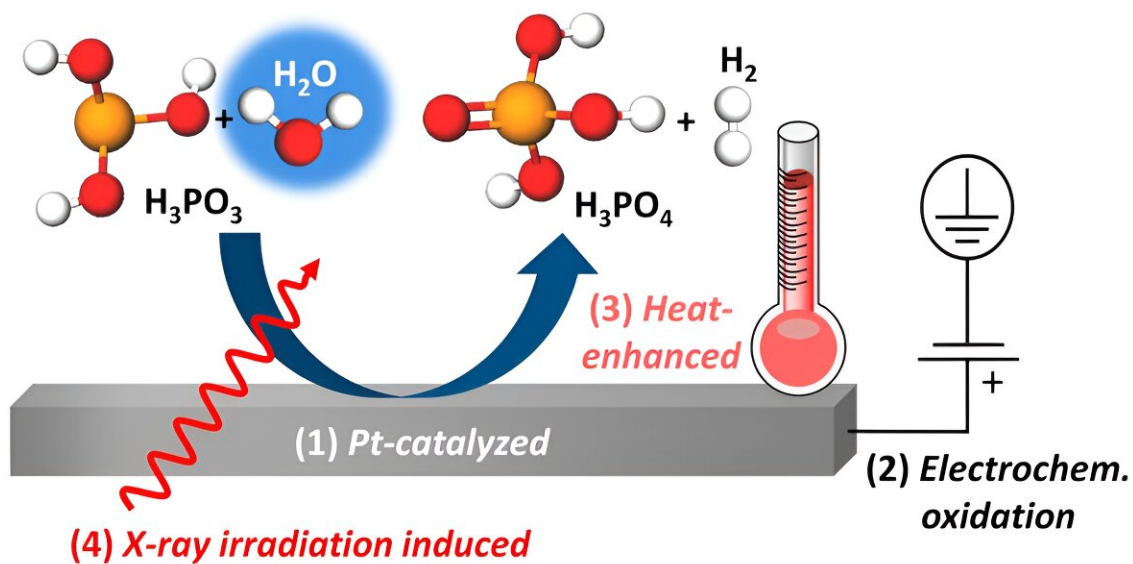


Fuel cells: Oxidation processes of phosphorous acid revealed by tender X-rays

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The illustration shows four different oxidation pathways (1-4) of aqueous phosphorous acid (H_3PO_3), which could be elucidated by XANES at BESSY II. All these reactions depend on the humidity present. Credit: HZB/JACS

The interactions between phosphorous acid and the platinum catalyst in high-temperature PEM fuel cells are more complex than previously assumed. Experiments at BESSY II with tender X-rays have decoded the multiple oxidation processes at the platinum-electrolyte interface. The

results indicate that variations in humidity can influence some of these processes in order to increase the lifetime and efficiency of fuel cells.

The work is [published](#) in the *Journal of the American Chemical Society*.

Hydrogen [fuel](#) cells convert [chemical energy](#) from hydrogen into [electrical energy](#) through separate reactions of hydrogen fuels and oxidizing agents (oxygen). Among hydrogen fuel cells, high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) are attractive for micro-stationary electricity sources. One disadvantage of these HT-PEMFCs is that the [phosphoric acid](#) (H_3PO_4) proton conductor leaches out of the H_3PO_4 -doped polybenzimidazole membrane and poisons the platinum catalyst.

Recent studies show further complications during the operation of the HT-PEMFC, where some of H_3PO_4 might be reduced to H_3PO_3 , which may further poison the platinum catalysts, leading to a significant loss of performance.

An earlier study by Prof. Dr. Marcus Bär's team showed that opposite processes also take place at the interface between Pt and aqueous H_3PO_3 and that the interactions between the platinum catalyst and the $\text{H}_3\text{PO}_3/\text{H}_3\text{PO}_4$ are very complex: While H_3PO_3 can lead to poisoning of the [platinum catalyst](#), at the same time platinum might catalyze the oxidation of H_3PO_3 back to H_3PO_4 .

Experiments under realistic conditions

In order to investigate the oxidation behavior of aqueous H_3PO_3 under conditions close to HT-PEMFCs working conditions, Bär's team has now analyzed the chemical processes using an in-housed designed heatable electrochemical cell compatible for in situ tender X-ray studies at the OÆSE end-station recently set up in the Energy Materials In-situ

Laboratory Berlin (EMIL).

They used intense X-ray light in the tender X-ray energy range (2 keV–5 keV), provided by the EMIL beamline at the X-ray source BESSY II. In this energy range, X-ray absorption near-edge structure spectroscopy (XANES) at the P K-edge is used to monitor [oxidation processes](#) from H_3PO_3 to H_3PO_4 .

Different oxidation reactions examined

"We have thus uncovered different processes for this oxidation reaction, including platinum-catalyzed chemical oxidation, electrochemical oxidation under positive potential bias at the platinum electrode, and heat-promoted oxidation. These in situ spectroscopic results are also confirmed by ion-exchange chromatography and in situ electrochemical characterizations," explains Enggar Wibowo, first author of the study and a Ph.D. candidate in Bär's team.

"Remarkably, all of these oxidation pathways involve reactions with water, which shows that the humidity inside the fuel cell has a significant influence on these processes."

In addition, the results also point to possible improvements of the operating conditions of HT-PEM fuel cells, e.g. by controlling the humidification to oxidize the H_3PO_3 back to H_3PO_4 .

"Corresponding adjustments to the operation conditions of HT-PEMFCs could be implemented to prevent catalyst poisoning by H_3PO_3 and enhance efficiency of those fuel cells," Wibowo points out.

"The work clarifies a key degradation pathway of fuel cells and is a contribution on the way to an H_2 -based energy supply," says Prof. Dr.-Ing. Marcus Bär. "It also shows the great benefit of tender X-rays,

and we are looking forward to BESSY III, which aims to close the tender X-ray-gap."

More information: Romualdus Enggar Wibowo et al, Elucidating the Complex Oxidation Behavior of Aqueous H₃PO₃ on Pt Electrodes via In Situ Tender X-ray Absorption Near-Edge Structure Spectroscopy at the P K-Edge, *Journal of the American Chemical Society* (2024). [DOI: 10.1021/jacs.3c12381](https://doi.org/10.1021/jacs.3c12381)

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