanometer to micrometer scale are especially important. The strength of chemical interactions, for example, between the ionomer and catalyst requires control over multiple interactions including tuning to provide robust materials while maintaining a catalyst surface for the desired reactions. Developing inks with precise catalytic and electrically conductive support materials can facilitate a deeper understanding of how the assembly process can be tuned. This PRO is related to that articulated more broadly in the recent BES BRN report on "Transformative Manufacturing."[78] This report identifies the opportunities specifically applicable to interfaces of multicomponent, multiphase systems.

3d. Potential Impacts

To elucidate and control interfacial phenomena with the fidelity needed to enhance carbon-neutral hydrogen technologies requires the development of new experimental and computational techniques, as well as coupling existing techniques in new ways. These techniques can facilitate unprecedented understanding and control over catalytic transformations and physical processes occurring near interfaces, with applications to hydrogen technologies and beyond. Breakthrough insights into the properties of solid–gas, solid–liquid, and solid–solid interfaces, and the subsequent leveraging of these hydrogen technologies, necessitates new approaches to predict and control interfacial structures and phenomena with unprecedented spatiotemporal resolution to reveal correlations and connections that would otherwise be obscured by the complexity of the system.

The combined insights can enable synthesis of interfaces with appropriate structures and control of local kinetic variables, to produce, store, and utilize hydrogen with high efficiency, durability, and scale. Methods of studying static interfaces now typically leverage both sophisticated DFT simulations and operando characterization methods. Emerging approaches can illustrate how interfaces structurally evolve in time and their dynamics, as well as how those processes influence properties and how they can be harnessed to improve performance.

Interface design within various components from the angstrom to micrometer scales can directly influence the activity, durability, efficiency, and cost of hydrogen technologies. Many interfaces in these systems and processes rely on a catalyst for reactions that occur at solid–liquid, solid–solid, or solid–gas interfaces. Tailored interfaces can expose larger catalyst surface areas, ameliorate surface poisoning, and enable faster transport of reactants and products, resulting in lower voltage losses.

The design of porous materials and their interfaces also impacts hydrogen storage technologies (see **PRO 2**) where, for example, open framework materials are used. Pore-scale phenomena occurring within and at the length scale of these pores, including the role of defects, chemisorption, thermodynamics, and kinetics of reaction pathways, are not well understood. Sorption/desorption, formation of hydrogen bonds, double layer formation, and the transition from long-range order to disorder are all important factors in interface design.

Many hydrogen technologies suffer from undesirable reactions that result in material loss, deactivation, and, broadly, component degradation (see **PRO 4**). Harsh environments, such as high or low pH, exposure to contaminants, radicals, and other stressors (thermal gradients, chemical potential gradients, pressure gradients, and mechanical stresses) affect materials and interfaces. Interfaces are especially susceptible to these changes because they are often driven far from equilibrium during operation, highlighting the need to leverage metastability of the interface to suppress undesirable reactions. Local pH, ion solvation, and electric double layers differ at interfaces compared to the bulk, creating gradients that act as driving forces for degradation. Tailored interfaces can serve as a protection layer for catalysts, and coatings can prevent intercalation or act as self-healing interfaces to reduce or eliminate dissolution and other degradation routes. Catalyst–support interactions are also critical for durability; in many applications catalysts are anchored on a support, and mechanical detachment is a key degradation mechanism.

PRO 4: Understand and Limit Degradation Processes to Enhance the Durability of Hydrogen Systems

Understanding and mitigating degradation is a formidable challenge in many hydrogen technologies. The lack of mechanistic understanding of multiple, simultaneous degradation phenomena at a molecular or atomic scale is exacerbated by their occurrence over long time periods and the complexity of operating environments. Recognizing the structure–function relationships that govern stability is essential, including performing operando process characterization at interfaces. Such understanding can lead to new design principles to guide the preparation of more robust, stable materials with significantly enhanced lifetimes, especially when synthesis and performance are coupled with predictive modeling.

4a. Summary

A primary challenge for many hydrogen technologies is understanding and mitigating degradation. Lack of fundamental understanding of degradation phenomena, exacerbated by their occurrence over long timescales and the complexity of their operando environments, limits our ability to deploy hydrogen technologies at scale. Combined experimental and computational investigations are needed to develop structure–function relationships important to materials stability, including the use of model systems and operando characterization of interfaces. Such studies can lead to new design principles for robust materials and improved screening methodologies to enable accelerated deployment.

Devices that generate and use hydrogen, e.g., electrolyzers and fuel cells, and the materials that comprise them, have evolved to significant levels of maturity in terms of their energy and fuel efficiency. Hydrogen materials and systems encompass a wide range that includes electrochemical, thermochemical, photochemical, and biochemical approaches that produce or use hydrogen. These approaches involve functional materials, such as catalysts, supports, and electrolytes, including heterogeneous and homogeneous catalysts and liquid, polymeric, and ceramic ion conductors. The interfaces between these and other functional materials and between the components of a system may be solid–solid, solid–liquid, or solid–gas in nature (see **PRO 3** and **Sidebar 6**). A fundamental and predictive understanding of the long-term stability of the materials and interfaces, however, is lacking. This mechanistic and energetic (kinetic and thermodynamic) understanding of degradation is needed to design robust hydrogen systems.

Degradation pathways include dissolution, migration and coalescence, redox reactions, and morphological evolution, all of which can affect catalysts, support materials, electrolytes, and the interfaces between them.[21,79–81] Degradation pathways can also be coupled, which challenges conventional experimental philosophies whereby mechanistic control is probed by altering a single variable at a time (e.g., temperature, pressure, pH, and electrochemical potential). More systematic and bottom-up approaches are needed to deconvolute the contributions of complex degradation mechanisms, which can be achieved through combined experimental, imaging, and computational investigations of model systems. The understanding from model systems can be used to systematically add layers of complexity, approaching the degradation phenomena experienced in real systems.

Degradation of hydrogen systems is also complex because of the dynamic nature through which most mechanisms proceed and evolve over time. Degradation can occur through rare events, competing with intended hydrogen processes, adding to the challenge of understanding degradation phenomena over long timescales. Investigations taking place over the timescales typically involved in real-world system degradation are impractical for developing a fundamental understanding. Methods through which degradation mechanisms of interest can be accelerated, without altering their nature, are needed. Similarly, methods that can isolate rare events or increase the likelihood of their occurrence are required to achieve the desired level of mechanistic understanding.

4b. Key Scientific Questions

- How can the complex mechanisms of degradation be identified and understood to obtain foundational knowledge that enables the predictive design of robust hydrogen systems?

- What approaches are needed to probe complex H_2 systems under the operando conditions where degradation processes occur?

- How can the time frame challenges of degradation processes in H_2 materials and devices be addressed?

- What combination and type of model systems, experiments, characterization/imaging, and computational approaches, including ML, will produce the atomic-level knowledge of degradation processes that can lead to the predictive design of systems with enhanced lifetimes?

