Non-precious Metal Catalysts for Hydrogen Oxidation Reaction in Alkaline Electrolytes

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Low-temperature hydrogen fuel cells show great promise for highly efficient and environmentally friendly energy conversion.[1] In addition to the 300 ~ 400 mV overpotential caused by the sluggish oxygen reduction reaction (ORR) at the cathode in both acidic and alkaline media, slow hydrogen oxidation reaction (HOR) on Pt in alkaline electrolytes compared to that in acids imposes extra cell voltage loss, which requires higher Pt loading on the anode.[2] Therefore, the demand for Pt-free catalysts for the HOR in alkaline medium arises in order to reduce the overall catalyst cost and the commercialization of alkaline or alkaline membrane fuel cells. Through the study of the reverse reaction i.e., hydrogen evolution reaction (HER) on a wide range of metal surfaces in base, we found the exchange current densities at the reversible hydrogen potential correlated to the calculated hydrogen binding energies (HBE) of these metal surfaces via a volcano relationship, as shown in Fig. 1.[3] This discovery suggests that HBE values can serve as a reaction descriptor for designing and searching for novel electrocatalysts for the HER/HOR in base.
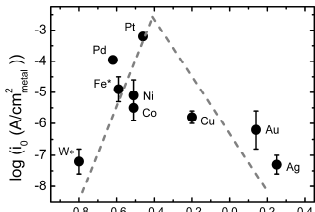

Figure 1. Exchange current densities, $\log(i_0)$ on mono metallic surfaces plotted as a function of the calculated HBE. The dashed lines are to guide the eyes.[3]

Guided by the DFT calculations, we calculated the HBE of Ni-based multi-metallic surfaces and found that a ternary nickel alloy, NiMN, had similar HBE value as Pt. We subsequently synthesized NiMN by electrodeposition and evaluated their HOR performance at different temperatures.

Fig. 2a shows that the HOR on NiMN outperforms Pt in 0.1 M KOH at 313 K and reaches the theoretical limiting current ~100 mV earlier than Pt. Both of the HOR and HER kinetic currents on NiMN are significantly higher than that on Pt (Fig. 2b).
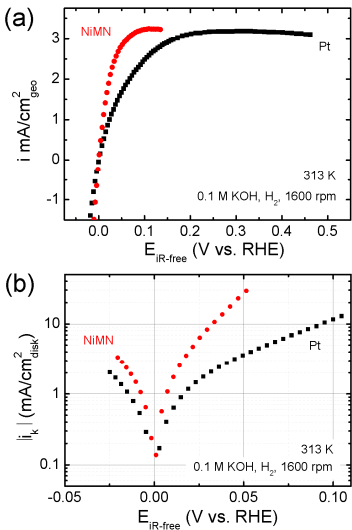

Figure 2. (a): steady state polarization curves of the HOR/HER on electroplated NiMN alloy (red) and Pt disk (black) in H_2-saturated 0.1 M KOH at 313 K. The polarization curves have been corrected for solution resistance; (b): kinetic currents of the HOR/HER on NiMN alloy (red) and Pt (black) at 313 K. The HOR kinetic currents were acquired using the Koutecky-Levich equation.

Simulated anode performance based on the HOR exchange current density on NiMN at 353 K, which is extrapolated from the measured exchange current densities at different temperatures, shows a nearly 100 mV reduction in the anodic overpotential. This promising material will greatly mitigate the catalyst cost issue raised by higher Pt loading in alkaline electrolytes for maintaining similar anode performance as in acids, which will facilitate advancing the alkaline or alkaline membrane fuel cell technology.

References

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