

New Catalyst Unveils the Hidden Power of Water for Green Hydrogen Generation

A European team of scientists led by ICFO (Barcelona) reports in Science a new milestone for the sustainable production of green hydrogen through water electrolysis. Their new catalyst design harnesses so far unexplored properties of water to achieve, for the first time, an alternative to critical raw materials for water electrolysis at industrial-relevant conditions.

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Hydrogen is a promising chemical and energy vector to decarbonize our society. Unlike conventional fuels, hydrogen utilization as a fuel does not generate carbon dioxide in return. Unfortunately, today, most of the hydrogen that is produced in our society comes from methane, a fossil fuel. It does so in a process (methane reforming) that leads to substantial carbon dioxide emissions. Therefore, the production of green hydrogen requires scalable alternatives to this process.

Water electrolysis offers a path to generate green hydrogen which can be powered by renewables and clean electricity. This process needs cathode and anode catalysts to accelerate the otherwise inefficient reactions of water splitting and recombination into hydrogen and oxygen, respectively. From its early discovery in the late 18th century, the water electrolysis has matured into different technologies. One of the most promising implementations of water electrolysis is the proton-exchange-membrane (PEM), which can produce green hydrogen combining high rates and high energy efficiency.

? To date, water electrolysis, and in particular PEM, has required catalysts based on scarc , rare elements, such as platinum and iridium, among others. Only a few compounds combi e the required activity and stability at the harsh chemical environment imposed by th s reaction. This is specially challenging in the case of anode catalysts, which have to operate t highly corrosive acidic environments - conditions where only iridium oxides have sho n stable operation at the required industrial conditions. But iridium is one of the scarce t elements on eart

. In search for possible solutions, a team of scientists has recently taken an important step o find alternatives to iridium catalysts. This multidisciplinary team has managed to develop a **novel way to confer activity and stability to an iridium-free catalyst by harnessing so far unexplored properties of water.** The new catalyst achieves, for the first time, stability in PEM water electrolysis at industrial conditions without the use of iridium.

This breakthrough, published in Science, has been carried out by ICFO researchers **Ranit Ram**, **Dr. Lu Xia**, **Dr. Anku Guha**, **Dr. Viktoria Golovanova**, **Dr. Marinos Dimitropoulos**, **Aparna M. Das** and **Adrian Pinilla-Sanchez**, and led by **Professor at ICFO Dr. F. Pelayo Garcia de Arquer**; and includes important collaborations from the Institute of Chemical Research of Catalonia (ICIQ), The Catalan Institute of Science and Technology (ICN2), French National Center for Scientific Research (CNRS), Diamond Light Source, and the Institute of Advanced Materials (INAM).

Dealing with the acidity

Combining activity and stability in highly acidic environment is challenging. Metals from the catalyst tend to dissolve, as most materials are not thermodynamically stable at low pH and applied potential, in a water environment. Iridium oxides combine activity and stability at these harsh conditions, and that is why they are the prevalent choice for anodes in proton-exchange water electrolysis.

The search for alternatives to iridium is not only an important applied challenge, but a fundamental one. Intense research on the look for non-iridium catalysts has led to new insights on the reaction mechanisms and degradation, especially with the use of probes that could study the catalysts during operation combined with computational models. These led to promising results using manganese and cobalt oxide-based materials, and exploiting different structures, composition, and dopants, to modify the physicochemical properties of the catalysts.

While insightful, most of these studies were performed in fundamental not-scalable reactors and operating at softer conditions that are far from the final application, especially in terms of current density. Demonstrating activity and stability with non-iridium catalysts in PEM reactors and at PEM-relevant operating conditions (high current density) had to date remained elusive.
To overcome this, the ICFO, ICIQ, ICN2, CNRS, Diamond Light Source and INAM researchers came up with a new approach in the design of non-iridium catalysts, achieving activity and stability in acid media. Their strategy, based on cobalt (very abundant and cheap), was quite different to the common paths.
i¿½Conventional catalyst design typically focuses on changing the composition or t e structure of the employed materials. Here, we took a different approach. We designed a n w material that actively involves the ingredients of the reaction (water and its fragments) in i s structure. We found that the incorporation of water and water fragments into the cataly t structure can be tailored to shield the catalyst at these challenging conditions, thus enabli g stable operation at the high current densities that are relevant for industrial applicationsi? ½, explains Professor at ICFO, Garcia de Arquer. With their technique, consisting n a delamination process that exchanges part of the material by water, the resulting cata yst present as a viable alternative to iridium-based cataly