4c. Scientific Challenges and Research Opportunities

Understanding the dynamic processes for individual hydrogen system components is paramount to designing durable systems with desired performance. Advances in degradation science based on theory, simulation, and advanced characterization can provide insight beyond observable phenomenological properties of systems to move toward the development of a detailed atomic-level comprehension of the mechanisms of individual and coupled processes that lead to system degradation and failure. This insight is needed to enhance stability, prevent failure, and enable the design, development, and even repair (including self-healing) of molecules and materials, as well as to define the operating conditions required for long-term performance and durability. As discussed in the following sections, research on the degradation of materials for hydrogen processes and systems is needed to accomplish the following:

- Understand degradation under operando environments

- Enable investigative methods to study slow or rare events that lead to degradation

- Overcome structured complexity to gain insight into degradation phenomena

- Combine experiments and computational approaches to produce atomic-level knowledge of degradation processes

Understand degradation under operando environments

A comprehensive mechanistic understanding of fundamental degradation processes in materials for hydrogen systems under operando environments represents an exceptional challenge because of the range of dynamic, operando environments these systems experience, the nature of degradation processes that occur, and the complexity of the materials within which they are occurring. The operando environment includes considerations for variable temperature, pressure, pH, and electrochemical potential, as well as other compositional or structural changes in local environments that impact degradation. Additionally, the nature of degradation processes, that can many times occur as relatively rare, local events at the atomic level (e.g., contamination, localized elemental diffusion/segregation) that compete with intended hydrogen processes, makes fundamental insights of degradation processes more difficult to obtain. Further, the potential competition between intended hydrogen processes and degradation results in compromises between activity and durability that have yet to be fully explored. Finally, the systems these processes occur inside are typically heterogeneous in composition with buried interfaces having a broad distribution of states that continuously evolve under dynamic conditions. The combination of these factors makes the scientific challenges of mechanistic understanding an area of critical focus that necessitates the development of new tools and systems for investigation.

The complexity of the operating environment of hydrogen systems, the interfacial nature of specific key processes, and, in many cases, their slow kinetics make operando characterization of degradation processes challenging.[82] Existing characterization techniques may lack the combination of necessary spatial and time resolution, the sensitivity to measure relevant concentrations of degradation products, the ability to penetrate through the surrounding media to probe the critical interfaces, and the ability to resolve the interfacial structure and chemistry from the bulk. For example, electron microscopy techniques can provide the necessary spatial resolution and interfacial specificity but lack the ability to penetrate through operando environments to probe materials during degradation processes in real time.[83] This limitation has prompted the use of identical location transmission electron microscopy techniques where the materials are periodically removed from the operating environment, and the same location is imaged before and after degradation events,[84–86] as demonstrated in **Figure 4-1** (2D)[86] and **Figure 4-2** (3D).[87] X-ray and neutron scattering and absorption techniques can, in many cases, penetrate through the operando environment to probe materials and components of interest,[88–90] as highlighted in **Sidebar 7** and **Sidebar 8**. Neutron scattering techniques are especially powerful for studying hydrogen systems because the incoherent scattering cross section of the hydrogen nucleus is more than an order of magnitude larger than most other elements.[91–93] Limitations of neutron scattering techniques, much like X-ray scattering methods for transition metals, are a lack of specificity to the materials and processes of interest (e.g., interfacial vs. bulk) and a lack of necessary (atomic) spatial resolution. This lack of specificity often necessitates the use of model systems with controlled geometries to selectively probe interfacial phenomena. An additional limitation of existing electron and X-ray techniques, especially when probing systems containing soft materials such polymers, can be alteration of the materials under study (i.e., beam damage).[94] The nondestructive nature of neutrons is an attractive property of neutron-based methods. Therefore, nondestructive tools are needed that can combine the advantages of existing techniques and selectively resolve chemical and structural degradation processes at interfaces and in the bulk with atomic- to micrometer-level spatial resolution and over the relevant timescales to gain new insight into degradation phenomena.

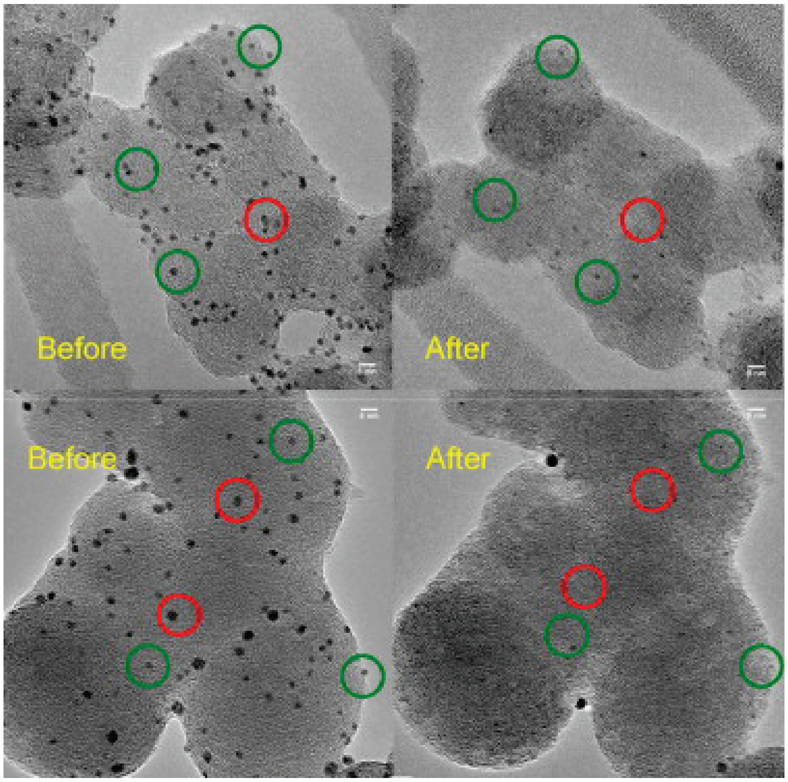


Figure 4-1. Identical location transmission electron microscopy images of a platinum/carbon electrocatalyst degradation acquired before and after an accelerated corrosion test (sample subjected to 3,000 cycles, 0.6–1.2 V at 200 mVs^{-1} in 0.1 M $HClO_4$). Red and green circles track the same platinum nanoparticles before and after cycling.[84] Reprinted with permission: F. Perez-Alonso, et al., *Journal of Power Sources*, **196** 6085-6091 (2011) Copyright 2011 with permission from Elsevier.

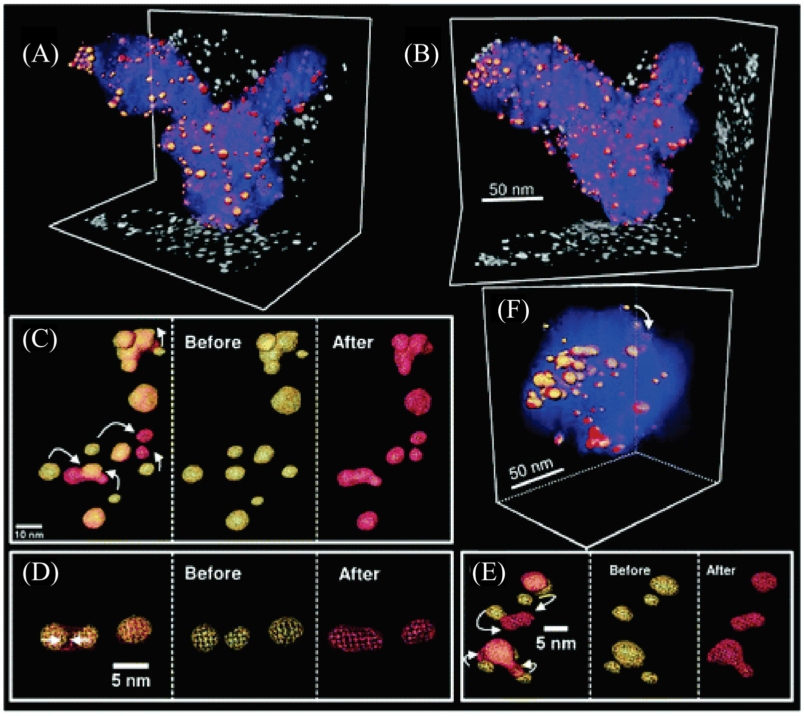


Figure 4-2. One-to-one correspondence of catalyst particles before (gold) and after (red) electrochemical aging, with the same color scheme used in all figures. (A) 3D reconstruction of catalyst particles on carbon support (blue) with projected 2D images shown on each side. (B) Alternate viewing angle. (C–E) Instances of catalyst particle coalescence and migration (particle positions indicated by arrows). (F) Example of cropped volume from (A,B) showing how one catalyst particle moves into the positive curvature (valley) from negative curvature (summit) of catalyst support. Arrow shows trajectory of the particle movement.[87] Reprinted with permission: Y. Yu, et al., *Nano Letters,* **12** 4417–4423 (2012), Copyright 2012, American Chemical Society.

