

Hydrogen: Water Splitting

from atomic scale understanding to design of advanced electrocatalyst materials for real application

Renewable energy plays a key role in achieving the energy and climate objectives of the European Union (EU). The EU strongly supports the adoption of very ambitious climate targets for 2030 aiming to carbon neutrality by 2050 [1].

Hydrogen produced by water electrolysis has high potential to become the core technology in a decarbonized global energy sector, since it enables transition of our energy system in multiple areas, from energy production, storage and distribution, to end-uses in transport, industry and heating [2] (► *figure 1*).

The EU Hydrogen Strategy has defined a renewable hydrogen production target for 2030 at around 10 million tonnes which is equal to total hydrogen production capacities at the moment.

Currently, the cheapest method of bulk hydrogen production is hydrocarbon reforming, and over 90% of hydrogen is produced from fossil fuels, while clean hydrogen (renewable or low-carbon) production capacities are lower than 1% of total hydrogen production [1,2] (► *figure 2*).

These numbers indicate the extent of the challenge which requires not only development of new renewable energy sources across the EU but also deploying new electrolyzers for on-site hydrogen production.

Moreover, clean hydrogen needs to become cost-competitive with conventional fuels [2]. In order to promote cost reductions the EU identified a set of measures including upscaling of electrolyzer/fuel cell equipment manufacturing and increasing research and development efforts for hydrogen technologies.

The development of Power-to-Hydrogen (PtH) projects with the focus on increasing energy efficiency and cost reductions along the whole value chain has pivotal importance for a sustainable development of the hydrogen sector and the number of such projects is rapidly increasing across the EU countries. About 96% of planned PtH capacity and 66% of planned projects are represented by six countries: the Netherlands, Spain, Germany, Denmark, France, and Portugal. The number and size of projects differ significantly across countries. For instance, in Germany ca.

1500 MW composed of 34 projects reaching 46 MW average project capacity, while Denmark's 1454 MW will be provided by eight projects with an average project size of 182 MW.

Majority of those projects plan to use the proton exchange membrane (PEM) technology, which is acidic water electrolysis, while 30% choosing alkaline electrolysis. The remaining 4.4% will involve solid oxide electrolysis (SO). However, PEM is often chosen for relatively small projects and its share in total capacity is only 21.4%, while 76% of the capacity will be provided by alkaline technology and 2.5% by SO [1].

Water electrolysis is a process in which water molecules are decomposed into hydrogen and oxygen by supplying electrical energy.

This can be achieved by the use of an electrolytic cell that consists of two electrodes separated by an electrolyte with sufficient ionic conductivity, e. g. acid or base.

In this processes catalyst materials are employed to achieve high rates of hydrogen and oxygen formation consuming lowest possible energy. Catalysts should be reactive and stable towards degradation to maintain high activity on a long-term.

Acidic and alkaline electrolyzers function in slightly different ways:

Alkaline water electrolysis is a well matured technology that enables hydrogen production up to the megawatt range. In alkaline electrolyzers two nickel-based electrodes immersed in a liquid alkaline electrolyte solution at a level of 20–30% potassium hydroxide. The two electrodes are separated by a diaphragm to prevent interaction between the product gases for the sake of efficiency and safety. The major issues of alkaline electrolyzers are typically associated with low partial load range, limited current density and low operating pressure [3].

In **acidic water electrolyzers** a polymer-electrolyte membrane enabling exchange of protons is used as an electrolyte.

Such membrane provides high proton conductivity, low gas crossover, compact system design, high efficiency and high pressure operation.



