

# Describing Charge Transfer Kinetics in Batteries and Electrocatalytic Systems with DFT

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## Abstract

Controlling charge transfer kinetics and thermodynamics with the electrode potential forms the very core of all electrochemical systems. While potential dependent thermodynamics of electrochemical reactions can usually be described using standard DFT, kinetics often call for advanced computational methods. Thus far, computational studies on charge transfer kinetics in electrocatalytic systems have focused almost entirely on adiabatic inner-sphere simultaneous proton-coupled electron transfer which can be treated using DFT and common transition state theory (TST).

Such conditions are too restrictive to understand electrochemical systems in general. Specifically, there are several important electrocatalytic reactions such oxygen reduction and evolution, where either the rate and/or potential determining step has been proposed to be a pure (outer-sphere) electron transfer or decoupled proton-electron transfer which can also be nonadiabatic; modelling such reactions call for methods and theories beyond basic DFT and TST. The possibility to include several charge transfer phenomena is not only scientifically interesting and important, but also opens new reaction pathways to enable design and understanding of advanced electrochemical systems.

In my presentation I will present our model and results for describing charge transfer kinetics using constrained DFT coupled with Marcus theory. This allows the treatment of both adiabatic and nonadiabatic reactions as well as outer-sphere reactions. For electrocatalytic systems, the solvent/electrode interface is treated within an implicit solvent model including ions and the Marcus picture is extended to the grand canonical formalism to describe the electrode potential explicitly.

Implementation of constrained DFT and implicit solvation in the GPAW code are briefly discussed. The newly developed methods are applied to i) charge transfer in lithium-sulfur batteries where the nonadiabatic are shown to be important and ii) electron transfer in oxygen reduction reaction in alkaline conditions.