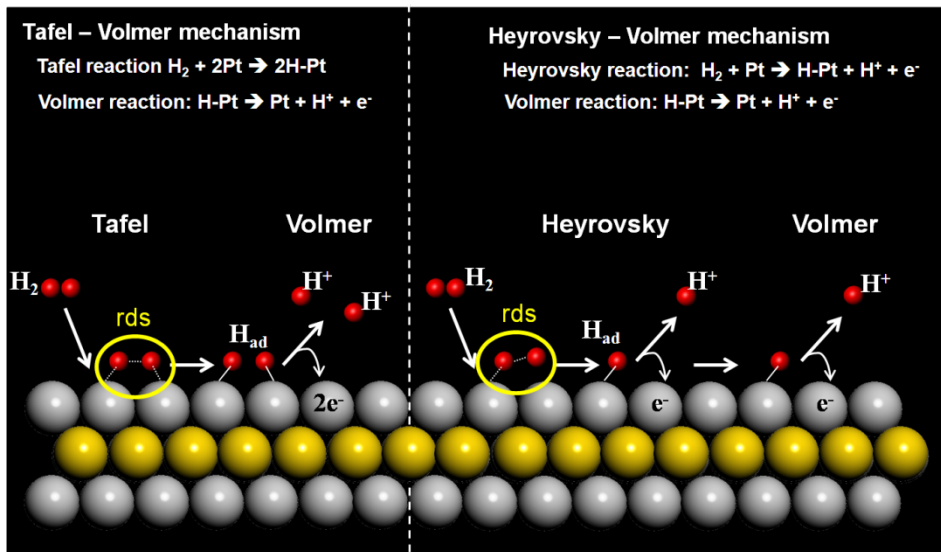


# 수소산화반응 촉매분야에서 분자 전자 촉매 설계의 최신 연구동향

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Fuel cells promising and worthy candidates for high efficiency and low emission energy conversion devices in mobile, stationary and portable application sectors and are expected to be one of the major clean energy sources in the near future. Despite important advancement in fuel cells investigation, there is the major impediment to the large-scale production and commercialization of such applications, as follows: the decreased catalytic activity by long-term operation, the high cost the electrocatalyst (Pt) required, and the deficiency of kinetic mechanisms on the electrocatalytic surface, which are the urgent issues to be addressed since they determine the efficiency and the cost of this energy source. In this chapter, we will explain a new approach about the designing electrocatalysts for hydrogen oxidation reaction (HOR) in polymer electrolyte fuel cells (PEFCs).

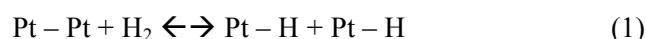


*Scheme 1. Elementary reaction steps for HOR*

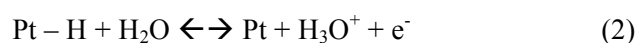
The anode reaction in PEFCs usually is referred to hydrogen oxidation reaction at the surface of the anode platinum electrocatalyst. The HOR and hydrogen evolution (HER) are by far the most thoroughly investigated electrochemical reaction system, and have assumed a new importance by virtue of renewed interest of fuel cells <sup>[1]</sup>. The mechanism of these processes is fairly well established and can be described by three elementary steps; 1) Tafel

step (or recombination reaction), 2) Volmer step (or charge transfer reaction), and 3) Heyrovsky step (or ion-plus-atom reaction). The overall process can be divided into 5 steps <sup>[2]</sup>.

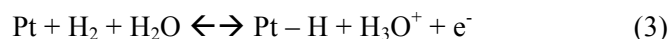
- 1) The transfer of the H<sub>2</sub> molecules to the platinum electrode via gas diffusion.
- 2) The adsorption of hydrogen molecules from the electrolyte onto the electrode surface through the electrolytical double layer.
- 3) The dissociative adsorption of hydrogen on platinum surface via Tafel reaction (or recombination reaction).



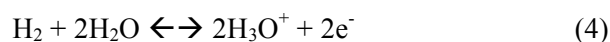
- 4) The ionization of H atom giving one electron to the electrode and a hydronium ion the solution, leaving an empty platinum site through the Volmer reaction (or charge transfer reaction).



or by direct reaction of hydrogen molecules through Heyrovsky reaction (or ion-plus-atom reaction)



- 5) Further step is the transport of the hydronium ions from the phase boundary to the electrolyte solution phase. Therefore, the overall charge reaction (or oxidation) can be expressed as:



The choice of platinum as an electrode material is only representative. The principal reaction steps should occur on any other noble metal electrode surface as well, but possibly under different conditions of the electrochemical potentials. For another electrode material and electrolyte, the rates of the reactions may be quite different, and the mechanism may be formed dominantly by Tafel/Volmer reaction steps or alternatively by Heyrovsky/Volmer reaction steps. Another less probable possibility is that the rates of all reactions are close to each other, so that a concerned mechanism is classified, in which only the reaction is studied. The overall reaction is classified as irreversible if the rate constant is small, or reversible if they are high enough to allow the treatment by Nernst equation.

