Modeling the Electrochemical Hydrogen Oxidation and Evolution Reactions on the Basis of Density Functional Theory Calculations

Density functional theory calculations have been performed for the three elementary steps—Tafel, Heyrovsky, and Volmer—involved in the hydrogen oxidation reaction (HOR) and its reverse, the hydrogen evolution reaction (HER). For the Pt(111) surface a detailed model consisting of a negatively charged Pt(111) slab and solvated protons in up to three water bilayers is considered and reaction energies and activation barriers are determined by using a newly developed computational scheme where the potential can be kept constant during a charge transfer reaction. We determine the rate limiting reaction on Pt(111) to be Tafel−Volmer for HOR and Volmer−Tafel for HER. Calculated rates agree well with experimental data. Both the H adsorption energy and the energy barrier for the Tafel reaction are then calculated for a range of metal electrodes, including Au, Ag, Cu, Pt, Pd, Ni, Ir, Rh, Co, Ru, Re, W, Mo, and Nb, different facets, and step of surfaces. We compare the results for different facets of the Pt electrode to experimental data. Our results suggest that the most important parameter for describing the HOR or the HER activity of an electrode is its binding free energy of H. We present a detailed kinetic model based entirely on the DFT reactions and show that the exchange current follows a volcano curve when plotted against the H adsorption free energy in excellent agreement with experimental data.

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