A DFT Study of H_2S Dissociation Reaction on Ni(111) and Ni(211)

Bohyun Hwang[1], Hyunguk Kwon[1], and Jeong Woo Han[1*]

[1]*Department of Chemical Engineering, University of Seoul, Seoul 02504, Republic of Korea*

*E-mail: jwhan@uos.ac.kr

Solid oxide fuel cells (SOFCs) offer great prospects for the efficient utilization of a wide range of chemical fuels from hydrocarbon fuels to carbonaceous solid fuels. [1] SOFCs also have desirable advantages compared to the other types of fuel cells due to low cost, high efficiency and low pollution emission. A Ni catalyst supported on yttrium-stabilized zirconia (YSZ) has been usually exploited as SOFC anode due to its higher catalytic activity with lower cost than other metals. However, the reaction on Ni/YSZ anode often accompanies the contaminants such as sulfur containing compounds which are difficult to remove economically. The development of sulfur-tolerant catalytic materials is therefore an urgent task for the efficient SOFC.

The mechanisms of interaction between H_2S and Ni or Ni-based bimetallic alloys surfaces (Cu/Ni, Rh/Ni, Pd/Ni, Ag/Ni, Pt/Ni, Au/Ni) were elucidated by density functional slab model calculations. All calculations were carried out with a Vienna ab initio simulation package (VASP) code. [2] The Perdew-Burke-Ernzehof (PBE) functional based on generalized gradient algorithm (GGA) was applied to relax geometries until the forces on all unrestricted atoms were less than 0.03 eV. In order to take into account the dispersion force, we used a semi-empirical DFT-D2 method proposed by Grimme. [3]

In this study, H_2S dissociation behavior is evaluated in two systems; (1) Ni(111) (or Ni-based bimetallic alloys) surface and (2) Ni(211) (or Ni-based bimetallic alloys). The (211) surface is a representative of undercoordinated site which can be frequently exposed at the nanoparticle shape. To investigate the mechanism of sulfur poisoning on both surfaces, we divided the process of H_2S dissociation into two sequential steps: $H_2S^* \rightarrow HS^* + H \rightarrow S^* + H^* + H^*$. The minimum-energy pathways (MEPs) and the energy barriers of H_2S dissociation were determined using the climbing image-nudged elastic band (CI-NEB) method.

Based on the results, we suggested a way of alleviating sulfur deposition by using Ni-based bimetallic alloys in comparison to the pure Ni. This study will be helpful to design sulfur-tolerant electrode materials in SOFC.

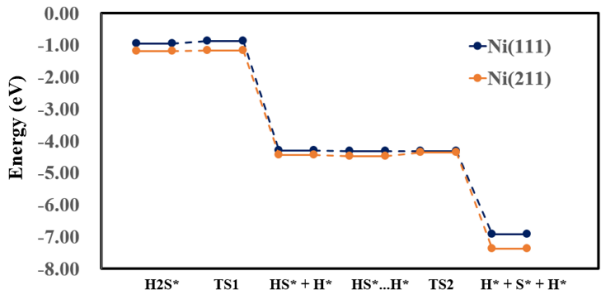

Fig. 1 Relative energy profile for decomposition of H_2S on Ni(111) and Ni(211). TS1 and TS2 indicate the transition state in $H_2S^* \rightarrow HS^* + H$ and $HS^* + H^* \rightarrow H^* + S^* + H^*$. respectively.

REFERENCES

[1] H. Kim, J.M. Vohs, R.J. Gorte, Chem. Commun., (2001) 2334.

[2] G. Kresse and J. Furthmuller, Phys. Rev. B: Condens. Matter Mater. Phys., 54 (1996) 11169.