Fully understanding degradation processes requires the coupling of operando studies with ex situ and in situ studies, pre- and postmortem characterization, carefully designed model systems, and computational modeling.

Sidebar 7: Operando X-ray and Neutron Scattering Methods

Operando X-ray scattering and X-ray absorption/fluorescence techniques can be used to track dynamic changes of materials in environments of interest and, by virtue of the strong interaction of X-rays with electrons, are particularly well suited to study high atomic weight materials, such as transition metals, in operating environments of low atomic weight materials (e.g., carbon, hydrogen, oxygen). X-ray methods have been used effectively to study electrocatalyst size, shape, crystalline structure, and compositional changes during potential cycling, which are critical experiments to assess catalyst stability under specific operational conditions, such as WEs and proton exchange membrane fuel cells (PEMFCs). Studies can be conducted on powder samples or electrode layers in MEAs. When coupled with high-resolution electron microscopy, electrochemical measurements, or both, insights about catalyst degradation mechanisms can be obtained at length scales ranging from the subangstrom (atomic structure) to nanometer level (individual nanoparticles) to 10–1,000s of micrometers (electrode layers). Small angle X-ray scattering combined with XAS provide averaged data on the simultaneous changes in the morphology (nanoparticle size, size distributions, and specific surface area) and composition (oxidation state, identity of nearest neighbors, such as alloying metals and bond distances) under operation-specific conditions. **Figure S7-1** shows the evolution of the particle size distribution of Pt nanoparticles during potential cycling of a Pt/C fuel cell electrocatalyst determined using anomalous SAXS, changes in coordination of oxygen with Pt nanoparticles during polarization, and changes in the O/Pt ratio induced by particle growth.[89] Studies combining X-ray scattering with X-ray spectroscopy provide mechanistic insight into the processes of catalyst degradation—in this case linking the extent of oxide formation with platinum dissolution resulting in particle growth by dissolution and redeposition.[95,96]

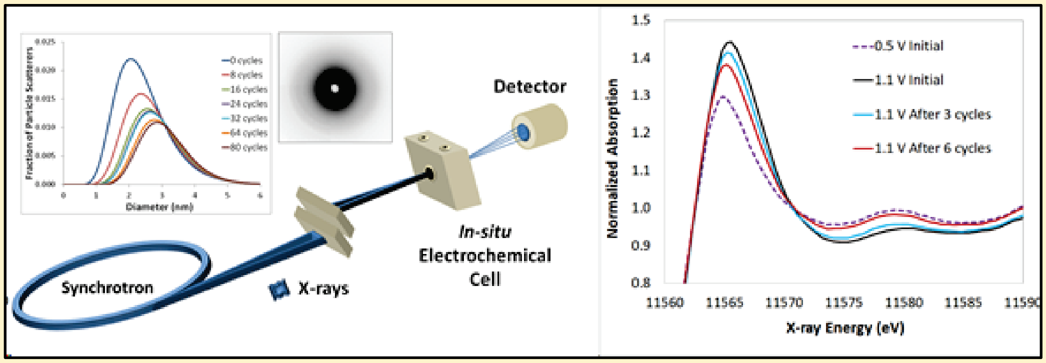


Figure S7-1. (*Left*) Schematic of operando synchrotron X-ray scattering, representative scattering data, and evolution of platinum electrocatalyst nanoparticle size distribution derived from X-ray scattering data as a function of potential cycling.[89] Reprinted with permission: J. Gilbert, et al., *Journal of the American Chemical Society*, **134** 14823-14833 (2012), Copyright 2012, American Chemical Society. (*Right*) Operando X-ray absorption near edge structure for a platinum/carbon as a function of potential during cycling. Image used with permission of Deborah Myers, Argonne National Laboratory.

Conversely, neutron scattering techniques can be used to track the dynamic changes of materials comprised of low atomic weight elements in operating environments comprised of higher atomic weight elements. For example, the atomic-level morphological changes of ionomers and membrane electrolytes during fuel cell or electrolysis operation can be probed with neutron scattering, as shown in **Figure S7-2** for a perfluorosulfonic acid membrane and ionomer in a PEM fuel cell.[97] Degradation associated with changes in the polymer structure impacting proton transport mechanisms can be probed using this operando technique. Neutron scattering is particularly powerful in resolving the structure of ionomers in catalyst–ionomer composite electrodes and changes in the catalyst–ionomer interface during electrochemical processes responsible for performance degradation.

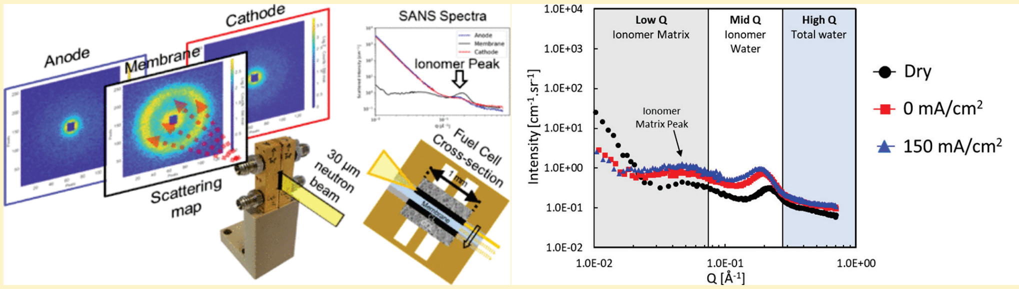


Figure S7-2. Schematic of operando small-angle neutron scattering of an operating fuel cell and representative scattering data showing evolution of the structure of the fuel cell membrane with cell current.[97] Reprinted with permission: J. Lee, et al., *ACS Applied Energy Materials*, **3** 8393-8401 (2020), Copyright 2020, American Chemical Society.

Sidebar 8: Operando X-ray Computed Tomography Methods

Operando X-ray computed tomography (CT) can be used to understand morphological changes of MEAs and other components within fuel cells and electrolyzers as they undergo degradation. Micro X-ray CT has been extensively used to understand membrane and catalyst layer degradation and wettability changes during accelerated stress tests. Synchrotron or laboratory-scale X-ray scanners are used for degradation studies. Synchrotron X-ray sources allow for high intensity X-ray beams, enabling subsecond imaging to understand dynamics of water formation or membrane swelling, for example. Since most degradation phenomena occur over longer timescales (hours to days), the advantages of dynamic imaging might not be needed, and laboratory-scale imaging could be more appropriate. In a typical micro X-ray CT experiment an operando cell is mounted onto a rotating stage and X-rays are transmitted through the cell; as the stage rotates 180°, the detector records radiographs of the transmitted signal. Micro X-ray CT beamlines typically have a resolution of ~1 µm and a field of view of 3 × 3 mm or a larger field of view for lower resolution. **Figure S8-1A** shows an example of the evolution of the PEMFC catalyst layer morphology during an accelerated stress test, where a significant number of cracks form as cycling progresses. The gray-scale images can be quantified into porosity maps and values via thresholding, as shown in **Figure S8-1B**.[98]