HZB

Dr. Olga Kasian
olga.kasian@helmholtz-berlin.de

Dr. Sonya Calnan

sonya.calnan@helmholtz-berlin.de

DLR

Dr. Syed Asif Ansar
syed-asif.ansar@dlr.de

Dr. Aldo Saul Gago Rodriguez
aldo.gago@dlr.de

Fraunhofer IEE

Jochen Bard
jochen.bard@iee.fraunhofer.de

Fraunhofer ISE

Dr. Tom Smolinka
tom.smolinka@ise.fraunhofer.de

IZES

Dr. Bodo Groß
gross@izes.de

FZ Jülich

Dr. Marcelo Carmo
m.carmo@fz-juelich.de,

Prof. Dr. Michael H. Eikerling
m.eikerling@fz-juelich.de

KIT

Prof. Dr. Thomas Jordan
thomas.jordan@kit.edu

ZAE

Maximilian Möckl
maximilian.moeckl@zae-bayern.de

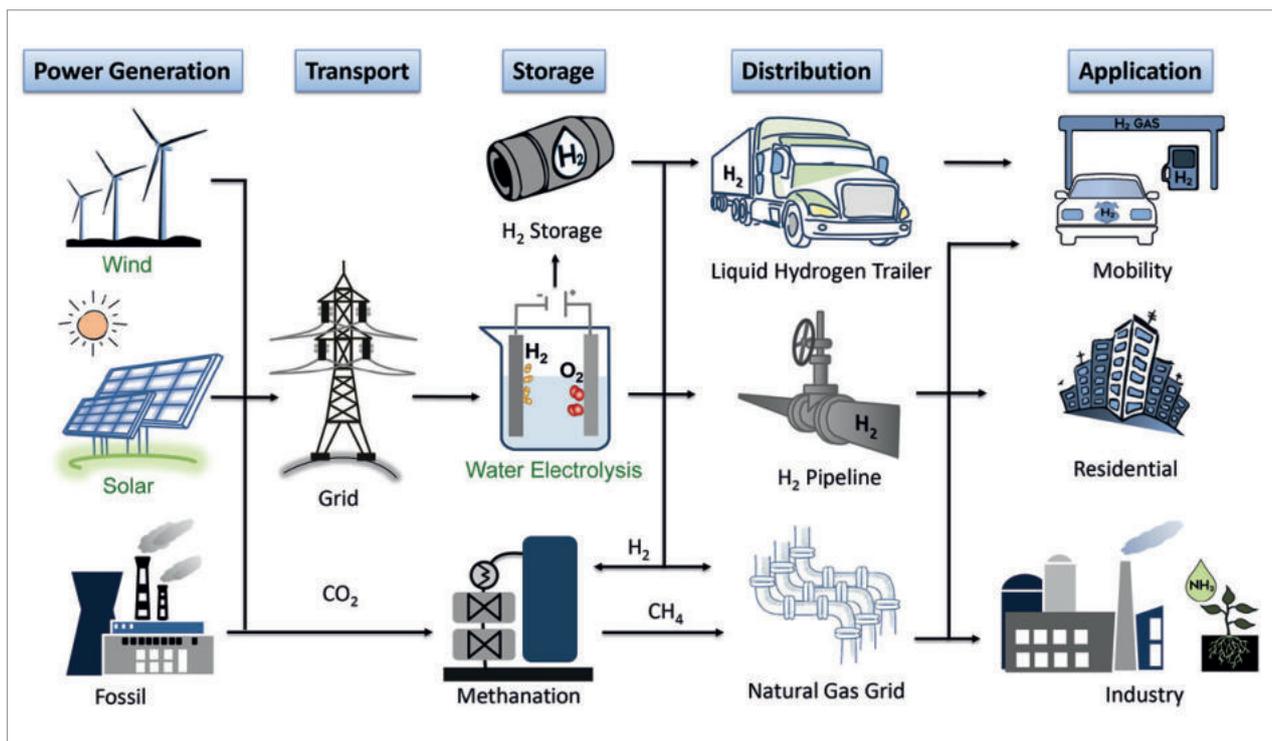


Figure 1
Coupling Renewable Energies and Water Electrolysis
 (Reference: Grube et al., Sustainable Energy Fuels, 2020)

However, use of scarce, expensive materials is required due to highly corrosive acidic environment and high applied voltage. In the state of the art PEM electrolyzers platinum and iridium are used to catalyze hydrogen and oxygen formation respectively, because these are nearly the only materials that can withstand such harsh corrosive conditions on a long-term [3]. Under dynamic operation conditions of an electrolyzer even platinum and iridium catalysts slowly degrade. This is especially crucial for anodic oxygen evolution because the reaction itself triggers oxidation and degradation of the catalysts and even stable iridium-based materials slowly undergo dissolution. This results in efficiency decrease and loss of expensive catalyst material [4]. Requirement of high corrosion resistance applies not only to the catalyst materials, but also to the current collectors and separator plates, which take up the major part of the stack costs. Several approaches to increasing service life and reducing the costs were discussed in literature [5,6].

