

수소발생 촉매분야에서 분자 전자 촉매 설계의 최신 연구동향

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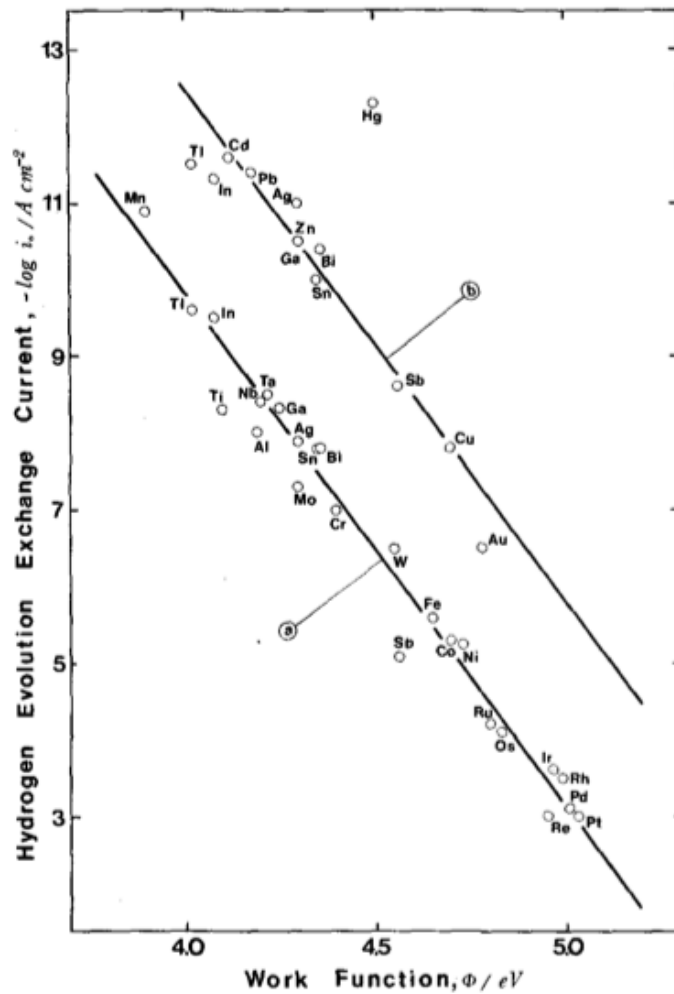


Figure 1. Exchange currents for electrolytic hydrogen evolution vs. values of the work function of metals.

Hydrogen production via water electrolysis is considered the ideal basis for the hydrogen economy in the near future due to its environmental friendliness and absence of any harmful

greenhouse gas emissions, unlike other technologies such as hydrocarbon reforming, coal gasification and biomass pyrolysis.^{1,2} However, several barriers to the commercialization of water electrolysis remain: (1) water electrolysis is expensive compared to hydrocarbon reforming which is the most widely used technology for hydrogen production, (2) HER can be started at large overpotential, and (3) the water electrolysis system suffers a stability problem over long-term and shut down operations.

In order to overcome these obstacles, studies have been conducted on various metals as a catalyst for HER.³⁻¹¹

