The ins and outs of hydrogen

Scientists are studying the effect of strain on the proton conductivity and proton-photon coupling. Here, **Dr Artur Braun** and PhD student **Qianli Chen** explain the complexities of one fundamental part of their study – hydrogen

Would you begin by outlining the significance of proton-photon coupling in your assay?

The economical and societal significance of protons can be seen in the context of the hydrogen economy. We want to modify ceramic materials so that we can better fit protons in and fit them out. Our findings suggest that epitaxial strain could be a key tool for accelerating protons.

What are the main activities of the Laboratory for High Performance Ceramics?

We belong to the Swiss Federal Laboratories for Materials Science and Technology (Empa), which is part of the Swiss ETH body. We are an industry-friendly synthesis and processing laboratory and provide solutions to problems across the ceramics market sector. Where necessary, we carry out fundamental studies to go beyond providing just better versions of readily-existing solutions. Influencing proton conductivity by strain engineering is a newly emerging field with new opportunities to manufacture protonic devices.

Does proton diffusion occur in other fields?

The water molecule is built from two protons and one oxygen ion. A scenario in which protons hop constantly from molecule to molecule was suggested by Theodor Grotthuss over 200 years ago and can in fact be observed in water. All organic and aqueous chemistry involves protons and proton transport.

Ambient humidity interacts with the surfaces of all materials and thus the water molecules may enter porous materials. Eventually, single water molecules may dissociate and the protons arrange with the crystal structure and reside there silently as protonic interstitials or defects. At elevated temperatures, they may develop some activity in these materials.

Biological cells manage their life by managing protons' transport, which is balanced by the corresponding electric charge from electrons. Photosynthesis shows a beautiful application of proton pumps at the molecular scale. For artificial photosynthesis, a prospective emerging field for solar fuel generation, management of proton transport could become important.

Our civilisation is well-developed with respect to managing electron transport, ie. electricity. We are less developed, however, when it comes to making devices that run on protons or hydrogen. This may change in the future and when we make protonic devices, we will need to understand and be able to control proton logistics.

What is Arrhenius' law and what other principles govern hydrogen utilisation?

Arrhenius' law describes how the kinetics of chemical processes increase with temperature. We observe Arrhenius' behaviour in proton conducting fuel cell solid electrolytes, where the protons provide electric transport. At low temperatures protons are bound to the oxygen ions in the crystal lattice, and they participate in the temperature activated lattice vibrations. These lattice vibrations are the phonons. At a certain temperature, the bonds between protons and oxygen break – these bonds are the thermally unstable hydrogen bonds – whereas the other bonds remain stable.

The coupling of the protons with the thermal activated lattice vibrations, the proton-phonon coupling, provides dynamics where at a certain temperature the protons leave their assigned position in the crystal lattice and become mobile charge carriers. We need to move this transition from bonded protons to mobile protons to lower temperatures. This requires manipulating the crystal lattice. This can be done by epitaxial strain in ultrathin films. While not yet established for proton or ion conductivity, our findings point in this direction.

Melting ice is a manifestation of the strong temperature dependence of the hydrogen bond. In ceramic proton conductors, the bonds between protons and the lattice are stronger and need a higher temperature to be broken. One important discovery of PROTONIQUE is that we can increase or decrease this characteristic temperature when we apply pressure or strain, respectively.

What are the current limitations of hydrogen technology?

Hydrogen storage for mobile, automotive applications is being addressed worldwide. Hydrogen production is also important: most hydrogen is still produced by steam reforming with fossil fuels, which is not a renewable approach, whereas electrolysis of water using renewable electric energy, such as solar cells, could be called 'green' hydrogen. High temperature fuel cells can operate in the reverse direction and then perform water vapour electrolysis. There, ceramic proton conducting membranes are prospective electrolytes. If we could engineer strained proton conducting membranes, we might be able to run the solid oxide fuel cells and electrolysers at lower temperatures. This would be a significant technological advance.

An exciting route for sustainable hydrogen production is artificial photosynthesis by solar water splitting in photoelectrochemical cells (PEC). For this we need the right high performance materials, such as metal oxides, further functionalised with motifs from photosynthesis proteins. Depending on the particular architecture of the PEC devices, proton barriers and proton conductors might be necessary components.

