Electrochemical Hydrogen Oxidation/Evolution Kinetics – New Insights into an Old Field

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The hydrogen oxidation/evolution reaction (HOR/HER) is a central reaction in both fundamental electrocatalysis and in electrochemical energy conversion devices, viz., in H_2/air fuel cells as well as in water electrolyzers. The most active catalyst for this reaction is platinum, and in acidic electrolytes its kinetics are so large, that their quantification by the commonly used rotating disk electrode (RDE) technique turned out to be compromised by unaccounted for mass-transport resistances. This will be outlined in this presentation, showing that the true HOR/HER kinetics of Pt in acidic electrolytes are about two orders of magnitude larger than previously assumed [1]. This explains why ultra-low loadings of platinum in H_2/air fuel cell anodes or in water electrolyzer cathodes are sufficient to sustain very high rates at very low overpotentials.

A mechanistically very interesting aspect of the HOR/HER reaction is that early *ab-initio* models predicted that its kinetics on platinum are independent of pH [2], which recently was shown to not be the case, as the HOR/HER kinetics on Pt are ≈100-fold lower in alkaline compared to acidic electrolytes [3]. The so far proposed explanations for this effect are an increased H/metal bond strength [3, 4], a change of the reaction mechanism from H^+ to H_2O activation requiring more oxophilic catalyst surfaces [5], and/or a change of the water configuration at the metal/electrolyte interface [6]. The consistency of these hypotheses with the HOR/HER kinetics on different metal electrodes will be discussed. One other fundamental question of interest is whether the hydrogen oxidation/evolution reaction on palladium catalysts actually occurs on metallic palladium (as assumed in calculations [3]) or on palladium-hydride, a question which we will try to address by means of *operando* X-ray absorption studies [7].

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