

Anionic Effect on Metal Pair of Se-doped Nickel Diphosphide for Hydrogen Evolution Reaction

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ABSTRACT

The actual chemical environment of metal phosphides or chalcogenides during hydrogen evolution reaction (HER) has been on debate. In this work, pyrite-phased NiP₂, Se-doped NiP₂ and NiSe₂ were investigated by means of *in-situ* and *ex-situ* characterizations to dynamically study the transformation during electrocatalysis. We found that doping with selenide would generate more vacancies to facilitate the activation on water molecule, in which hydroxide poisoning on active site would be suppressed by the presence of selenide. Furthermore, the radial distance of Ni-Ni pair can serve as a descriptor to identify the mechanism of HER. For NiP₂ and Se-doped NiP₂, the radial distance of the metal (Ni-Ni) pair during HER is identical to the as-prepared one, implying the HER active site is on single metal site with a Heyrovsky step. A drastic bond contraction of Ni-Ni pair on NiSe₂ indicates dual site activation correlated with a chemical desorption of Tafel step. The role of anion effects and metal sites are comprehensively investigated to further gain the fundamental insights from the point of view on improving HER electrocatalytic performance.