A new approach: the delamination process
To obtain the catalyst, the team looked into a particular cobalt oxide: cobalt-tungsten oxide (CoWO4), or in short CWO. On this starting material, they designed a delamination process using basic water solutions whereby tungsten oxides (WO42-) would be removed from the lattice and exchanged by water (H2O) and hydroxyl (OH-) groups in a basic environment. This process could be tuned to incorporate different amount of H2O and OH- into the catalyst, which would then be incorporated onto the anode electrodes.
The team combined different photon-based spectroscopies to understand this new class of material during operation. Using infrared Raman and x-rays, among others, they were able to assess the presence of trapped water and hydroxyl groups, and to obtain insights on their role conferring activity and stability for water splitting in acid. i¿½Being able to detect t e trapped water was really challenging for usi¿½, continues leading co-author Dr. Anku G ha. i¿½Using Raman spectroscopy and other light-based techniques we finally saw that the e was water in the sample. But it was not i¿½freei¿½ water, it was confined wateri¿½; so ething that had a profound impact on
erformance. From these insights, they started working closely with collaborators experts in catalyst modelling. "The modeling of activated materials is challenging as larg structural rearrangments take place. In this case the delamination employed in the activati n treatment increases the number of active sites and changes the reaction mechanism r ndering the material more active. Understanding these materials requires a detailed map

ing between experimental observations and simulations", says Prof. Nuria Lopez from ICIQ. Their calculations, led by a leading co-author Dr. Hind Benzidi, were crucial to unders and how the delaminated materials, shielded by water, were not only thermodynamical y protected against dissolution in highly acidic environments, but lso active. But, how is this possible? Basically, the **tungsten oxide leaves a hole behind**, exactly where it was previously located. Here is where the i¿½magici¿½ happens: **water and hydroxide**, which are vastly present in the medium, spontaneously **fill the gap**. This in turn **shields the sample**, as it renders the cobalt dissolution an unfavorable process, effectively holding the catalyst components together.

Then, they assembled the delaminated catalyst into a PEM reactor. The initial performance was truly remarkable, achieving higher activity and stability than any prior art. i¿½ e increased five times the current density, arriving to 1 A/cm2- a very challenging landmark in the field. But, the key is, that we also reached more than 600 hours of stability at such high density. So, we have reached the highest current density and also the highest stability for non-iridium catalystsi¿½, shares leading co-author Dr. Lu Xi

. i¿½At the beginning of the project, we were intrigued about the potential role of water it elf as the elephant in the room in water electrolysisi¿½, explains Ranit Ram, first author of t e study and instigator of the initial idea. i¿½No one before had actively tailored water and interfacial water in this wayi¿½. In the end, it turned out to be a real game ch nger. Even though the stability time is still far from the current industrial PEMs, this represents a big step towards making them not dependent on iridium or similar elements. In particular, their work brings new insights for water electrolysis PEMs design, as it highlights the potent al to address catalyst engineering from another perspective; by actively exploiting the prop rties of

Towards the industrialization

The team has seen such potential in the technique that they have already applied for a patent, with the aim of scaling it up to industry levels of production. Yet, they are aware of the non-triviality of taking this step, as Prof. Garcia de Arquer notices: i¿½Cobalt, being mo e abundant than iridium, is still a very troubling material considering from where it is obtaine . That is why we are working on alternatives based on manganese, nickel and many oth r materials. We will go through the whole the periodic table, if necessary. And we are going o explore and try with them this new strategy to design catalysts that we have reported in o r studyi?