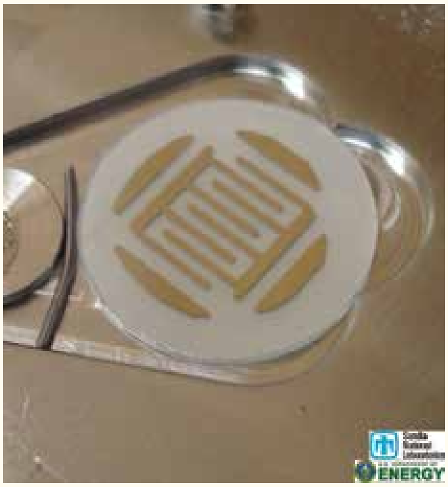
PROTONIQUE

A team from the **Laboratory for High Performance Ceramics (Empa)** is at the forefront of research on ceramic proton conductors. Their PROTONIQUE study seeks to understand how changing the lattice volume can affect the proton mobility and thus the operating temperatures of solid oxide fuel cells and electrolysers

PROTONS ARE THE positive charge carriers for the hydrogen fuel economy and are essential in hydrocarbons and water molecules. They close the electric cycle in Nature – such as in photosynthesis – and also in technology – for instance, in fuel cells and electrolysers. There is hope that ceramic proton conductors can become efficient electrolytes for solid oxide fuel cells (SOFC) and electrolysers (SOEC). The electric conductivity due to protons in ceramic materials begins at temperatures around 400-500 °C, whereas conventional ceramic electrolytes are based on oxygen ion conductivity, which requires temperatures from 600-1,000 °C.

To further improve proton conductors and make them competitive with existing standard oxygen ion conducting electrolytes, it has been suggested to lower their activation energy by strain engineering their materials. While a standard approach to increase the performance of solid electrolytes is based on grain boundary engineering, and more recently interface engineering, it will ultimately be bulk strain engineering which can provide faster proton transport through layers. But this requires precise understanding of the chemical and vibrational interactions of water vapour and protons with the crystal lattice of the proton-conducting metal oxides used in this application under extreme environments. Dr Artur Braun is a Principal Investigator at the Laboratory for High Performance Ceramics (Empa) and works with PhD student Qianli Chen to conduct a project called PROTONIQUE, which has empirically shown that the application of strain alters the proton conductivity activation energy, an effect which can be exploited for protonic devices. Scientific analyses underpinned by the basic principles of condensed matter physical chemistry show that, with the application of strain, the proton-phonon coupling can be manipulated.

Proton conductor pellet with interdigited gold electrodes, ready for combined in-situ ambient pressure XPS and impedance analyses.



NOVEL TOOLS FOR RESEARCH

Impedance spectroscopy is a major analytical tool for fuel cell researchers and electric engineers. "We want to know how our proton-conducting electrolytes behave in operation, or in situ," explains Braun, "and this means we have to connect the proton conductor electrically, heat it to approximately 500 °C and supply it with water vapour so that the protons from the water molecules can enter the crystal lattice. This is where a new challenge comes in: we have to simultaneously apply a very high mechanical pressure such as 1 Gigapascal to the proton conductor." This means the team has to acquire a massive cell housing that is capable of providing these conditions. Fortuitously, the Geophysics Institute at Goethe University of Frankfurt in Germany has such a housing.

A more challenging situation has been the team's in situ neutron experiments, which were necessary in order to understand the proton dynamics. While neutrons are the best probes for protons, they have to be able to pass through the massive cell housing without losing the information they carry, after passing and probing the proton conductor inside. This is a technically very intricate and challenging business, but fortunately the team's engineers did eventually provide the solution. "In order to be scientifically competitive, we have to go for in situ and operando analytical methods because we need to understand how materials in a device behave under realistic and extreme working conditions," notes Braun.

PROTONIQUE'S ENGINEERING APPLICATIONS

The investigation holds potential for new engineering applications and to benefit the efficiency of industrial technologies. The first suggested application is an ultrathin strained proton-conducting film; the advantage of this is its calculated lower activation energy than that of existing bulk proton conductors. Due to its lower activation energy, the strained proton-conducting electrolyte can carry out its function at a significantly lower temperature, or be better conducting at standard temperatures of 400-600 °C. This would be a great advance for ceramic fuel cell and electrolyser technology. There are other applications of the technique than simply making protons faster. For instance, the researchers can slow down or stop protons completely by compressing the crystal lattice.

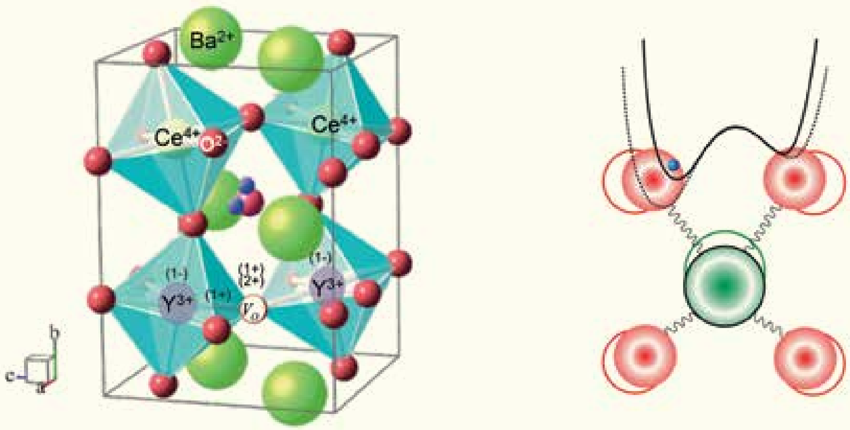
In terms of the wider repercussion of this work, the group could well be on the cusp of discovering some truly fascinating applications. For example, the management of proton transport is important in devices for solar water splitting. Therefore, this could become a relevant issue, for example, in artificial photosynthesis.

