

Understanding the pH Dependence of Reversible Hydrogen Reactions

The kinetics of HER/HOR on Pt and other catalysts is fast at low pH, however, reaction rates are found to be several orders of magnitude slower in base. The explanation for this unusual pH dependence has been a matter of debate within the scientific community. Traditionally, hydrogen binding energy (HBE) has been used as the lone activity descriptor, independent of electrolyte pH [1]. This alone, however, is not sufficient to describe the pH dependence of the HER/HOR activity on metals other than Pt. Markovic et al. have proposed that hydroxide adsorption is necessary to facilitate water recombination/dissociation in base [2].

In this work, our aim is to determine if adsorbed hydroxide plays an active or spectator role in HER/HOR kinetics combining electroanalytical techniques with microkinetic modeling. We use expressions for time-dependent current and voltage as a function of hydrogen and hydroxide binding strength for the indirect (hydroxide-mediated) and direct (hydroxide-as-spectator) Volmer steps in base to simulate cyclic voltammograms. The simulated results are compared to experimental cyclic voltammograms of H-UPD on Pt(110). The free energy of hydroxide adsorption is controlled experimentally by the electrolyte cation via changes in cation solvation strength [3]. Varying the sweep rate results in greater peak separation that can be used to extract rate constants for the adsorption reaction via traditional electroanalysis [4].

Our computations show that at both slow and fast scan rates, either the direct or indirect mechanism can describe the peak potential splitting and peak current. However, hydroxide binding strength affects the mechanisms differently. In the indirect mechanism, stronger hydroxide binding reduces overpotential and, therefore, peak splitting. In the direct mechanism, stronger hydroxide binding decreases available surface sites, leading to lower exchange current densities and greater overpotential. Comparison with experiments show that from 0.1M KOH to 0.1M LiOH the peak potential location decreases while peak potential splitting increases. This trend shows that stronger hydroxide binding has detrimental effects on H-UPD kinetics, and that the direct mechanism is therefore more likely to dominate observed behavior.

Our results strongly suggest that weakening OH binding strength should increase availability of sites for H adsorption. This study contributes to resolving a long-standing paradox in electrocatalysis and surface science by determining that oxophilicity is not an accurate descriptor for alkaline hydrogen electrocatalysts. Other parameters, such as water orientation and non-covalent interactions, might be playing a greater role in the overall activity.

References:

- (1) Durst et al. *Energy Environ. Sci.* 2014, 2255.
- (2) Strmcnik et al, *Nat. Chem.* 2013, 1.
- (3) Danilovic, N. et al. *Electrocatalysis* 3, 2012, 221.
- (4) Angerstein-Kozłowska et al. *J. Electroanal. Chem. Interfacial Electrochem.* 1979, 1.