The Tafel/Volmer mechanism, with the Tafel reaction being the rate determining step,

has been proposed for H<sub>2</sub> reaction in strong acids on a platinum electrode and the reaction is considered as reversible. The kinetic equations employed for analysis are <sup>[3]</sup>

$$E = E_1 - 2.303 \frac{RT}{nF} \log \frac{(i_L^c)^2 (i_L^a - i)}{(i_L^a) (i - i_L^c)^2} \quad (1.13)$$

where  $i_L^c$  and  $i_L^a$  are the cathodic and anodic limiting current. In the case of strong acid solution ( $|i_L^c| \gg i$ ), the equation becomes

$$E = E_1 - 2.303 \frac{RT}{nF} \log \frac{(i_L^a)^2 - i}{(i_L^a)} \quad (1.14)$$

where  $E_1$  is the equilibrium potential and

$$E_1 = E_0 - 2.303 \frac{RT}{nF} \log \frac{C_R^\infty}{(C_O^\infty)^2} \quad (1.15)$$

in which  $E_0$  is the formal potential, and  $C_R^\infty$  and  $C_O^\infty$  are equilibrium concentrations of reductant and oxidant, in this case, H<sub>2</sub> and H<sup>+</sup> or hydronium.

When the fuel used in PEFCs is impure hydrogen produced by reforming other fuels, such as methanol, ethanol, or natural gas, trace amount of CO is difficult to avoid. CO molecules will preferentially adsorb on platinum active sites, thus block the sites for hydrogen adsorption, and consequently decreases the fuel cell energy conversion efficiency <sup>[3]</sup>. CO-tolerant electrocatalysts have been searched to overcome the negative effects of CO poisoning. Generally, these electrocatalysts are combinations of platinum and oxophilic elements, such as ruthenium, tin, molybdenum, osmium, etc., in binary, ternary, or quaternary alloys <sup>[4],[5],[6]</sup>. The alternative way to increase CO tolerance of the electrocatalyst is to deposit sub-monolayer of platinum on ruthenium nanoparticles. One of the main advantages of the sub-monolayer platinum electrocatalyst is to reduce the amount of platinum used by more than 10 times in comparison with commercial platinum alloy electrocatalyst <sup>[7]</sup>. The additional elements are placed to promote the electro-oxidation of CO to CO<sub>2</sub> through the so called bifunctional mechanism, which involving spillover process of CO to the OH species formed on the oxophilic sites <sup>[8]</sup>. The presence of the second element can also lead to a weaker platinum-CO bonding due to an electronic effect introduced by the second element, and resulting in an enhancement of CO tolerance <sup>[9]</sup>.

The electrocatalytic properties of bimetallic surfaces on single crystal metal surface have been extensively studied in ultra-high vacuum systems <sup>[10],[11],[12],[13]</sup>. In many cases, the formation of the bimetallic surfaces significantly changed the geometric and electronic

properties of the primary metal, and pronounced differences were observed in the electrocatalytic reactivity of some transition metal monolayers on various primary metal substrates<sup>[10]</sup>.

Recently, Nørskov advanced a new theory to elucidate simply the adsorption properties of metal atoms and small molecules on transition metal surfaces<sup>[14]</sup>. In this theory, instead of the density of states at Fermi level, the d-band center (average energy of the whole d-band) is used to elucidate the catalytic reactivity of the reaction sites on the metal surface. Density function theory calculations showed that the binding energies and catalytic reactivity of small atom or molecule adsorption on strained surfaces correlate well with the position of d-band center of surface metal atoms. The surface bond lengths changes in orbital overlap due to strain effect and modifies the electronic structure of the metal. According to this argument, when the surface atoms are subjected to tensile strain, the d-orbital overlap is decreased, resulting in a sharpening of the d-band and an up shift of the d-band center, which indicates a stronger adsorption energy. On the other hand, when the surface atoms are under compressive strain, the d-orbital overlaps are increased, resulting in a broadening of the d-band and a lowering of its average energy. Consequently the presence of other metals around a metal atom changes its electronic environment and modifies its electronic structure and its chemical properties. These results show the theoretical possibility to design the outstanding electrocatalyst and agree with data from many experimental researches<sup>[15],[16],[17]</sup>.

Therefore, next generation HOR electrocatalysts should either consist of moderate to low-cost materials that exhibit a catalytic activity at least equal to that of platinum or so-called “zero cost” materials<sup>[18]</sup>. In recent years, several researchers have identified several alternative electrocatalysts in various forms including metal alloys<sup>[19],[20]</sup>, metal oxides<sup>[21],[22],[23]</sup> and both organic and inorganic and metallic complexes<sup>[24],[25]</sup>. However, these anodes generally exhibit a lower activity than Pt. Recently, three groups have identified a family of Pd-based alloy electrocatalysts that have shown great promise for the HOR<sup>[26],[27],[28]</sup>. A significant amount of work remains to completely characterize these materials including clarifying the role of composition on the catalytic activity, testing performance stability and elucidation of the mechanism.

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