Even though catalysts are not the most expensive components of the electrolyzers, their stable operation is crucial. Development of approaches to hindering catalyst degradation requires deep understanding of underlying processes at the atomic level, because only the topmost atomic layers of the electrocatalysts govern the mechanism and kinetics of hydrogen and oxygen formation. In time the surface atoms undergo changes induced by the

reactions, they can be poisoned, oxidized or even lose connection with underlying layers and dissolve. The oxidation and dissolution reactions are often linked. Theoretical studies and modelling provide understanding of interconnection between these processes. In case of platinum catalysts theory predicts that oxidation of platinum surface eventually leads to its dissolution and that dissolution is favorable when a half of the atomic monolayer is covered by oxygen [7]. Translating these observations to real application, dissolution of platinum occurs under the conditions prevailing during start-up and shutdown of the electrolyzer [8].

Similar tendency is observed for iridium catalyst during water splitting to oxygen. With the aid of atom probe tomography, which is a mass-spectrometry technique that allows to map the distribution of individual atoms within the surface in three dimensions it was proven that under the oxygen evolution metallic iridium transforms into stable rutile oxide. Such transformation happens via formation of a few atoms in size metastable clusters containing iridium and oxygen in 1:1 ratio, that are extremely reactive but very unstable [9].

Further employment of advanced electrochemical methods revealed that reactions of oxygen formation and catalyst degradation are linked via common intermediates [4], denoting that more active catalyst

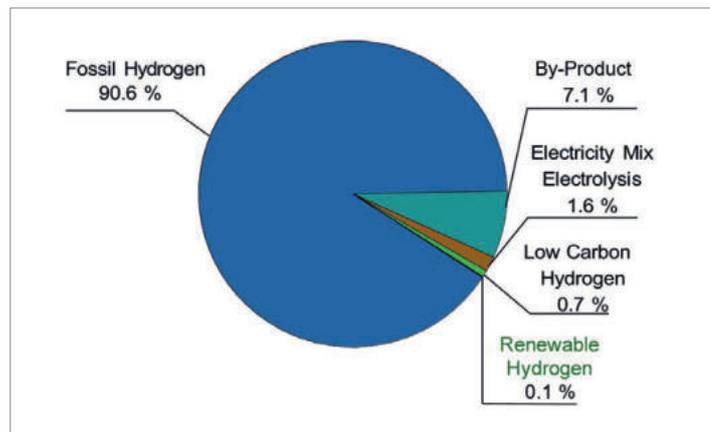


Figure 2

Hydrogen Production capacity(Reference: <https://www.hydrogeneurope.eu/>)

materials are less stable. In order to hinder the degradation reactions, it is, therefore, crucial to identify these intermediates and develop the strategy how to stabilize them on the surface. This can be achieved with the aid of advanced electrochemical methods combined with surface sensitive techniques, e.g. synchrotron based methods. The most reactive catalysts suffer from additional degradation pathways. Stability drops when the oxygen atoms in the catalyst are replaced by those from water. In case of extremely reactive oxide catalysts, the oxygen molecule can be released directly from the oxide lattice, without water contribution [10].

Iridium dioxide, which is the most stable oxygen evolution catalyst known, also experiences ongoing structural changes during water splitting. Surface restructuring affects two nanometers of the oxide due to a constant exchange between oxygen atoms between the catalyst and water, as revealed by isotope labelling and atom probe tomography [11].

There are several approaches to decreasing loading of precious metals and durability improvement. Without sacrificing stability the efficiency of the catalyst utilization can be improved if the catalytically active noble metal or oxide is dispersed over a support material [12].

Another approach relies on so-called synergy effects in alloys or mixed oxides where the functional properties of resulting mixtures would be superior compared to individual components. Ideally, theory and modelling should be used to find the best combinations. In this approach, reactivity of iridium catalyst is improved by alloying with ruthenium (Ru) or nickel (Ni) [13,14].

