

Probing the potential and pH dependence of HER kinetics from first principles via intrinsic reaction barriers

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The hydrogen evolution reaction (HER) has been extensively studied for decades. However, several questions regarding the HER mechanism remain unanswered. In particular, the dramatic decrease in intrinsic reaction rate in alkaline media is not completely understood. Previous experimental work reported an HER activation barrier of 0.30 eV on Pt in alkaline media.¹ Recent theoretical studies argue that the activation barriers are the same in acidic and alkaline media, and that the sluggish HER kinetics in alkaline electrolytes is a consequence of an increased entropic barrier through the outer Helmholtz plane.²

Herein, we implicitly study the effect of pH on the Volmer, Heyrovsky and Tafel steps of the HER mechanism within the density functional theory framework by changing the proton donor and environmental parameters. We use the solvated jellium model (SJM) - a method developed in our group - to study the potential- dependence of the elementary steps of the HER mechanism. This method allows for the addition/subtraction of electrons (or fractions thereof) to/from the unit cell in order to keep the potential constant. As a consequence, intrinsic reaction barriers in an electrochemical environment are directly and efficiently accessible via e.g. nudged elastic band (NEB) calculations.

The first elementary step of HER in any aqueous electrolyte is the Volmer step, i.e. proton discharge from the electrolyte to form adsorbed hydrogen. The second elementary reaction could be either the Heyrovsky or the Tafel step. The former describes hydrogen gas formation from an adsorbed hydrogen atom and a proton-electron pair from the electrolyte/circuit, whereas the latter is a purely chemical step between two adsorbed hydrogen atoms. One can thus expect the Tafel step to be independent of the applied potential save for field effects. Hence, we will report on the relative barrier heights of the Heyrovsky and Tafel steps in acidic and alkaline media, and determine whether a potential window within which one could expect a change in HER mechanism exists.

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2. Rossmeisl, J.; Chan, K.; Skúlason, E.; Björketun, M.; Tripkovic, V., *Catalysis Today*, 2016, 262,36-40