THE BENEFITS OF COLLABORATION

Due to the extensive crossdisciplinary nature surrounding the work of PROTONIQUE, it has become necessary that Braun and Chen collaborate with other research groups. As a result, new and special expertise has been brought to the project's neutron, synchrotron, Raman and impedance studies.

This work required the project members to place ceramic proton conductors under high mechanical pressure and then analyse the material and its interaction with protons in standard SOFC operation conditions. Typically, studies of materials under high pressure are a domain of geology. It is not surprising, therefore, that PROTONIQUE consulted and collaborated with geologists. For example, the high pressure impedance studies were carried out by Chen at the University of Frankfurt, and the high pressure Raman spectroscopy experiments at Stanford University and the University of Hawaii.

For the neutron scattering work, Empa's High Temperature Integrity expert Dr Stuart G Holdsworth along with Chen designed a unique neutron scattering cell in collaboration with staff at the neutron sources in Switzerland, Germany and France. This project has also coincided with the availability of novel synchrotron facilities in Berkeley, California where the researchers had the unique opportunity to combine X-ray photoelectron spectroscopy (XPS) with impedance analyses on proton conductors in situ, under water vapour pressure. This allowed them to investigate the chemical interaction of the proton-conducting metal oxides with oxygen, hydrogen and water vapour. There, the researchers were able to observe operando how oxygen vacancies in the proton conductors were filled when they supplied water vapour, and how at higher temperature the oxygen-hydrogen bonds broke. It was then possible to quantitatively correlate these observations with the structural evolution of the ceramic, the onset of the proton conductivity with temperature and the conjugated changes in



(Left): Snaphot schematic of water molecule, filling oxygen vacancy in the $BaCe0.8Y0.2O3-\delta$ proton conductor.
(Right): Lattice vibrations promote proton conductivity.

the electronic valence band. A true highlight not observed before.

Even further still, PROTONIQUE also worked with collaborators in China, Korea, Japan, Sweden and the UK. These partners provided specially synthesised specimens, methods and scientific advice. Overall, the activities of the Empa team in Switzerland have been truly global and collaborative.

CHALLENGES AND LOOKING TO THE FUTURE

For all the team's success, along with its global collaborators, there have also been considerable challenges. To put their work into context, for investigations on hydrogen and protons, neutrons happen to be the most sensitive probes. This is why they extensively utilised neutron scattering. However, some of these experiments required large samples, and therefore, they could not investigate thin strained films with quasielastic neutron scattering (QENS), despite the fact that such an experiment would have been key to developing and analysing superprotonic electrolytes in novel micro fuel cells or electrolysers.

However, it is the difficulties that have already been faced that will shape the future work of PROTONIQUE. Along with experts based at the neutron sources, the project members hope to further develop QENS for thin films, and therefore increase the success they have already enjoyed in the field of proton-activated fuel cells.

PROTONIQUE

OBJECTIVES

Investigation of the proton conductivity in ceramic membranes at the molecular scale with state-of-the-art laboratory methods and with novel neutron and X-ray scattering and spectroscopy methods shows how protons couple with the strain field in ceramics.

KEY COLLABORATORS

Dr Stuart Holdsworth, Empa • **Professor Nikolai Bagdassarov**, Goethe University Frankfurt, Institute of Geosciences • **Professor Wendy Mao**, Stanford University • **Professor Murli H Manghnani**, Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa • **Dr Simon M Clark**, California High Pressure Observatory and Advanced Light Source • **Dr Jan Embs; Dr Thierry Strässle; Dr Vladimir Pomjakushin**, Paul Scherrer Institute • **Professor Joel Mesot**, ETH Zurich and Paul Scherrer Institute • **Dr Antonio Cervellino**, Swiss Light Source, Paul Scherrer Institute • **Professor Wayne Stolte**, University of Nevada Las Vegas and Advanced Light Source • **Dr Zhi Liu**, Advanced Light Source • **Dr Cristian D Savaniu**, University of St Andrews • **Professor Sigitas Tamulevicius**, Kaunas University • **Dr Bernhard Frick**, Institute Laue Langevin, Grenoble • **Professor Bongjin S Mun**, Hanyang University • **Professor Dr Xinyu Zhang**, Yanshan University • **Professor Dr Shu Yamaguchi**, University of Tokyo • **Dr Farid El Gabaly**, Sandia National Laboratories

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QIANLI CHEN finished her doctoral thesis at Empa Laboratory for High Performance Ceramics and graduated recently from ETH Zürich with a DSc. She holds an MSc from KTH Royal Institute of Technology and a BEng from Southeast University.