One of the promising ways to enhance stability is the formation of mixtures in which the noble catalyst element is 'dissolved' in the non-noble matrix of more stable metals or metal oxides. For example, mixtures

of iridium with titanium oxides containing at least 50 at.% of iridium exhibit reactivity comparable to iridium dioxide, while exceed it in stability. Such superior performance governed by the atomic scale structure in which metallic iridium matrix providing high reactivity mixed with titanium oxide enriched clusters ensuring stability towards dissolution [15].

Extremely reactive and stable catalysts tested in laboratory scale often cannot find application in real electrolyzers. This is mainly due to limitations of experimental methods for stability estimation. Moreover, the same catalyst with the same composition prepared by different procedures may show different performances. For instance, iridium-ruthenium mixed oxides prepared by different approaches show a different performance in both laboratory test cells and PEM electrolyzers [16]. This highlights the importance of membrane electrode assembly tests as single cells and stacks, especially at conditions of high current density [6,17].

Summary

Development of the catalyst materials with superior performance demands deep understanding of the reactivity and stability at the atomic level. To ensure the technological relevance of the catalysts tested in the laboratory scale, durability should be then verified in both short stacks and the test systems operating at the kW level. This requires joint efforts of fundamental research, applied research and engineering.

Apart from the listed above problems, the use of clean hydrogen needs adaptations in production schemes, in the infrastructure and in the deployment of hydrogen by the end users. The implementation of the different hydrogen strategies requires a systematic change on research, private, national and European level.

References

- [1] Clean hydrogen monitor 2020, Hydrogen Europe, Belgium 2020, 106 p., www.hydrogeneurope.eu/wp-content/uploads/2021/04/Clean-Hydrogen-Monitor-2020.pdf
- [2] Grube et al., Sustainable Energy Fuels, 2020, 4, 5818, <https://doi.org/10.1039/D0SE00896F>
- [3] Carmo et al. Int. J. Hydrogen Energy 2013, 38, 4901, <https://doi.org/10.1016/j.ijhydene.2013.01.151>
- [4] Kasian et al. Angew. Chemie 2018, 130, 2514 <https://doi.org/10.1002/ange.201709652>
- [5] Ayers et al. Annu. Rev. Chem. Biomol. Eng. 2019, 10, 219, <https://doi.org/10.1146/annurev-chembioeng-060718-030241>
- [6] Lickert et al. Int. J. Hydrogen Energy 2020, 45, 6047, <https://doi.org/10.1016/j.ijhydene.2019.12.204>
- [7] Eslamibidgoli et al. Electrocatalysis 2016, 7, 345, <https://doi.org/10.1007/s12678-016-0313-2>
- [8] Cherevko et al. Nano energy 2010, 29, 275, <https://doi.org/10.1016/j.nanoen.2016.03.005>
- [9] Li et al. Nature Catalysis 2018, 1, 300, <https://doi.org/10.1038/s41929-018-0108-3>
- [10] Kasian et al. Energy & Environmental Science 2019, 12, 3548, <https://doi.org/10.1039/C9EE01872G>
- [11] Schweinar et al. J. Phys. Chem. Lett. 2020, 11, 5008, <https://doi.org/10.1021/acs.jpcclett.0c01258>
- [12] Saveleva et al. ACS Catal. 2020, 10, 4, 2508, <https://doi.org/10.1021/acscatal.9b04449>
- [13] Baroody et al. Electrochim. Acta, 2018, 283, 1006, <https://doi.org/10.1016/j.electacta.2018.06.108>
- [14] Buvat et al., ACS Appl. Energy Mater. 2020, 3, 5229, <https://doi.org/10.1021/acsaem.0c00069>
- [15] Kasian et al. J. Phys Energy 2020, <https://iopscience.iop.org/article/10.1088/2515-7655/abbd34/meta>
- [16] Wang et al. Nano Energy, 2017, 34, 578, <https://doi.org/10.1016/j.nanoen.2017.02.050>
- [17] Möckl et al. Int. J. Hydrogen Energy 2020, 45, 1417, <https://doi.org/10.1016/j.ijhydene.2019.11.144>