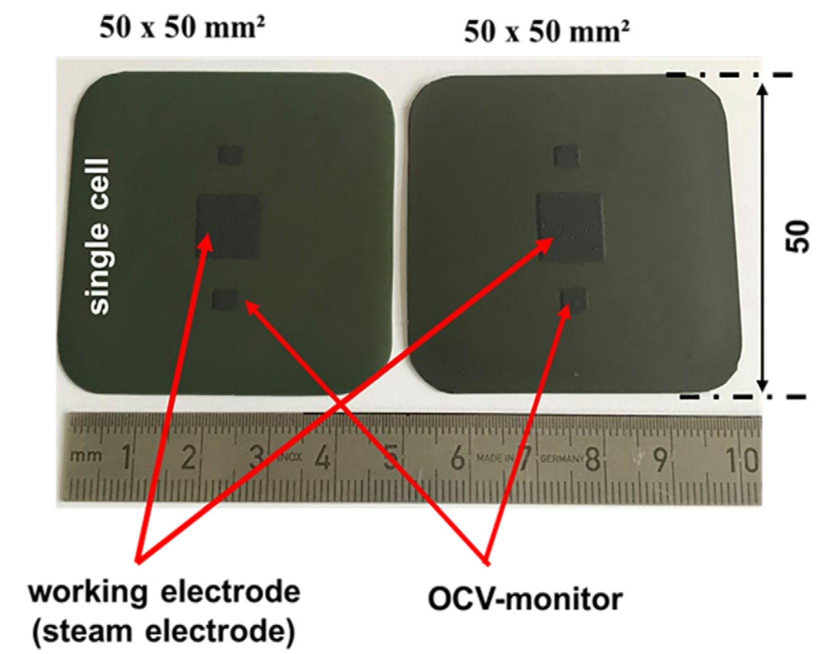
New steam electrolysis devices for efficient hydrogen production

Hydrogen plays a major role in future renewable energy strategies, and the process of steam electrolysis is essential if we are to transition to a hydrogen-dependent future. However, until now, despite numerous attempts, most devices rely on techniques that require either high temperatures with costly system components that are prone to degrade rapidly or a complex setup that does not readily translate into broader industrial uses. Dr Kwati Leonard, Assistant Professor at the International Institute for Carbon-Neutral Energy Research, Kyushu University, has devoted his research to the pursuit of manufacturing ceramic proton conductor membranes for hydrogen production, which are suitable for industrial use. His work led him to fabricate new ceramic protonic devices using a tape casting approach, providing excellent results.

Hydrogen has long been considered a promising energy carrier for a sustainable, clean, secure, and affordable future. Despite this great promise, however, its production is costlier than other fossil fuel alternatives, making the widespread societal transition to hydrogen very difficult.

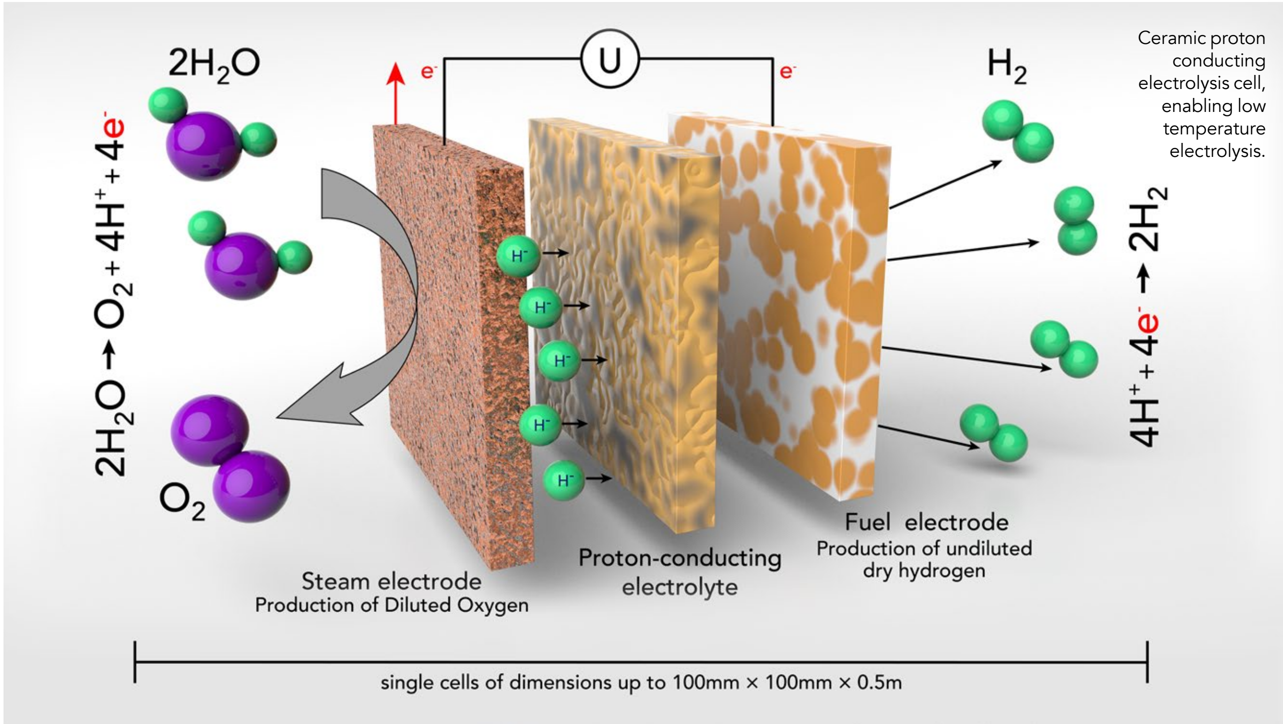
One proposed way to secure robust and clean hydrogen production is via steam electrolysis, a technique for producing hydrogen at very high temperatures. Unfortunately, these high temperatures are inimical with a broad industrial setup. The solution for lowering the temperature can be addressed using ceramic proton-conducting electrolytes. However, manufacturing this type of electrolyte in an upscale manner for industrial use comes with a panoply of obstacles and disadvantages. Addressing this issue, Dr Kwati Leonard, Assistant Professor at the International Institute for Carbon-Neutral Energy Research, Kyushu University, focuses on the fabrication of multi-layered devices that can work at low temperatures with excellent efficiency via a cost-effective sequential tape casting approach.



