

## Beyond current frontiers of electrocatalysis

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One of the key reasons why the deployment of sustainable energy systems is at a standstill are the unusually complex phenomena of energy conversion at electrified solid/liquid interfaces. Namely, conversion of electric energy into chemical energy, and vice versa, comprises of interfacial processes whose mechanisms are still beyond comprehension. An important example is the electrolysis of water, where after decades of research it is still not clear how to significantly enhance efficiency of electricity-driven water splitting into gaseous hydrogen and oxygen. At the very core of energy conversion process are electrochemical reactions known as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which intrinsic kinetics determines energy conversion efficiency. In order to further accelerate water electrolysis or other processes important for energy conversion devices (e.g. fuel cells, batteries etc.), central practical task is to design highly active and stable electrocatalysts.

If we ask a key question from a conceptual point of view, namely: what are the origins of electrocatalytic activity? - the answer will be, in most cases, as it was 70 years ago. Namely, the paradigm of electrocatalysis is Sabatier principle, which suggests optimal ("not too strong, not too weak") binding of intermediates as the main prerequisite for a high reaction rate. This viewpoint is usually supported by the Brønsted-Evans-Polanyi (BEP) relation, which imply that the tuning of adsorption energy of intermediates is essential for lowering of activation energy and ultimately enhancing reaction rate. However, recent systematic experimental analysis indicates that the lowering the activation energy is not necessarily beneficial for increasing the rate of electrocatalytic reaction.

Therefore, in this lecture, some fundamentally important questions about the nature of electrocatalytic activity will be raised with intention of establishing of links between material properties, interfacial structural dynamics and reaction rate. Identifying and analyzing these important links can give necessary momentum towards efficient water electrolysis as well as towards more comprehensive understanding of electrocatalysis.

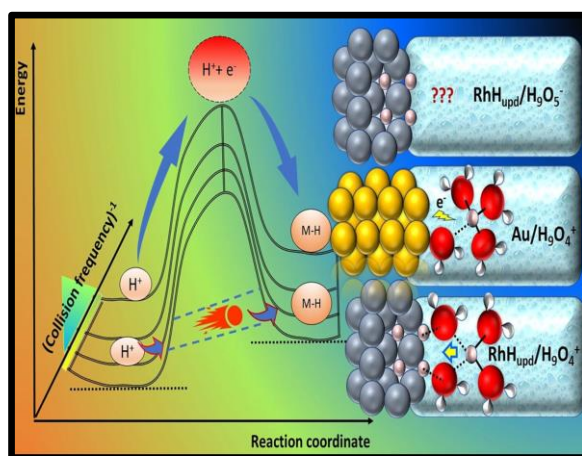


Figure 1. Illustration of how metals with specific interfacial water structure could behave as efficient electrocatalysts for hydrogen evolution reaction (HER) where high reaction rate, despite of relatively high activation energy, is possible to achieve via high values of preexponential factor by proton tunnelling. Adopted from [5] Copyright (2022) , with permission from Wiley.

### References

1. A.R. Zeradjanin, *Encyclopedia of Solid-Liquid Interfaces* (2024) 36 <https://doi.org/10.1016/B978-0-323-85669-0.00110-0>
2. A.R. Zeradjanin, *Nature Catalysis* **6** (2023) 458 <https://doi.org/10.1038/s41929-023-00973-w>
3. A.R. Zeradjanin, P. Narangoda, J. Masa, R. Schlögl, *ACS CATALYSIS* **12** (2022) 11597 <https://doi.org/10.1021/acscatal.2c02964>
4. P. Narangoda, I. Spanos, J. Masa, R. Schlögl, A.R. Zeradjanin, *ChemElectroChem* **8** (2021) 1 <https://doi.org/10.1002/celec.202101278>
5. P. Narangoda, I. Spanos, J. Masa, R. Schlögl, A.R. Zeradjanin, *ChemElectroChem* **9** (2022) <https://doi.org/10.1002/celec.202200008>
6. A.R. Zeradjanin, J. Masa, I. Spanos, R. Schlögl, *Frontiers in Energy Research* **8** (2021) 613092. [doi:10.3389/fenrg.2020.613092](https://doi.org/10.3389/fenrg.2020.613092).