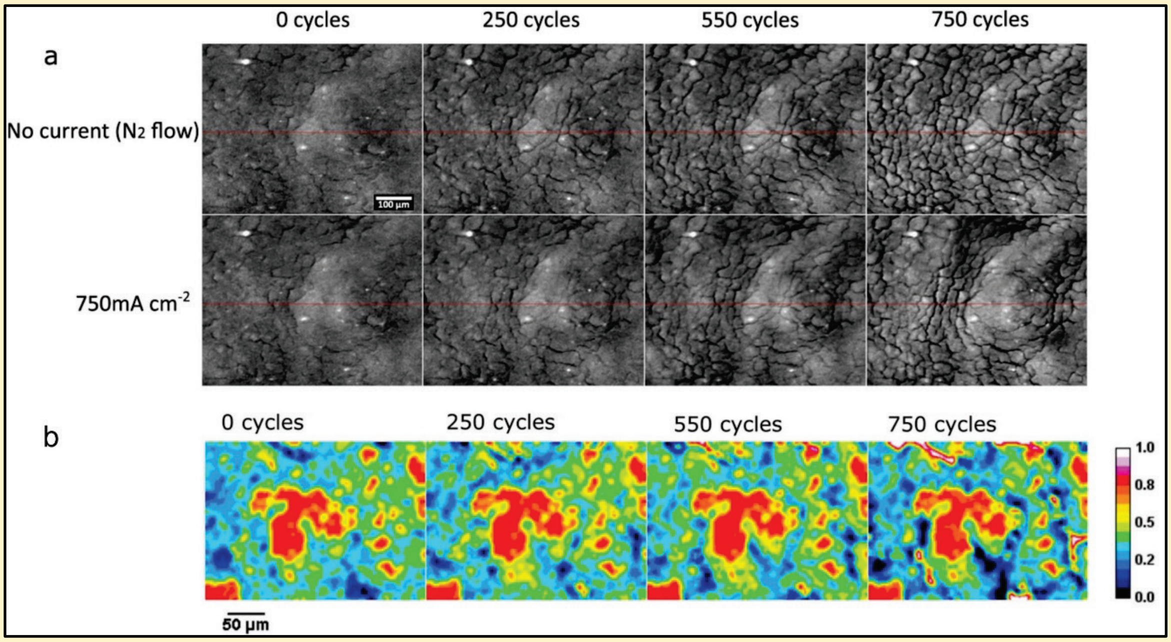


Figure S8-1. Morphology changes of PEMFC catalyst layer during voltage cycling using operando X-ray CT. (A) In-plane gray-scale tomographs show crack evolution with cycling for dry (*top*) and wet (*bottom*) conditions. (B) Color-coded porosity of cathode layer at 0 cycles and after 250, 550 and 750 cycles.[98] Reprinted with permission: R.T. White, et al., *Scientific Reports,* **9** 1843 (2019) under Creative Commons Attribution 4.0 International (CC BY 4.0). Copyright 2019.

Although micro X-ray CT has been extensively used for operando experiments, nano X-ray CT has limited implementation in operando studies because of several challenges, including a small field of view (~80 µm) and a high brightness X-ray beam focused onto a small spot potentially causing beam damage to the membrane and ionomer. Nano X-ray CT has a resolution of 30 nm and has been used to study catalyst morphology degradation ex situ. Beam damage for nano X-ray CT can be overcome by using beamlines that rely on Kirkpatrick–Baez mirrors, for example, at the European Synchrotron Radiation Facility (ESRF) where imaging can be conducted at 17.5 keV. Kirkpatrick–Baez mirrors enable imaging from the micro- to nanoscale. **Figure S8-2** shows gray-scale tomographs of the operando nano X-ray CT at ESRF for multiple resolutions on the same beamline without any observed beam damage.[99] As the community develops operando cells for nano X-ray CT imaging it may become possible to resolve catalyst layer morphology changes during operando experiments, as well as understand water or other species distributions and how these change over time.

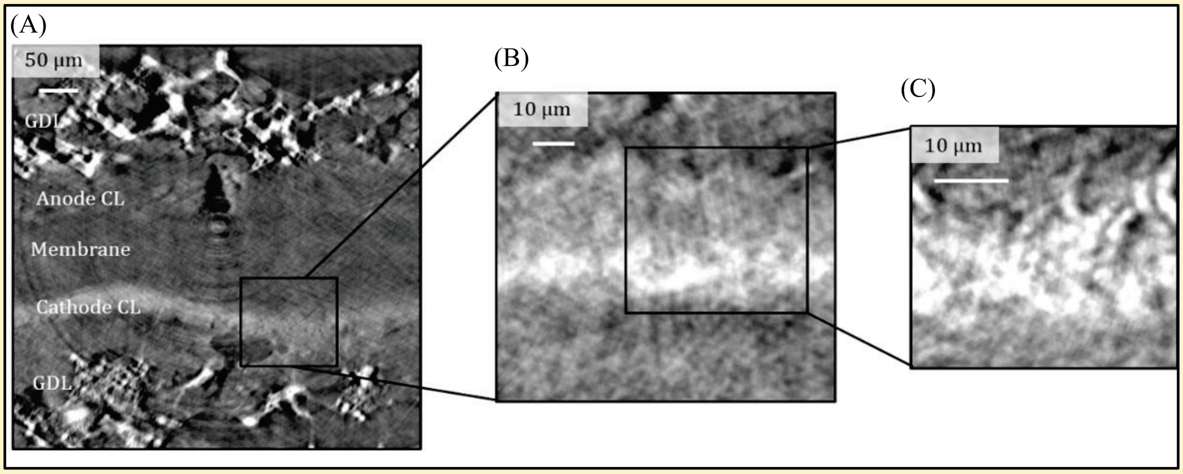


Figure S8-2. Operando nano X-ray CT experiment of a PEMFC at ESRF beamline ID16B showing (A) micro X-ray CT mode, (B) intermediate mode (100 nm resolution), and (C) nano X-ray CT mode (50 nm resolution). Cell operated at a potential of 0.1 V.[99] Reprinted with permission: D. Kulkarni, et al., *Journal of Physics: Energy,* **2** 044005 (2020) under Creative Commons Attribution 4.0 International (CC BY 4.0). Copyright 2020.

Enable rapid investigation of slow or rare events that lead to degradation

The descriptions of the degradation reactions that are observed in hydrogen materials suggest that they are discrete phenomena that can be identified, predicted, and controlled using experiments conducted over typical laboratory time frames with rigorously defined and controlled parameter spaces; however, this is not the case largely because the time frames over which alterations in materials composition, structure, and morphology occur often span tens of thousands of hours. Conducting experiments to investigate, predict, and control materials alterations over these time frames is difficult or impossible.

Consequently, research approaches are needed that can effectively address the time frame challenges by manipulating the kinetics of materials alterations to enable observation of slowly progressing reactions.[100,101] The conventional approach for probing slow reactions is to use operating conditions in which a single reaction condition is varied in an incremental fashion while observing changes in composition, structure, or reactivity. However, this strategy is very difficult to execute because multiple coupled reactions can occur simultaneously. Furthermore, changing reaction conditions to accelerate a targeted rate-controlling reaction inevitably changes the rates of both competing and coupled reactions. Research is needed to identify the relative rates of competitive and coupled reactions as a function of the microscopic environments relevant for hydrogen materials. Note that if specific reactions could be selectively accelerated, it would lessen the need to understand the complete ensemble of reactions; thus, research focused on activating individual reaction mechanisms is of strong interest.

Increasing the harshness of the chemical environment to enhance rates of chemical and morphological modification of hydrogen materials may activate competing reactions that are deleterious and furthermore, are not representative of processes that occur under less aggressive conditions. This can result in acceleration of reactions that proceed via mechanisms that are not relevant to the degradation reactivity occurring over long time periods. For example, oxygen-conducting SO-WE cells undergo degradation at the electrolyte–anode interface at 778°C, as shown in **Figure 4-3**,[102,103] but at 850°C they can display predominant degradation of the catalyst-support materials used in the cathodes (not shown).[82,104] Research is needed to enable accurate assessment of the responses of coupled and competitive reactions to variations in the reactive environments of hydrogen materials.

