



New Avenues in the Theoretical Description of Energy Storage and Conversion Processes

Kai S. Exner^{1,2,3}

¹University of Duisburg-Essen, Faculty of Chemistry, Theoretical Catalysis and Electrochemistry, Essen

²Cluster of Excellence RESOLV, Bochum

³Center for Nanointegration (CENIDE) Duisburg-Essen

Time: Monday, June 17, 2024, 15:30

Location: Joseph Loschmidt Lecture Hall

9. Währinger Str. 42, Faculty of Chemistry, ground floor/ intermediate floor

Since the birth of the computational hydrogen electrode (CHE) approach,¹ it is considered that the activity trends of electrocatalysts in a homologous series can be quantified by thermodynamic considerations, analyzing the adsorption free energies of reaction intermediates by density functional theory (DFT) calculations. Although the application of the CHE method in conjunction with heuristic activity descriptors to capture activity trends is popular,² this framework has several shortcomings:

- A) While the CHE approach relies on a canonical formalism (constant charge), electrochemical experiments are conducted at constant potential. To close this gap, grand canonical approaches are required to model catalytic processes at electrified solid/ liquid interfaces.³
- B) Given that the adsorption free energies of reaction intermediates are inspected under equilibrium conditions, overpotential and kinetic effects are not considered in the analysis.⁴ This assumption is only valid if the Tafel slope of electrocatalysts in a homologous series is constant and therefore underlines the need to identify activity descriptors that go beyond this simplified formalism.^{5,6}
- C) The interaction of reaction intermediates with the surrounding aqueous electrolyte is usually described by implicit solvation methods or is completely ignored by reference to gas-phase DFT calculations. Only the coupling of ab initio molecular dynamics simulations with DFT calculations allows the quantification of surface reconstructions based on the interaction of the electrode surface with the electrolyte, which can alter active sites and activity trends at electrified solid/ liquid interfaces.⁷
- D) The mechanistic picture of electrocatalytic processes is somewhat simplified, since usually a single reaction mechanism is investigated to approximate the electrocatalytic activity. This assumption is not fulfilled for highly active materials where a switch in the preferred reaction mechanism with increasing overpotential has been reported.⁸ Consequently, it is necessary to include a variety of different pathways in the mechanistic assessment to evaluate limiting reaction steps and activity trends.⁹
- E) While most theoretical studies aim at describing activity or selectivity trends, the evaluation of electrocatalyst stability is still in its infancy. Thermodynamic considerations are a first approach to assess the stability of different active sites under applied bias.¹⁰

In my talk, I will discuss our in-house methods aimed at modeling catalytic processes at electrified solid-liquid interfaces to address the above-mentioned challenges. My concepts could open new avenues in the theoretical description of electrocatalytic processes, from which the Cluster of Excellence "Materials for Energy Conversion and Storage" will substantially benefit for paving society's future to renewable energy.

1. Nørskov, J. K. et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* 2004, 108, 17886–17892.
2. Seh, Z. W. et al. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Science* 2017, 355, eaad4998.
3. Sokolov, M. et al. Best practice of materials modeling in electrocatalysis exemplified by oxygen evolution reaction on pentlandites. *Phys. Chem. Chem. Phys.* 2024, submitted.
4. Exner, K.S. Does a Thermoneutral Electrocatalyst Correspond to the Apex of a Volcano Plot for a Simple Two-Electron Process? *Angew. Chem. Int. Ed.* 2020, 59, 10236–10240.
5. Exner, K.S. A Universal Descriptor for the Screening of Electrode Materials for Multiple-Electron Processes: Beyond the Thermodynamic Overpotential. *ACS Catal.* 2020, 10, 12607–12617.
6. Razaq, S.; Exner, K.S. Materials Screening by the Descriptor $G_{\max}(\eta)$: The Free-Energy Span Model in Electrocatalysis. *ACS Catal.* 2023, 13, 1740–1758.
7. Razaq, S. et al. MXenes form Active and Selective Single-Atom Centers under Anodic Polarization Conditions. *ACS Energy Lett.* 2024, submitted.
8. Exner, K.S. On the mechanistic complexity of oxygen evolution: potential-dependent switching of the mechanism at the volcano apex. *Mater. Horiz.* 2023, 10, 2086–2095.
9. Usama, M. et al. Oxygen evolution reaction on IrO₂(110) is governed by Walden-type mechanisms. *Nat. Comm.* 2024, in revision.
10. Cho, J. et al. Importance of Broken Geometric Symmetry of Single-Atom Pt Sites for Efficient Electrocatalysis. *Nat. Comm.* 2023, 14, 3233.

As part of the presentation, there will be a teaching demonstration on the topic "Einstein and Debey Model".