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Operando Surface Hydrogen Analysis by Plasmon Spectroscopy

Andreas Borgschulte*, Emanuel Billeter, and Selim Kazaz

**Correspondence:* PD Dr. A. Borgschulte, E-mail: andreas.borgschulte@empa.ch, Laboratory for Advanced Analytical Technologies, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf

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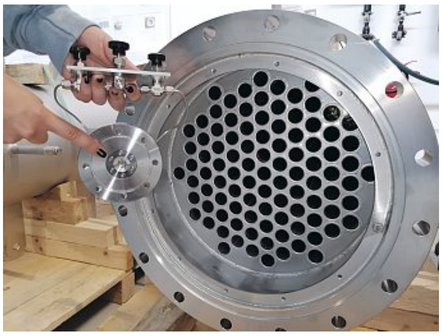
Hydrogen is a ubiquitous element in the environment. The element plays a key role in biology, chemistry, and physics: It is involved in numerous chemical reactions, from photosynthesis to the combustion of its products, and plays an essential role in the chemical industry and corrosion. The fast diffusion of hydrogen in most materials, including nonorganic matter such as metals and oxides, makes hydrogen an omnipresent impurity. Hydrogen is used on large scale as a process gas in chemical industry. Understanding the interaction of hydrogen with matter is crucial for any technology, with hydrogen involved as reactant, intermediate, or product. Needless to say that hydrogen-solid interactions gain relevance with the upcoming renewable hydrogen energy technology.

Hydrogen quantification in bulk materials is relatively straightforward. However, the analysis of hydrogen at the surface is much more difficult but no less important as it is the precursor of bulk hydrogen. Electron spectroscopy is the usual tool to characterize surfaces; however, the most common one, X-ray photoelectron spectroscopy, is a suboptimal technique for hydrogen detection due to the lack of a hydrogen core electron. The dependence of plasmon excitation on the hydrogen content as measured by reflecting electron energy loss spectroscopy (REELS) was found to be a reliable method to determine the sub-surface hydrogen concentration, from which the surface hydrogen-pressure composition isotherms are determined. The stability of hydrogen at the surfaces of hydrogen selective membranes is still controversially debated and thus the ideal system to be studied by the method. The Figure below shows the surface hydrogen pressure composition isotherms of vanadium membranes as a proof of principle of the technique. The energy dependence of REELS reveals that the VH_x layer formed at higher pressures exhibits a hydrogen concentration gradient at the surface. The experimental results deliver the input parameters to model and eventually improve hydrogen-selective membranes.



Size comparison between a test device for measuring the permeability of hydrogen selective membranes and a small industrial reactor. In industrial membrane reactors, the membranes are designed as tube bundles, while a flat design (a flat membrane is inserted at the location indicated by index finger) is chosen for scientific characterisation. The need for cheap membrane materials is obvious.

Apart from hydrogen membranes, the laboratory-based REELS method to analyze hydrogen at the surface of metals and alloys is highly relevant for additional applications such as hydrogen storage and hydrogen sensing.

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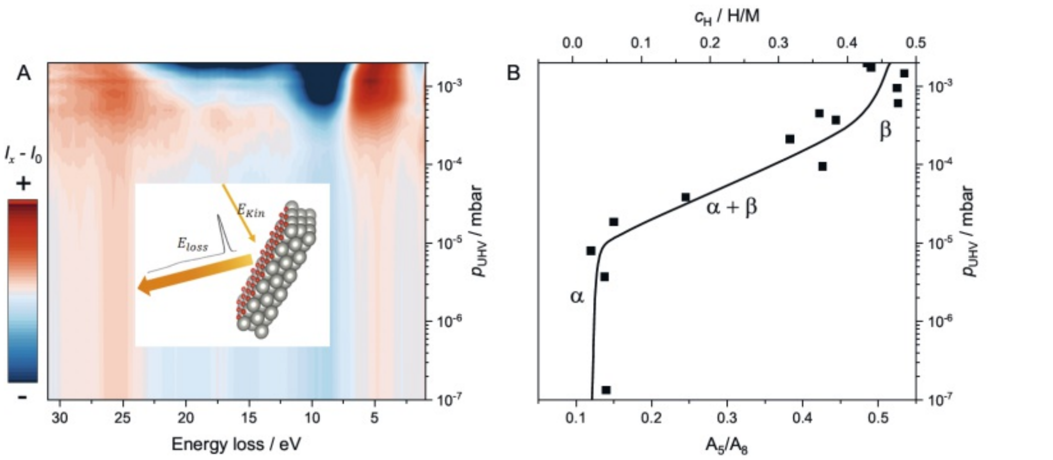
Reference

E. Billeter, S. Kazaz, A. Borgschulte, *Adv. Mater. Interf.* **2022**, *9*, 2200767, https://doi.org/10.1002/admi.202200767.



Left: Principle of reflecting electron energy loss spectroscopy (REELS) inset. Left and right: REELS difference spectra of the downstream surface of a vanadium membrane at 100 °C exposed to incrementally increased hydrogen pressure as 2D-contour plot showing the continuous change of the spectra upon hydrogen uptake particularly strong at 5 and 8 eV. The corresponding pressure surface composition isotherms are derived from the area ratio at these loss energies and the measured permeate pressure.

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