Size of the steam electrode on a single cell.

Previously, Leonard's research team experimented with solid oxide electrolysis cells (SOECs), which are environmentally friendly alternatives for the electrochemical conversion of steam into hydrogen. Importantly, this technology can be operated reversibly as a solid oxide fuel cell (SOFC) using the generated hydrogen to co-generate electricity and heat, meaning a combined device could efficiently convert between electrical and chemical energy.

The process of constructing the devices has yielded several complexities, however. The fabrication of multi-layered devices is affected by stresses due to shrinkage and complications involving the kinetics of sintering (the process of forming a solid mass through heat or pressure without heating to the point of liquefaction). Here we look at the advantages of these devices and consider how Leonard's team is working to overcome the difficulties inherent in their fabrication.



CERAMIC PROTON CONDUCTORS

Ceramic proton conductors are perovskites type oxides with mixed proton and oxygen ion conductivities. They can be used as electrolytes in electrochemical devices that directly convert stored chemical energy to usable electrical energy and vice versa. These devices operate with many distinct advantages, with several vital industrial uses.

Firstly, even if steam electrolysis requires extremely high temperatures, reaching 1,000°C, the ceramic proton conductors can operate in the intermediate temperatures, between 400°C and 600°C. Secondly, this class of electrolytes is particularly favoured for their relatively high ionic conductivity with low activation energy (<0.5 eV) for proton conduction, making them perfect candidates. Third, they rely on membrane technologies, meaning that they can produce hydrogen of remarkably high purity, as they selectively separate hydrogen from the supplied steam. This is a unique characteristic, as other existing devices, based on oxide-ion electrolytes, produce hydrogen mixed with steam, requiring an additional separation step. The challenge now focuses on creating devices that can work at these low temperatures, with high efficiency, and with the best possible setup that could be readily translated into a broader industrial context.

DEVICES FOR INDUSTRIAL USE

Typically, current devices are mostly small-scale single cells, having relatively small overall sizes and similarly small electrode surface areas. Although these small-sized protonic cells can successfully be used to reach very high hydrogen production performance, their fabrication techniques are not yet entirely rational at an industrial scale. To fabricate devices with a commercial target in mind, there is a need for larger devices, and these devices are generally categorised as *tubular* or *planar* depending on their shape and size.

> ***This proof of concept might be the key towards a sustainable hydrogen-dependent future.***

The planar type is generally preferable for operation due to several benefits related to size and area. Previous studies, such as that undertaken by Dailly and Marrony, have highlighted the advantages of planar-type proton-conducting electrolyte cells with an active working area of ~12–20 cm². However, for the successful fabrication of such devices, given their thin electrolyte layer, the electrode's microstructural integrity is critical. In addition, the surface will crucially affect the thin electrolyte layer's quality.

Leonard and team fabricated devices that could be used in an industrial set up using an innovative and low-cost process known as inverse tape casting. Broadly conceived, the process of tape casting generally refers to casting slurry onto a thin layer before drying and sintering. However, Leonard's advanced casting technique inverts a more traditional tape casting approach to produce homogeneous and large-area ceramic films. As with other forms of casting, this method of manufacturing devices uses a slurry formulation to produce the different layers. This method has previously been used for the fabrication of solid oxide-oxygen ions as well as hydrogen and oxygen separation membranes. A great advantage of this technique is its potential to minimise manufacturing costs, as multi-layer components are laminated and co-sintered in a single step.