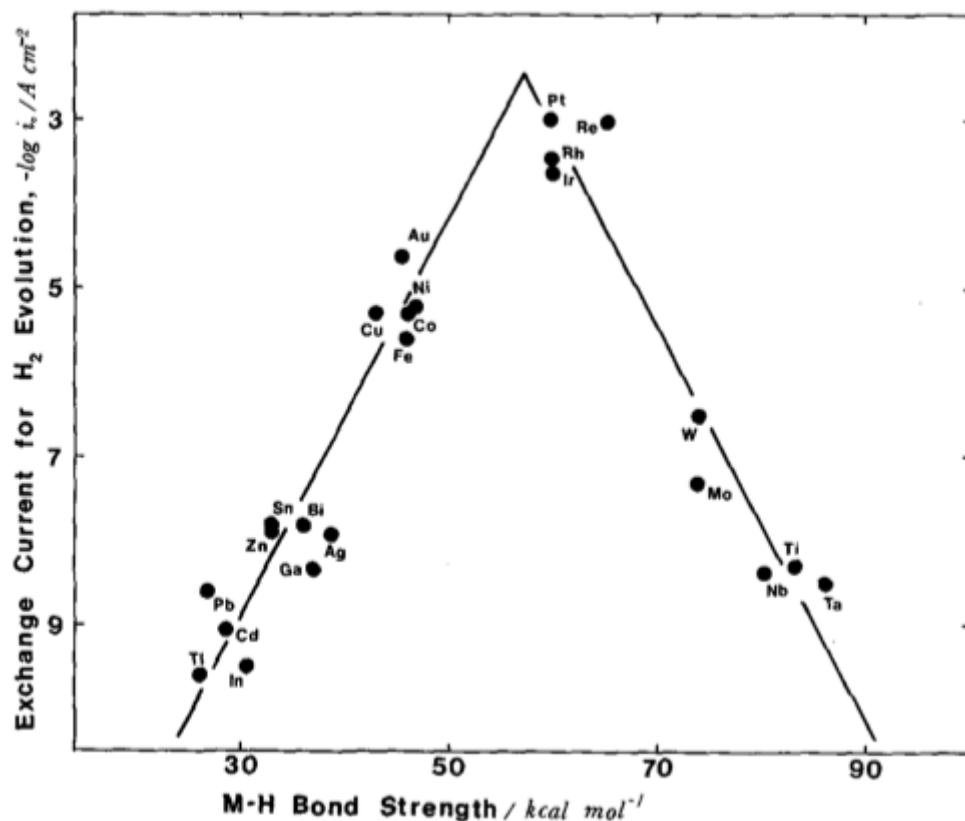


Figure 2. Exchange currents for electrolytic hydrogen evolution vs. strength of intermediate metal-hydrogen bond formed during electrochemical reaction itself. E(M-H) from Krishtalik.

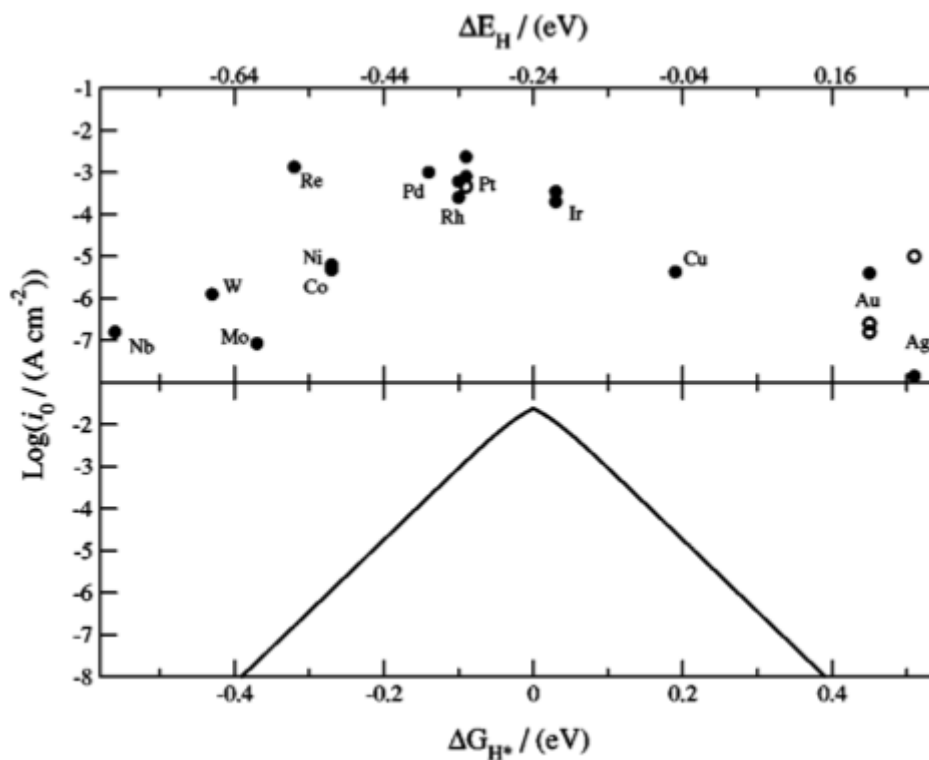


Figure 3. Experimentally measured exchange current, $\log(i_0)$, for hydrogen evolution over different metal surfaces plotted as a function of the calculated hydrogen chemisorption energy per atom.

Trasatti *et al.* and Nørskov *et al.* explained the catalytic performance of various candidates by using a volcano plot obtained from the exchange current density of HER as a function of the calculated hydrogen adsorption energies.⁴⁻⁶ If the binding between the adsorbed hydrogen and metal surface is too weak, activation of the hydrogen to the metal surface is difficult. On the other hand, strong hydrogen binding on the metal surface blocks the available reaction sites.