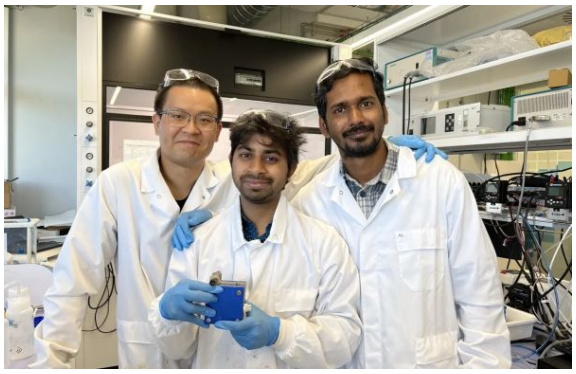
½. Despite the new challenges that will for sure arise, the team is convinced of the potentia of this delamination process and they are all determined to pursue this goal. Ram, in particu ar, shares: i¿½I have actually always wanted to advance renewable energies, because it wil help us as a human community to fight against climate change. I believe our studies contr buted one small step into the right directi

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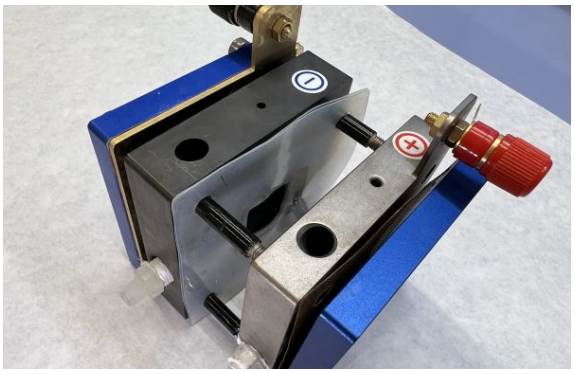
½. ### Refe**Water-hydroxide trapping in cobalt tungstate for proton exchange membrane water electrolysis**, Ranit Ram, Lu Xia, Hind Benzidi, Anku Guha, Viktoria Golovanova, Alba Garzon, Manjon, David Llorens Rauret, Pol Sanz Berman, Marinos Dimitropoulos, Bernat Mundet, Ernest Pastor, Veronica Celorrio, Camilo A. Mesa, Aparna M. Das, Adrian Pinilla-Sanchez, Sixto Gimenez, Jordi Arbiol, Nuria Lopez, F. Pelayo Garcia de Arquer, 2024, Science, https://doi.org/10.1126/science.adk9849

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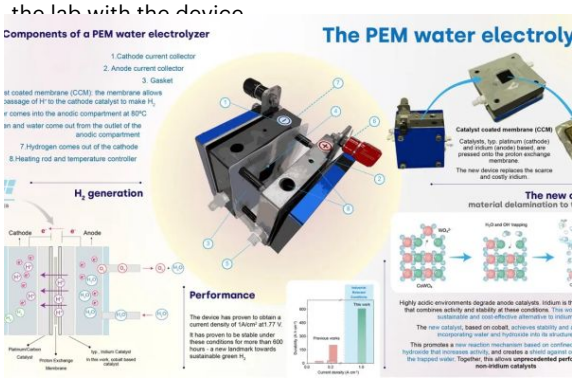
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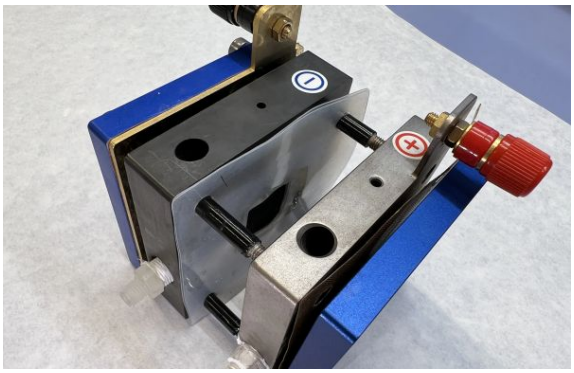
from left to right: Lu Xia, Ranit Ram and Anku Guha, in the lab with the device



The device and its components



Infographic explaining the PEM water electrolyzer



Video Abstract