The process requires a lot of attention to avoid bending and cracking due to

Hydrogen will be essential for future clean energy strategies.

shrinkage mismatch and the difference in sintering kinetics of the respective layers. Despite the challenges, Leonard and his group have managed to successfully obtain single cells of dimensions up to 100 mm × 100 mm × 0.5 mm with diminished warping. Additionally, they successfully managed to have minimum wrapping, which ultimately means there is no cracking in the final device.

PERFORMANCE

The performance of the fabricated device was spectacular. The morphology and microstructure of the layered half-cells were analysed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along with energy-dispersive X-ray spectroscopy.

Leonard managed to fabricate a flat tri-layer 50 x 50 mm^2 planar barium cerium yttrium zirconate device, or $BaZr_{0.44}Ce_{0.36}Y_{0.2}O_{2.9}$ (BZCY$(54)_{8/9}$2), that could perform at lower temperatures and with excellent efficiency. Specifically, the temperature was as low as 1,350 °C, which is about 200 °C lower than current sintering temperatures. This low sintering behaviour directly results from careful control over slurry viscosities, thicknesses of individual layers, and firing temperature. Shrinking the NiO-$SZr_{0.5}Ce_{0.4}Y_{0.1}O_{2.95}$ support during the co-sintering process facilitated the densification of the electrolyte layer, which resulted in this remarkably reduced temperature. What was more remarkable was that the devices could perform excellently at 600 °C, achieving ~81.5 and 83.1% current efficiencies with the present devices. Based on the above results, the calculated amount of electricity to produce 1 Nm^3 of H_2 is around 3.8 kWh, which is at least 25% reduced from the conventional low-temperature water electrolysis.

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In summary, Leonard's work sheds light on the processing of planar electrode-supported half cells using a cost-effective tape casting approach which promises ready translation into broader industrial use. By analysing the processing parameters, the research team were able to obtain defect-free single cells with diminished warping. In addition, tri-layered green tapes proved appropriately dense and gas-tight electrolyte layers after co-sintering at 1,350 °C/5h. The low sintering behaviour directly results from careful control over slurry viscosities, thicknesses of individual layers, and firing temperature.

WHAT THIS MEANS FOR THE FUTURE

Leonard's pioneering work is now more crucial than ever. A device such as the one proposed by his group can efficiently and directly convert between electrical and chemical energy, and as such has considerable potential for supporting the emerging hydrogen economy and reducing dependence on fossil fuels. Furthermore, these devices could be used in an industrial context, since low temperature is ensured, and maximum performance could be achieved. These results pave the way towards low-cost fabrication of large-sized protonic ceramic conducting electrolysis cells (PCECs). This proof of concept might be the key towards a sustainable hydrogen-dependent future.

Behind the Research

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Research Objectives

Dr Kwati Leonard and his team produce ceramic proton conductor membranes for efficient hydrogen production.

Detail

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Bio

Dr Kwati Leonard is presently an assistant professor at the International Institute for Carbon-Neutral Energy Research, Kyushu University. He received his PhD in applied chemistry in 2011 at the University of Kagoshima, Japan. In the same year, he obtained a JSPS Post-Doctoral Fellowship for Foreign Researchers and joined Kyushu University, where he worked on energy conversion devices. In 2012 he received a Young Scientist Award from the International Conference on Nanostructure-Enhanced Photo-energy Conversion in Tokyo, Japan. His work is presently devoted to processing ceramics proton conductor membranes for use in electrochemical devices.

Collaborators

Professor Wilhelm A Meulenberg, Dr Mariya E Ivanova, Dr Norbert H Menzler, all from the Institute of Energy and Climate Research IEK-1, Forschungszentrum Jülich. Professor Tatsumi Ishihara and Hiroshige Matsumoto, International Institute for Carbon-Neutral Energy Research

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Personal Response

Are there any other improvements you are considering which might further enhance the efficiency of these devices?

Yes, definitely. As mentioned above, ceramic proton-conducting electrolytes operate at a lower temperature (400 to 600°C). This operating regime would dramatically reduce materials costs, degradation rates, and start-up times and require new air electrodes tailored to the protonic electrolytes. In addition, most of the presently used air electrodes display sluggish kinetics for the oxygen evolution and oxygen reduction reaction certainly due to the limitation of the electrocatalysis, occurring only at the triple phase boundary (TPB). Therefore, new electrodes are highly desirable. We are currently performing an integrated computation-driven search and experimental input targeting new highly active electrode materials.