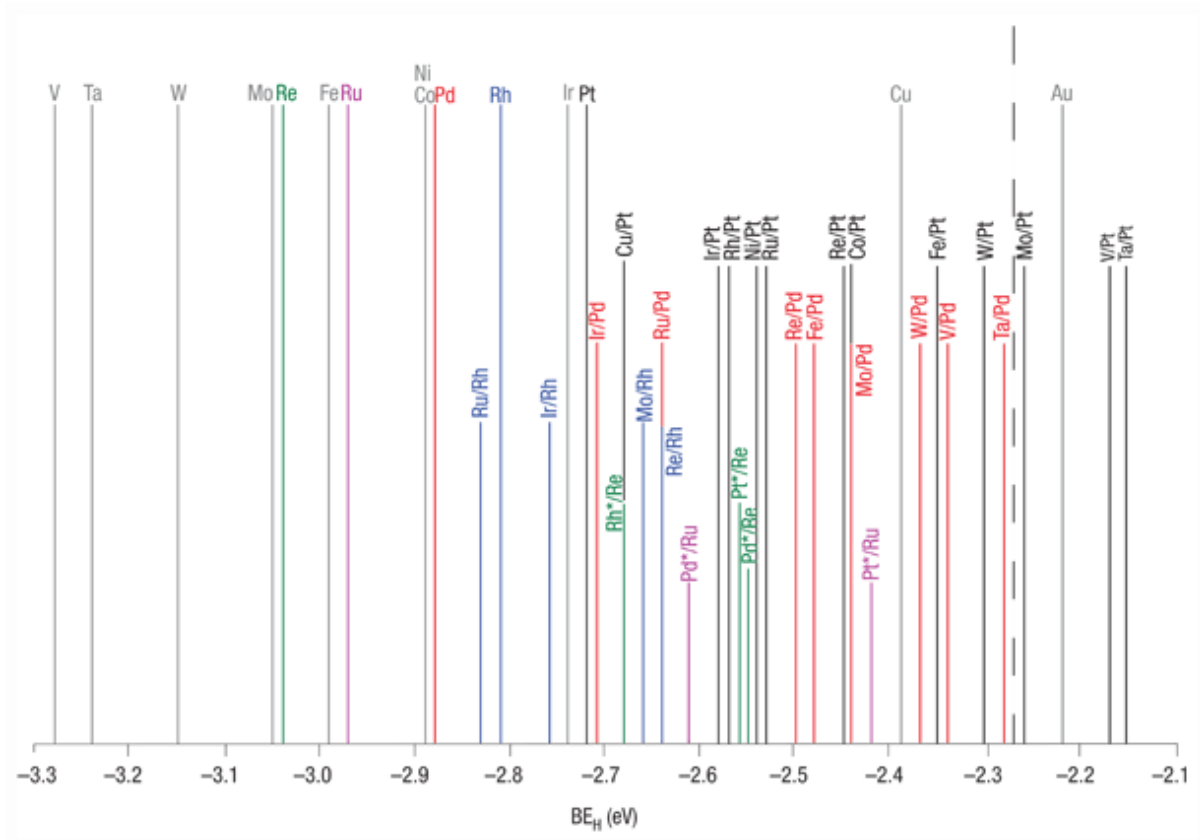


Figure 4. Referenced to a clean metal slab and a gas-phase hydrogen atom ($H(g)$) at infinite separation from one another. The height of the bars associated with the various alloys and pure metals is arbitrary and is varied only for clarity. The vertical dashed line at -2.28 eV corresponds to thermoneutral $H_2(g)$ dissociation (the gas-phase H_2 bond energy is 4.57 eV).

Investigations have determined that Ni has the highest catalytic activity for HER among the non-noble metals due to the proper hydrogen adsorption energy on its surface.^{7,8}

As well as the kind of metals, the physical properties of the catalysts, including size, shape and crystallographic structure, also affect their catalytic activity.¹² The size and shape are closely related to the surface area, which affects the catalytic activity. In addition, controlling the orientation of the metal catalyst surface is effective in improving the catalytic properties. The type of crystal orientation affects the kinetic behavior of electrochemical reactions

because the activation energy for adsorption of reactants on the metal surface is a function of the distance between adjacent atoms.^{13,14} Ferrin *et al.* reported the morphological effect of methanol electrooxidation on eight transition metals between the (111) and (100) facets.¹⁵ The activity of the oxygen reduction reaction with Pt is increased in the following order of facets: (110) > (111) > (100).^{16,17} Gómez *et al.* reported different catalytic activity for HER on Pt (100) and Pt (111) facets.^{9,10}

Reference

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