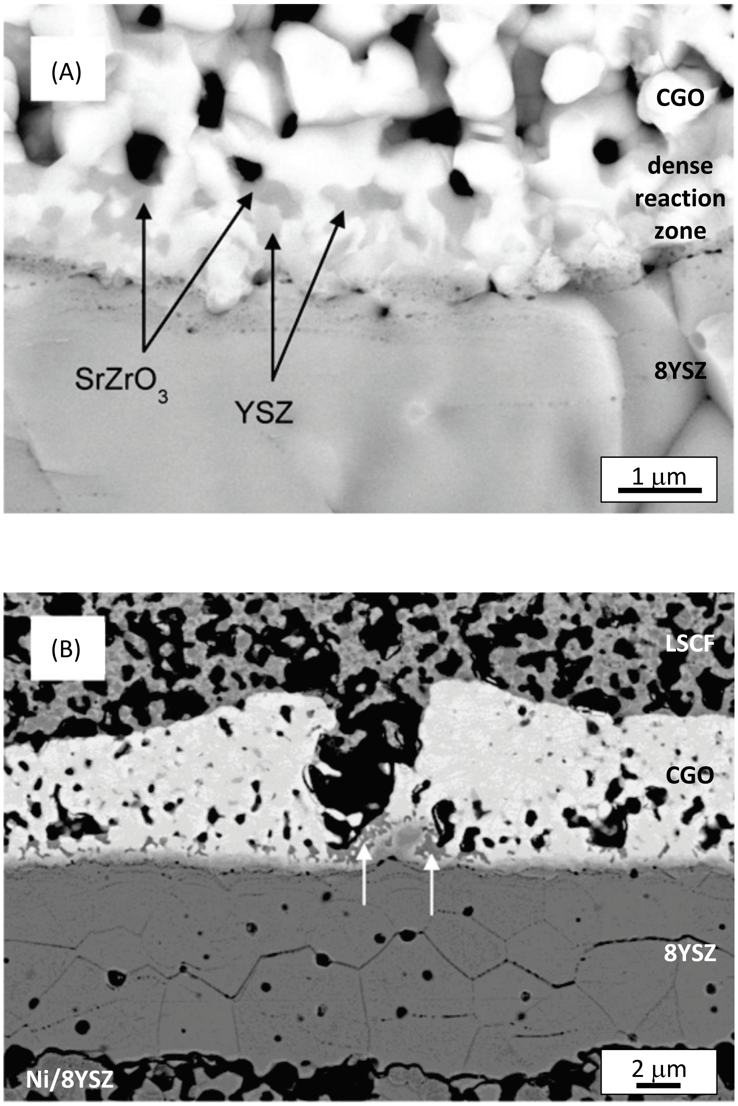


Figure 4-3. Backscatter electron microscopy images of an 8YSZ/$Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) interface acquired from a Ni-8YSZ/YSZ/GDC/$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ SOE cell operated for 9,000 hours. Galvanostatic at 1 Acm^{-2}, 778°C, and an 80% steam feed. (*A*) Enlarged area of image (*B*) showing formation of $SrZrO_3$ due to the diffusion of YSZ into the CGO layer and horizontal pore structure along the interface. (*B*) Micrometer-sized pores formed in CGO layer with enhanced $SrZrO_3$ formation (shown by arrows) at the sintering cracks in the CGO layer where the cathode was in direct contact with YSZ. Gray scale gradient at the 8YSZ/CGO interface indicates the diffusion of Zr and Y into the CGO layer.[102] Reprinted from F. Tietz, et al., *Journal of Power Sources*, **223** 129-135 (2013) with permission from Elsevier.

Ongoing degradation reactions occurring in hydrogen materials can be benign for long periods of time, resulting in insignificant changes. However, these processes can be precursors for catastrophic events like the loss of conductivity in the electrolyte or fracturing at the electrolyte–electrode interfaces, completely degrading device performance.[104–108] Approaches for understanding the time constants for these rare events are needed; thus, research directed at correlating the occurrence and rates of degradation mechanisms with catastrophic failures are necessary. A related need is the ability to measure the progress of the chronic processes over long time periods.

The application of transient variations in reaction conditions may hold potential for accelerating degradation reactions without inducing irrelevant mechanisms and without inducing catastrophic events. Application of periods of higher, lower, or dynamic voltage, current density, temperature, or chemical concentration gradients can result in changes to electrode and electrolyte materials that may be representative of "normal degradation rates," which if followed by periods of normal operation would allow the device to return to the previous level of performance with the imposition of apparent aging. Research into the effects of transient periods of harsh operation, their periodicity, and amplitude are current research gaps.

Overcoming structured complexity to gain insight into degradation phenomena

Model systems have been broadly used in many aspects of hydrogen technology development, creating structure–function relationships based on material descriptors that guide design.[109,110] The success of such efforts is served by using model systems that allow quantitative and fundamental information to be more readily obtained and used to develop mechanistic interpretations. For electrocatalytic performance such systems have been proposed and explored, as highlighted in **Figure 4-4**.[111] Similar model systems are yet to be applied with the same rigor to understand the scientific fundamentals of degradation challenges faced in carbon-neutral hydrogen technologies; current approaches to investigate degradation mechanisms typically involve the use of real systems in which multiple degradation mechanisms simultaneously occur and influence each other. Such a top-down approach, although valuable for applied investigations of degradation, limits the ability to derive fundamental and mechanistic information. The use of model systems with well-defined materials and systems that are systematically interrogated using a suite of experimental tools affords a more systematic bottom-up approach. Distinct degradation mechanisms can be more readily isolated and quantitatively investigated, facilitating the fundamental understanding of degradation mechanisms. A bottom-up approach also affords the ability to add complexity, one "layer" at a time, each in the form of another model component or system. Ultimately, sufficient layers of complexity can be combined to understand the interplay between degradation mechanisms at an atomistic scale, as well as approach the complexity of a real device, as illustrated in **Figure 4-5**,[7] demonstrating the predictive capability of fundamentally derived degradation models.

