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First-principles based kinetic analysis of the
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Polymer electrolyte membrane fuel cells (PEMFC) are promising energy conversion devices in which the chemical energy of low-carbon or zero carbon fuels (e.g. methanol or hydrogen) is converted to electricity at low temperature. A major obstacle for wide-scale deployment of PEMFC technology is the development of active, inexpensive, and stable catalysts for the oxygen-reduction reaction (ORR). Platinum and Pt-based alloys currently set the standard for ORR catalysts as they are active and stable, though there is room for improvement on both issues. Pt-skin alloys of Pt$_3$M are particularly interesting; recent studies[1-2] have shown that Pt-skinned Pt$_3$M alloys have shown improved activity for oxygen reduction reaction compared to pure Pt or bulk Pt alloys. As Pt skin alloys (Pt$_3$M) consist of a pure Pt surface, they are in many ways similar to pure Pt, but the subtle changes in electronic and geometric structure arising from the alloyed second or third atomic layers with a transition metal M give rise to a significant improvement in ORR catalytic activity.

A detailed understanding of the relevant intermediates of ORR on these surfaces can aid in the design of better catalysts. Here, we present a first-principles based kinetic-analysis of the electrochemical discharge of water on Pt skin alloys.

Adsorbate-adsorbate interactions during relevant ORR conditions play a large role in ORR activity. The approach presented in this paper is based on a micro-kinetic micro-dynamics model which uses energies computed using Density Functional theory (DFT). DFT-calculated angular resolved adsorbate-adsorbate interactions account for the complex adsorbate structure and the non-linearity of the adsorbate interactions. These interactions are used in combination of equilibrium Monte Carlo and dynamic Monte Carlo to perform first principle simulations of the electrochemical discharge of water. The two electron transfer steps $H_2O \leftrightarrow OH + H^+ + e^-$ and $OH \leftrightarrow O + H^+ + e^-$ are treated kinetically while the fast steps like diffusion, rotation of adsorbed species are treated in equilibrium. The kinetics of the electron transfer reactions is computed using Local Reaction Center theory[3], as implemented in the Convergent Iterative Constrained Variation (CICV) method[4]. The effects of solvation, the electric field and entropy are accounted for by shifting the activation energy curves to their thermodynamic reversible potential computed from DFT[5].

The results of the adsorbate coverage from the electrochemical discharge of water on Pt$_3$Ni(111) surface in 0.1 M HClO$_4$ solution is shown in Fig 1. Similar results will be presented for other Pt skin alloys (Pt$_3$Fe, Pt$_3$Ti). The results show that there is a coexistence of OH$_{(ads)}$ and O$_{(ads)}$ at high potentials. These adsorbates

adsorb on on-top and fcc sites, respectively, resulting in an adsorbate surface structure that impacts the nature of the ORR reaction; motivating the need for a theoretical framework that accurately describes adsorbate structure – not only to understand ORR kinetics on different surfaces but also to design improved materials.
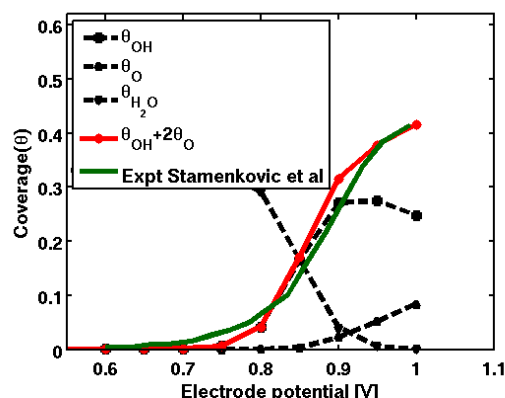

Fig 1: Results of the simulation of the electrochemical discharge of water on Pt$_3$Ni(111) in 0.1M HClO$_4$.

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