

Multiple proton-coupled electron transfer in electrocatalysis: theory vs experiment

Marc T.M. Koper

*Leiden Institute of Chemistry, Leiden University
PO Box 9502, 2300 RA Leiden, The Netherlands
m.koper@chem.leidenuniv.nl*

This talk will outline a simple but general theoretical analysis for multiple proton-electron transfer reactions, based on the microscopic theory of proton-coupled electron transfer reactions, recent developments in the thermodynamic theory of multi-step electron transfer reactions, and the experimental realization that many multiple proton-coupled electron transfer reactions feature decoupled proton-electron steps in their mechanism. It is shown that decoupling of proton and electron transfer leads to a strong pH dependence of the overall catalytic reaction, implying an optimal pH for high catalytic turnover, and an associated optimal catalyst at the optimal pH. When more than one catalytic intermediate is involved, scaling relationships between intermediates may dictate the optimal catalyst and limit the extent of reversibility that may be achievable for a multiple proton-electron-transfer reaction. These scaling relationships follow from a valence-bond-type binding of intermediates to the catalyst surface. The theory is discussed in relation to the experimental results for a number of redox reactions that are of importance for sustainable energy conversion, primarily focusing on their pH dependence.