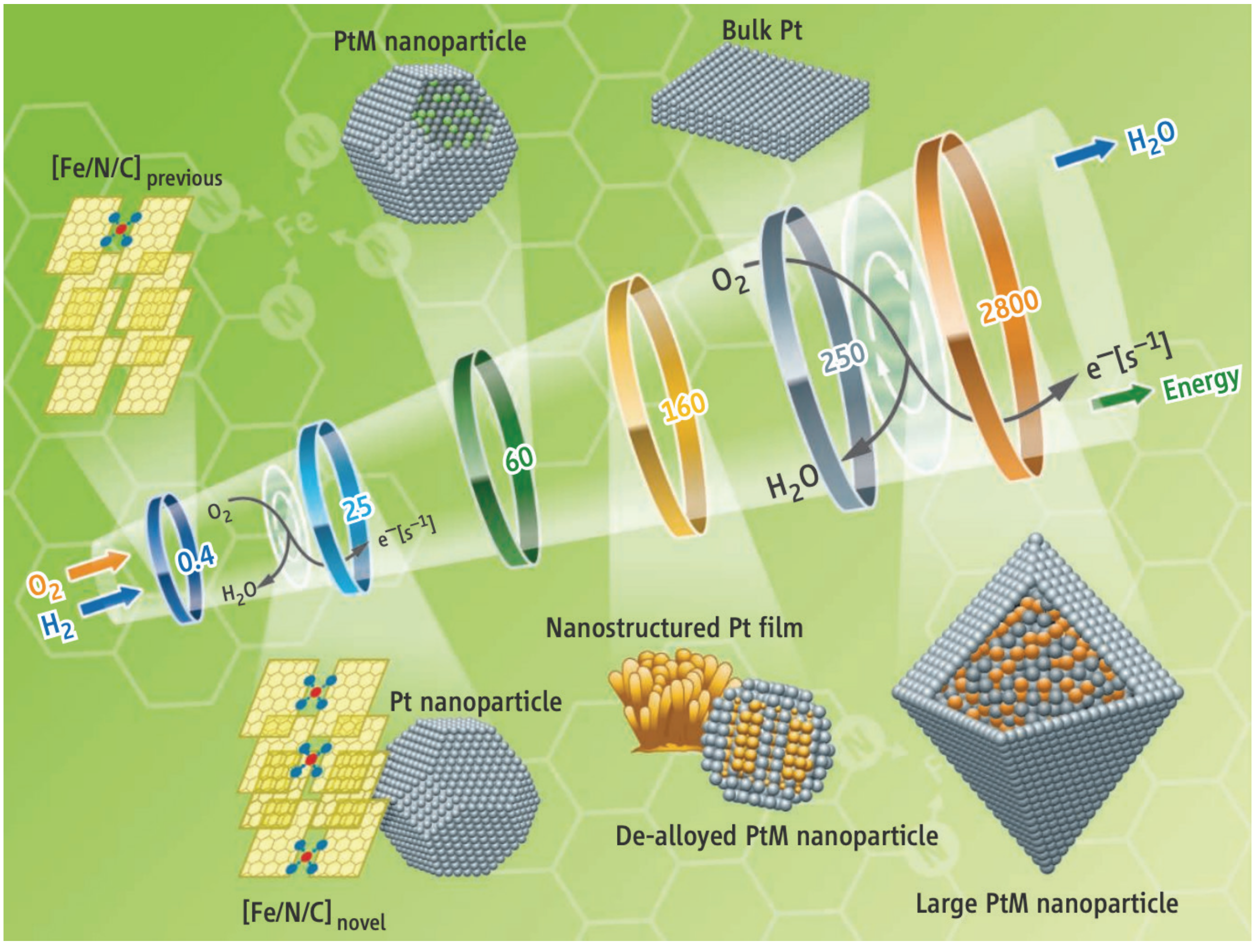


Figure 4-4. Illustration of different model oxygen reduction reaction electrocatalysts with increasing turnover frequencies targeting improved electrocatalytic performance.[111] Illustration by Aaron Ashley.

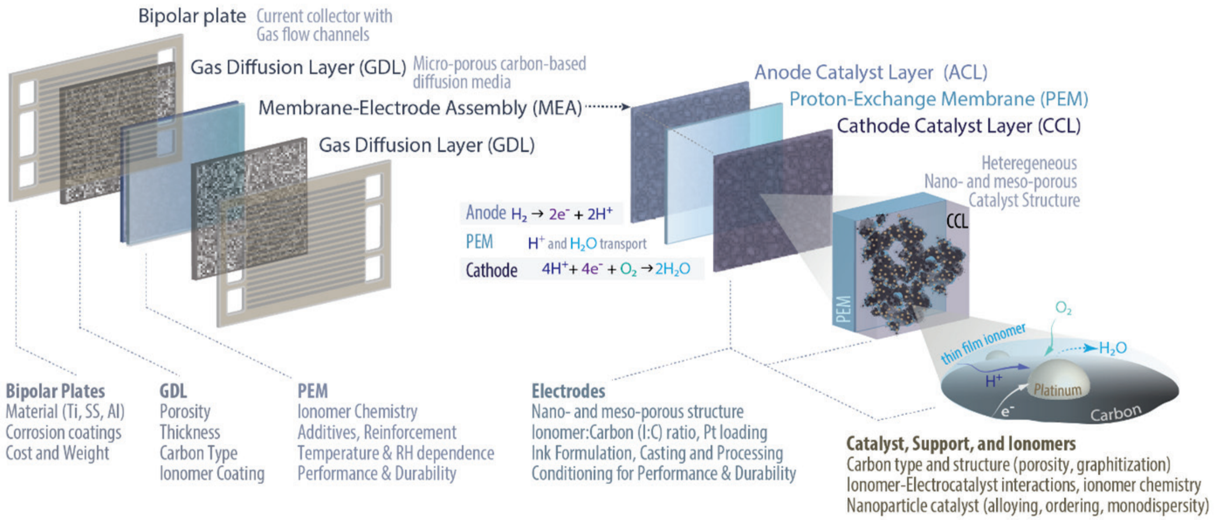


Figure 4-5. Representation of a PEMFC stack showing components and complexity of a functioning device including bipolar plates, gas diffusion layer, PEM, and electrodes.[7] Reprinted with permission: D.A. Cullen, et al., *Nature Energy*, **6** 462-474 (2021) Copyright 2021.

Combine experiments and computational approaches to produce atomic-level knowledge of degradation processes

Combined computational and experimental research of degradation mechanisms is needed to develop a mechanistic understanding and provide fundamental insight into the thermodynamic and kinetic landscape of various degradation modes. The use of model systems greatly facilitates the inclusion of computational research of degradation, as well as the ability to combine experimental and computational investigations. Well-defined model systems can be computationally simulated in contrast to real-world systems, which have highly complex environments that prohibit the development of representative computational models. Single crystal structures can serve as simplified model systems for the catalyst surfaces in hydrogen systems and processes, for example, and are readily simulated in computational environments. Single crystals also lend themselves to various characterization methods that support operando studies of structural, compositional, and electronic changes.[112,113] Access to data sets that span a large array of experimental degradation information (e.g., catalytic activity, material crystallinity, conductivity, electrolyte chemical composition) can enable the use of ML and other data science tools to identify non-obvious trends that inform the mechanistic information. The study of degradation involves a large parameter space, which can be prohibitive to probe experimentally at the level needed to develop quantitative understanding. Constant feedback between early experimental information and ML models can help focus parameter spaces of interest for further experimental resources and efforts. There also exists a need for a feedback loop involving device performance, in situ characterization methods, and computational modeling to interrogate degradation mechanisms at the atom scale. Ex situ characterization can yield misleading interpretations of degradation because materials and their evolution are highly sensitive to their environment.

A particular research need for computational investigations of degradation is the development of computational tools and methods that can operate across multiple timescales. Modeling of chemical events at the atom scale through first principles methods is typically done at fractions of a second, largely because of the intensive computational resources required. Degradation events must be captured over multiple length- and timescales. Combining energetic information derived from computational calculations can be incorporated into thermodynamically consistent kinetic models that predict degradation behavior over timescales relevant to experimental applications.

4d. Potential Impact

The ability to understand, predict, and ultimately mitigate degradation mechanisms can transform the viability of large-scale deployment of carbon-neutral hydrogen technologies. Developing stable materials for hydrogen systems and processes can enable the reduction or elimination of platinum group metal loadings while also dramatically shifting the trade-offs between performance and durability such systems currently experience. Predictive understanding of degradation mechanisms can also accelerate the design cycle, thereby transforming the cost and timeline associated with bringing future hydrogen technologies to market. Advancements in understanding degradation mechanisms is of significant relevance to other scientific areas, where technologies required for a carbon-neutral future also face issues of performance and long-term stability. Characterization tools developed, in particular operando and in situ methods, are broadly applicable to other areas of scientific research needed to understand atomic level interactions.

3. Closing Remarks

This report describes the existing knowledge gaps, scientific and technical challenges, and importantly, the fundamental science needs for successfully developing and implementing energy-efficient, carbon-neutral hydrogen materials, systems, and processes. These needs are summarized in the four PROs presented herein that are designed to accelerate discovery and set research priorities for hydrogen over the next decade. The PROs build upon—and go well beyond—established research directions outlined in previous BES workshops and reports and provide a framework for the basic research needed to identify and understand the fundamental principles of hydrogen production, storage, and utilization that are essential to achieve DOE's aggressive goals of establishing a carbon-neutral, hydrogen-driven energy and chemical infrastructure as outlined in the Hydrogen Shot. The impact of these basic science efforts can be increased by effective coordination with the applied research programs to enable a DOE-wide approach to tackle the most important environmental issue facing the nation: reversing the impacts of climate change through implementation of clean energy innovations such as carbon-neutral hydrogen technologies.

