

Hydrogen oxidation and evolution reactions in fuel cells slow down because of hydrogen binding

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(Phys.org)—As scientists look for alternative energy sources, fuel cells that operate in a basic environment have garnered much attention. Typically fuel cells require an expensive catalyst, such as platinum. Hydroxide exchange fuel cells involve the movement of hydroxide ions (OH^-) across a polymer membrane. The alkaline environment is conducive to the oxidation and reduction reactions without the need for expensive metals. However, these reactions are quite slow requiring a better catalyst.

In order to make a better catalyst for these fuel cells, Jie Zheng, Wenchao Sheng, Zhongbin Zhuang, Bingjun Xu, and Yushan Yan from the University of Delaware and Columbia University studied the factors that affect the hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER) in a hydroxide exchange [fuel cell](#). Their previous studies showed that the dominant controlling factor in the HOR/HER reactions is hydrogen adsorption on the platinum electrode, i.e., hydrogen binding energy. In this study they determined that the hydrogen binding energy was directly related to electrolyte pH, not metal identity or the metal's oxophilicity. Their work appears in *Science Advances*.

Previous studies have shown that there is some correlation between the hydrogen oxidation reaction, hydrogen binding energy, and electrolyte pH. These factors seemed to be independent of the metal's properties. In

this study Zheng, et al. sought to better understand the effect of pH on hydrogen binding energy and how hydrogen binding energy affects the HOR/HER kinetics. They tested this by investigating current densities over a large pH range on carbon-supported platinum-metal nanoparticles (e.g., Pt, Ir, Pd, and Rh).

Using cyclic voltammetry, Zheng, et al. determined desorption peak potentials for deposited hydrogen on each of the supported metal nanoparticles at various pH values. They observed a similar linear correlation for all of the metals in which higher pH lead to a positive shift. The results of this study indicate that there is a generalizable trend between hydrogen binding energy and [electrolyte](#) pH that is independent of the metal used.

If pH affects hydrogen binding energy, then does it also affect the hydrogen oxidation and evolution reactions? In order to relate pH to HOR/HER activities, they used a rotating disk electrode and calculated exchange current density. They found that as pH increased, current density decreased, demonstrating that, indeed, higher hydrogen binding energy leads to lower HOR/HER activity.

Armed with this data, Zheng, et al. then used mathematical manipulations to generalize the trends between exchange current density and hydrogen binding energy. From these they could calculate the activation energy of the hydrogen oxidation and evolution reactions in 0.1M KOH for all of the metal nanoparticles. Their results verify that the reaction's high activation energy is due to hydrogen binding energy, and therefore, it is the dominant factor in HOR/HER kinetics in alkaline electrolytes.

Finally, their last study looked at whether hydroxide ions played a role in the hydrogen oxidation reaction. Since hydrogen binding to the metal electrode is the key factor in HOR kinetics, Zheng, et al. wanted to

determine whether adsorbed hydroxide ions also affected the kinetics. By looking at potentials where carbon monoxide is stripped from the electrode, they were able to deduce that hydroxide likely does not play a key role in HOR/HER activities.

This research provides important insight into why the reaction kinetics is significantly slower in hydroxide exchange fuel cells. The pH apparently affects hydrogen [binding energy](#), which directly affects HOR/HER kinetics. Of particular significance is that this trend holds regardless of the platinum-group metal used. Further research will look into ways to tailor hydrogen adsorption.

More information: J. Zheng et al. Universal dependence of hydrogen oxidation and evolution reaction activity of platinum-group metals on pH and hydrogen binding energy, *Science Advances* (2016). [DOI: 10.1126/sciadv.1501602](https://doi.org/10.1126/sciadv.1501602)

Abstract

Understanding how pH affects the activity of hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) is key to developing active, stable, and affordable HOR/HER catalysts for hydroxide exchange membrane fuel cells and electrolyzers. A common linear correlation between hydrogen binding energy (HBE) and pH is observed for four supported platinum-group metal catalysts (Pt/C, Ir/C, Pd/C, and Rh/C) over a broad pH range (0 to 13), suggesting that the pH dependence of HBE is metal-independent. A universal correlation between exchange current density and HBE is also observed on the four metals, indicating that they may share the same elementary steps and rate-determining steps and that the HBE is the dominant descriptor for HOR/HER activities. The onset potential of CO stripping on the four metals decreases with pH, indicating a stronger OH adsorption, which provides evidence against the promoting effect of adsorbed OH on HOR/HER.

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