

Reaction Mechanism of Hydrogen Evolution over MoS<sub>2</sub> : Tafel vs. Heyrovsky

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Molybdenum disulfide (MoS<sub>2</sub>)-based materials have emerged as promising catalysts for hydrogen evolution reaction (HER). However, the reaction mechanism has been still questionable as such whether HER follows Volmer-Tafel or Volmer-Heyrovsky routes. In this work, we aim to settle the controversial issue by clearly describing the thermodynamic predominance of one type mechanism over the other via the density functional theory calculation. In order to describe the solid-electrolyte interface, the periodic MoS<sub>2</sub> slabs and explicit solvated protons were initially modeled with implicit water environment. Subsequently, by varying the number of solvated protons in the electrolyte layer, the reaction energetics and activation barriers were investigated as a function of electrode potential, which was determined by the work-function calculation. By comparing the free energy barrier at the rate-determining step of each reaction, we found that Volmer-Heyrovsky mechanism is predominant in the HER. In addition, to study the size-dependent HER activity, the reaction barriers of monolayer and bulk MoS<sub>2</sub> were also investigated. These fundamental understandings into the underlying mechanism and size effects in the HER will surely help the design of advanced HER catalysts.