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Appendix A.

Roundtable on Foundational Science for Carbon-Neutral Hydrogen Technologies

Background and Roundtable Charge

August 2–5, 2021 (Zoom virtual meeting)

Background: Hydrogen is an energy-rich molecule that can be produced from processes involving water splitting, fossil fuels, microbial reactions, and biomass feedstocks. Hydrogen has the potential to become an increasingly crucial component of energy systems, both as a clean energy carrier for transportation/energy storage and as chemical feedstocks for industrial, residential, and agricultural sectors. Hydrogen is currently an important target in energy research and development, as illustrated by productive efforts of U.S.-based research and development by single investigators and larger teams (centers), demonstration projects, and international research initiatives. Today, there is a compelling opportunity to create hydrogen energy systems that do not generate carbon dioxide or other greenhouse gases. Although notable progress has been made in hydrogen research over the previous two decades, further scientific progress is required to overcome technical hurdles to economically viable hydrogen production, storage, and utilization in systems that operate under carbon-neutral conditions.

Multiple approaches are being considered for carbon-neutral hydrogen production. One strategy is to build on technologies that convert renewable energy into the electricity required for electrolysis to split water and produce hydrogen gas. However, hydrogen can be produced not only from electrolytic or photolytic water splitting but also from hydrogen-rich hydrocarbons such as methane, as well as from biomass through integrated catalytic processes that must be made highly selective to achieve carbon-neutral emissions. Microorganisms can be used to produce hydrogen through biological reactions under mild reaction conditions.

In addition, for many applications, hydrogen must be safely transported and then stored using novel materials and chemical storage strategies. Many technological advances have been achieved, but more fundamental research is necessary to gain new knowledge that can lead to discovery or development of novel solid-state and molecular hydrogen storage media including adsorbents, metal hydrides, and organic liquids. Deep phenomenological understanding is likewise needed for novel approaches to low- and high-temperature membranes for purification, separation, and production processes.

Basic research to identify and understand the fundamental principles of hydrogen production, storage, and utilization is essential to achieve a carbon-neutral, hydrogen-driven energy and chemical infrastructure. This roundtable is intended to take advantage of the strong foundation of current and past Office of Basic Energy Science (BES) research, in coordination with existing research and development activities supported by the Energy Efficiency and Renewable Energy and Fossil Energy Offices, to assess the critical steps needed to overcome the scientific and technical complexities and successfully design carbon-neutral hydrogen materials and processes.

Roundtable Charge: This roundtable will discuss scientific and technical barriers associated with carbon-neutral hydrogen production, chemical- and materials-based hydrogen storage, and the integration for hydrogen technologies. It will identify priority research opportunities (PROs) for fundamental science that will accelerate progress toward energy-efficient, carbon-neutral cycles for hydrogen processes. Although carbon capture and sequestration technologies are critical to implementing many carbon-neutral cycles, such as in thermoelectric power plants that use fossil fuels, these will not be a topic of discussion in this roundtable. The roundtable will build upon—and go beyond—the established research opportunities outlined in previous workshops related to this topic as well as recent U.S. Department of Energy reports, to determine the most significant avenues for discovery and development of *selective*, *stable*, *and efficient chemical and materials systems*. The roundtable will address the basic research challenges in hydrogen production, storage, and utilization, together with cross-cutting opportunities that can provide synergy among these challenges, as described below.

- **Production** of hydrogen: Extraction of hydrogen from molecular carriers in an energy-efficient and selective manner becomes a greater research challenge as the complexity and heterogeneity of the feedstock increases, as well as with the added requirement for carbon neutrality. Research paths to innovative and efficiently extract hydrogen, especially those that increase yields and concomitant reduction of energy spent for by-product treatment or greenhouse gas emissions, will be evaluated. Another topic for consideration is how to unravel the mechanisms of electrochemical, photo-driven, biological, and thermal reactions occurring in complex environments. One goal for consideration is discovery of fundamental design principles for coupled molecular/materials systems that selectively extract hydrogen from complex sources under milder and more energy-efficient conditions.
- **Storage** of hydrogen: To achieve the purity and quantity of hydrogen required for many applications, storage currently involves energy-intensive processes that impose limitations on the viability of hydrogen as an energy carrier and commodity chemical. In principle, hydrogen may be transported and stored efficiently by the suitable atomic/molecular level design of environments and materials that contain hydrogen. Today, hydrogen interactions with a wide range of materials and chemicals are still not understood, including systems involving novel membranes, solvents, sorbents, molecular cages, hierarchical structures, and metallic alloys. Additionally, elucidation of transport phenomena, from dynamics at the molecular scale to macroscopic processes, under electrical, thermal, or other applied potentials is needed. The design of novel, durable molecular and materials systems, including consideration of temperature extremes, is required to attain consistently controlled properties appropriate for hydrogen storage or delivery.
- **Utilization** of hydrogen: Hydrogen plays an important role as an energy carrier (e.g., in fuel cells and combustion turbines) and as a chemical reagent (e.g., in chemical or materials manufacturing). Increasing the efficiency of electrochemical fuel cells and electrolyzers has several structural and chemical challenges, such as enhancing the stability of catalysts, optimizing electrode architectures, and developing new

electrolytes/membranes. A major impediment to more widespread use of fuel cells is the use of precious metal catalysts for both the oxidation of hydrogen and reduction of oxygen. Significant gaps in scientific knowledge remain on how to achieve competitive current densities and durability using earth-abundant catalysts, chemicals, and materials. Likewise, increasing the efficiency, activity, and selectivity of hydrogenation and hydrogenolysis reactions presents further challenges, such as the need to discover stable earth-abundant catalysts and resilient, molecularly selective membranes. For all areas of hydrogen utilization, research is required to develop a molecular or atomic-level mechanistic understanding of the pathways that lead to activation of hydrogen, activation and deactivation of substrates, and synthesis and deactivation of materials and membranes.

- **Cross-cutting** opportunities: This roundtable will identify fundamental science challenges that are common across the hydrogen technology landscape, from production and storage to "real-world" use, as well as the research approaches needed to address common scientific challenges (e.g., theory, modeling, data science, synthesis, and characterization). These research challenges present many opportunities to leverage and coordinate synthesis, characterization, and simulation platforms to gain further insight into relevant hydrogen-based reactions and processes. Cross-cutting research approaches might play a key role in developing a mechanistic understanding of critical reactions and processes include:
    - theory and simulation of multiscale phenomena, from ab initio electronic structure calculations to molecular models, solid state and fluid modeling and simulation, and computational approaches for energy and charge transfer
    - advancing chemical and materials knowledge representations for data science approaches, machine learning, deep learning, and reinforcement learning; synthesis of complex materials and ligand design for hydrogen storage, molecular or ionic transport in fuel cells, selective catalysts, and membrane chemistries
    - conducting in situ and operando spectroscopy, microscopy, and neutron and X-ray scattering experiments for processes important in hydrogen reactivity, such as hydrogen-materials interactions, solvent and cage effects, and bond scission and formation.

The roundtable will produce a report to BES that identifies PROs for a coordinated effort to enable accelerated realization of future hydrogen technologies.

Chairs:	Morris Bullock (PNNL) and Karren More (ORNL)
Estimated Size:	Approximately 30 participants plus additional observers • Participants include scientists and engineers from academia, DOE national and federal laboratories, and industry • Representatives from DOE, other Federal agencies, and DOE national labs will be invited as observers
Breakout Panels:	Three topical focus areas and a cross-cutting panel to identify common research opportunities.

Appendix B.

