First-Principles Study on Poisoning Tolerance of Pt Alloy Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell Anode

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A recent polymer electrolyte fuel cell requires development of anode materials with high tolerance to poisoning by adsorption of impurities such as CO and H_2S in the fuel, which degrades activity of the anode. Here, Shi and Uchida et al. developed PtFe, PtCo, and PtNi alloy nano-particles with two atomic layers of stabilized Pt skin (Pt_{2AL}-PtM[M = Co, Fe, Ni]), and showed that the order of tolerance to CO poisoning is Pt_{2AL}-PtFe > Pt_{2AL}-PtCo > Pt_{2AL}-PtNi > Pt [1]. In order to develop an anode catalyst with high tolerance to both CO and H_2S poisoning, it is important to understand adsorption states of CO and H_2S on Pt_{2AL}-PtM nano-particles. In this study, to elucidate the catalyst with the high impurity tolerance, we investigated adsorption states of CO and H_2S molecules on Pt_{2AL}-PtM(111)[M = Co, Fe, Ni] by first-principles calculation.

At first, to compare the tolerance of Pt_{2AL}-PtM(111) and Pt(111) to CO poisoning, we calculate the adsorption energy of CO. Here, the ratio of Pt to alloy atoms in the alloy layer is 1:1. The model of Pt_{2AL}-PtM(111) is presented in Fig. 1 and the calculated adsorption energies of CO are shown in Table 1. The adsorption energy of CO on Pt_{2AL}-PtFe(111) is 31.94 kcal/mol, which is lower than that on Pt(111) of 47.25 kcal/mol. The result indicates more difficult adsorption of CO on Pt_{2AL}-PtFe and the higher tolerance to CO poisoning than pure Pt. The adsorption energy on Pt_{2AL}-PtCo(111) is 32.61 kcal/mol and slightly higher than that on Pt_{2AL}-PtFe(111). These adsorption energies indicate that the order of CO tolerance is Pt_{2AL}-PtFe > Pt_{2AL}-PtCo > Pt, which is good agreement with the experiment [1]. In the case of Pt_{2AL}-PtNi(111), the Pt skin layer is collapsed by CO adsorption and the adsorption energy is not obtained. Here, lattice constants of PtFe, PtCo, PtNi, and Pt are 3.862, 3.835, 3.811, and 3.924 Å, respectively. Then, we suggest that much difference of the lattice constant between PtNi and Pt leads to the unstable Pt skin layer and the collapse by CO adsorption.

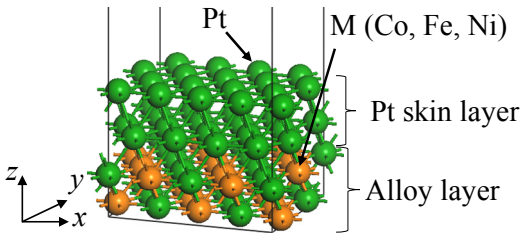

Fig. 1 Pt_{2AL}-PtM(111)[M= Co, Fe, Ni] surface model.

TABLE 1 Adsorption energy of CO and H_2S on Pt(111) and Pt_{2AL}-PtM(111)[M= Co, Fe, Ni]

	CO	H_2S
Pt(111)	47.25	25.32
Pt_{2AL}-PtFe(111)	31.94	21.28
Pt_{2AL}-PtCo(111)	32.61	20.17
Pt_{2AL}-PtNi(111)	-	-

Next, to investigate the tolerance of Pt_{2AL}-PtM(111) to H_2S poisoning, we calculate the adsorption energy of H_2S (Table 1). To compare the tolerance with pure Pt, we also calculate the adsorption energy on Pt(111). The adsorption energies of H_2S on Pt(111), Pt_{2AL}-PtFe(111), and Pt_{2AL}-PtCo(111) are 25.32, 21.28, and 20.17 kcal/mol, respectively. This result shows that Pt_{2AL}-PtFe(111) and Pt_{2AL}-PtCo(111) are more tolerant to NH_3 poisoning than Pt(111). Here, H_2S adsorption collapses the Pt skin layer of Pt_{2AL}-PtNi(111). Then, in our investigated surfaces, we suggest that Pt_{2AL}-PtFe(111) and Pt_{2AL}-PtFe(111) show higher tolerance to CO and H_2S poisoning than pure Pt(111).

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