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Guiding principles for hydrogen evolution reaction on nickel-based catalysts in aqueous electrolytes

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The development of catalytic materials for the hydrogen evolution reaction (HER) has been closely tied to the well-known concept of volcano plot, where the metal-H_{ad} bond energy is used as a single activity-descriptor. Although from a thermodynamic point of view it should make no difference whether hydrogen is produced from protons or water, there is a huge impact on the kinetics of the HER, which on most metal catalysts in alkaline media is about 2-3 orders of magnitude slower than in acid solutions, a phenomenon that cannot be explained solely by the metal-H_{ad} energetics [1]. We have persistently drawn attention to the importance of the kinetic synergy (bifunctional nature) of the HER in alkaline electrolytes, wherein both the beneficial OH_{ad}–M and H_{ad}–M energetics are necessary for achieving a highly effective catalyst. A specific example is a controlled decoration of Pt(111) surfaces by nanometer-scale $Ni(OH)_2$ clusters that manifests a factor of 8 activity increase in catalyzing the HER, compared to corresponding bare Pt(111) [2].

In recent years, many academic debates have been revived, focusing on the two aspects: *i)* the previously mentioned variation in HER kinetics between acidic and base environments, and *ii)* the impact that the spectator species have on the kinetics of electrochemical reactions. Here, we aim to highlight the contribution of 4 key factors governing the rate of HER in aqueous solutions on Ni-based catalysts. The interest in the electrochemical behavior of nickel arises from its industrial use as the cathode material in the water-alkaline electrolyzers.

Our study starts with the extended surfaces, affording insight into the fundamental kinetics of cathodic processes on the atomic/molecular level, which in the case of the Ni polycrystalline system are quite complex owing to the existence of several possible oxidation states of the metal, including numerous species such as Ni^0, $Ni(OH)_2$, NiO, NiOOH, hydride, *etc.* as well as their corresponding (pseudo)polymorphs.

We demonstrate the significance of water as a vital hydrogen-donor molecule that promotes the rate of transformation of reaction intermediates into the molecular hydrogen in alkaline electrolytes. Furthermore, a delicate balance between the availability of active sites on Ni electrode surface (the $1-\Theta_{ad}$ term) and the energetics of the activated water complex (the $\Delta G^{0\#}(H_2O)$ term) appears to be the key to maximizing the rate of the HER [3,4]. By careful design of our experiments, we were able to decouple these two factors and show their individual contribution to the rate of HER. This, in turn leads us to identifying the active sites for the HER and emphasize that the surface reactivity for the HER on Ni can be improved by simply tailoring the nature and coverage of adsorbates.

References

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