Foundational Science for Carbon-Neutral Hydrogen Technologies Roundtable Attendees

Roundtable Co-Chairs

Morris Bullock, Pacific Northwest National Laboratory
Karren More, Oak Ridge National Laboratory

Plenary Speakers

Kathy Ayers, Nel Hydrogen "Challenges of Large-Scale Water Electrolysis and Implications for Advanced Water Splitting Technologies"
Tom Baker, University of Ottawa "Cavendish + 255: What's Next for H2 Science?"
Levi Thompson, University of Delaware "Challenges and Opportunities for Hydrogen Utilization"

Invited Roundtable Participants

Hydrogen Production Panel (Panel Lead: Jinguang Chen, Columbia University)
Omar Abdelrahman, University of Massachusetts
Kathy Ayers, Nel Hydrogen
Marcetta Darensbourg, Texas A&M University
Jing Gu, San Diego State University
Eranda Nikolla, Wayne State University
Jenny Yang, University of California, Irvine

Hydrogen Storage Panel (Panel Lead: Krista Walton, Georgia Institute of Technology)
Tom Autrey, Pacific Northwest National Laboratory
Tom Baker, University of Ottawa
Tabbetha Dobbins, Rowan University
Diego Gomez-Gualdron, Colorado School of Mines
Craig Jensen, University of Hawaii
Jose Mendoza-Cortes, Michigan State University
Tina Nenoff, Sandia National Laboratories

Hydrogen Utilization Panel (Panel Lead: Bryan Pivovar, National Renewable Energy Laboratory)
Lauren Greenlee, Pennsylvania State University
Gary Groenewold, Idaho National Laboratory
Shanna Knights, Ballard Power Systems
Khartish Manthiram, California Institute of Technology
Levi Thompson, University of Delaware
Adam Weber, Lawrence Berkeley National Laboratory

Cross-Cutting Panel (Co-Leads: Aleksandra Vojvodic, University of Pennsylvania and Daniel Resasco, University of Oklahoma)
Simon Bare, SLAC
Shannon Boettcher, University of Oregon
Jeff Greeley, Purdue University
Suljo Linic, University of Michigan
Christos Maravelias, Princeton University
Deborah Myers, Argonne National Laboratory
Iryna Zenyuk, University of California, Irvine

U.S. Department of Energy (DOE) Participants
Chris Fecko, BES
Bruce Garrett, BES
Allison Hahn, NE
Kerry Hochberger, BES
Linda Horton, BES
Jason Marcinkoski, NE
Eric Miller, EERE
Eva Rodezno, FECM
Robert Schrecengost, FECM
Andy Schwartz, BES
Athena Sefat, BES
Michael Sennett, BES
Sunita Satyapal, EERE

Invited Observers
Michelle Buchanan, DOE Oak Ridge Site Office
Dong Ding, Idaho National Laboratory
Zak Fang, ARPA-E
Greg Fiechter, BES
Kelly Gaffney, SLAC
William Gibbons, EERE
Chris Guenther, National Energy Technology Laboratory
Gregory Hackett, National Energy Technology Laboratory
Daniel Haynes, National Energy Technology Laboratory
Brittany Hidges, Idaho National Laboratory
Helen Kerch, BES
Mike Markowitz, BES
Dan Matuszak, BES
Gail McLean, BES
Karen Mulfort, Argonne National Laboratory
Long Qi, Ames National Laboratory
Molly Roy, Office for Science and Energy
Viviane Schwartz, BES
Sanjaya Senanayake, Brookhaven National Laboratory
Jacob Spendelow, Los Alamos National Laboratory
Vitalie Stavila, Sandia National Laboratories
Ned Stetson, EERE

Peter Sushko, Pacific Northwest National Laboratory
Thiyaga Thiyagarajan, BES
Francesca Toma, Lawrence Berkeley National Laboratory
Jao VandeLagemaat, National Renewable Energy Laboratory
John Vetrano, BES
James Vickers, EERE
Christina Wildfire, National Energy Technology Laboratory
Brandon Wood, Lawrence Livermore National Laboratory
Michael Zachman, Oak Ridge National Laboratory
Xiaolin Zheng, SLAC

Appendix C.

DOE-BES Virtual Roundtable on Foundational Science for Carbon-Neutral Hydrogen Technologies

Platforms: Zoom and XLeap (for brainstorming)

August 2–5, 2021

Day 1: Monday**, **August 2, 2021

All times indicated are Eastern

2:45–3:00 PM	**Log-In**
3:00–3:10 PM	Welcome to the Plenary Session and Introduction of Speakers Morris Bullock (PNNL) and Karren More (ORNL)
3:10–3:45 PM	*Challenges of Large-Scale Water Electrolysis and Implications for Advanced Water Splitting Technologies* Kathy Ayers, Nel-Hydrogen (25 min presentation + 10 min Q&A)
3:45–4:20 PM	*Cavendish + 255: What's Next for H_2 Science?* Thomas Baker, University of Ottawa, Canada (25 min presentation + 10 min Q&A)
4:20–4:55 PM	*Challenges and Opportunities for Hydrogen Utilization* Levi Thompson, University of Delaware (25 min presentation + 10 min Q&A)
5:00 PM	Adjourn

Day 2: Tuesday**, **August 3**, **2021

10:45–11:00 AM	Log-in to *Zoom*
11:00–11:40 AM	Welcome Linda Horton, Director, Office of Basic Energy Sciences Sunita Satyapal, Director, Hydrogen & Fuel Cell Technologies Office
11:40–12:00 PM	Welcome, Roundtable Goals and Logistics Morris Bullock, PNNL Karren More, ORNL

12:00–12:30 PM	**Break** (30 min)
12:30–4:00 PM	Breakout *Session I—Science Focus (Panels will be provided with XLeap link)* Panel on Hydrogen Production Panel on Hydrogen Storage Panel on Hydrogen Utilization Panel on Cross-cutting Research - panelists will directly participate and interact on other panels: 12:30-2:00 panelists participate in specific/assigned panels (Production, Storage, Utilization) 2:00-4:00 panelists return to Cross-cutting panel with notes to coordinate ide*as across panels*
4:00–4:30 PM	**Break** (30 min)—Panel Leads prepare panel reports (suggested PROs from panel discussions)
4:30–6:00 PM	Plenary Session I—Panel Reports: Identification of Potential PROs and Discussion
6:00 PM	Most attendees adjourn; panel leads and co-chairs meet to consolidate responses in preparation for Day 3

Day 3: Wednesday, August 4, 2021

10:45–11:00 AM	**Log-In**
11:00–11:15 AM	Introduction to Day 3—goals, PROs, logistics
11:15 AM–3:30 PM	*Breako*ut Session II—Panels re-assigned to focus on potential PROs (panelists take a 15 min. break 1:30-1:45 PM) (panel le*ads meet with Co-chairs and BES, 1:45-2:00 PM and provide update on progress)*
3:30–4:30 PM	**Break** (60 min) **** Panel leads meet with co-chairs and BES to collate feedback from Plenary Session II****
4:30–6:00 PM	Plenary Session III—Presentation of PROs by Panel Leads to Roundtable Closing Remarks—Morris Bullock and Karren More
6:00 PM	**Adjourn**

*Day 4: Thursday, August 5, 2021 ***Roundtable chairs, panel leads and designated writers only****

10:45–11:00 AM	**Log-In**

11:00–11:30 AM	Introduction of writing assignments/writing groups
11:30 AM–1:00 PM	**Writing/editing session 1**
1:00–2:00 PM	**Break** (60 min)
2:00–6:00 PM	**Writing/editing session 2**

Day 5: Monday, August 16, 2021 ***Roundtable chairs, panel leads and designated writers only***

10:45–11:00 AM	**Log-In**
11:00–11:30 AM	Discussion and updates on writing progress
11:30 AM–3:30 PM	**Writing/editing session 3**

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