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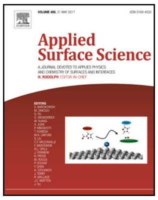

Full Length Article

Density functional theory study for the enhanced sulfur tolerance of Ni catalysts by surface alloying

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ABSTRACT

Sulfur compounds in fuels deactivate the surface of anode materials in solid oxide fuel cells (SOFCs), which adversely affect the long-term durability. To solve this issue, it is important to design new SOFC anode materials with high sulfur tolerance. Unfortunately, it is difficult to completely replace the traditional Ni anode owing to its outstanding reactivity with low cost. As an alternative, alloying Ni with transition metals is a practical strategy to enhance the sulfur resistance while taking advantage of Ni metal. Therefore, in this study, we examined the effects of transition metal (Cu, Rh, Pd, Ag, Pt, and Au) doping into a Ni catalyst on not only the adsorption of H_2S, HS, S, and H but also H_2S decomposition using density functional theory (DFT) calculations. The dopant metals were selected rationally by considering the stability of the Ni-based binary alloys. The interactions between sulfur atoms produced by H_2S dissociation and the surface are weakened by the dopant metals at the topmost layer. In addition, the findings show that H_2S dissociation can be suppressed by doping transition metals. It turns out that these effects are maximized in the Au-doped Ni catalyst. Our DFT results will provide useful insights into the design of sulfur-tolerant SOFC anode materials.

1. Introduction

Sulfur poisoning causes the deactivation of heterogeneous catalysts by blocking the active sites for catalytic reactions, leading to scientific and industrial problems in a variety of device applications [1–3]. In particular, the phenomenon causes performance degradation of solid oxide fuel cell (SOFC) anodes, resulting in undesirable effects on the long-term stability and cost of fuel cells. SOFCs with fuel-flexibility can be powered by oxidizing a variety of fuels, including hydrogen, hydrocarbons, biogas and syngas, at the anode, either with or without pre-reforming of them [4,5]. Unfortunately, sulfur compounds which are present as an impurity in the fuels significantly deteriorate the rate of the electrochemical reaction at the anode [6,7]. These poisoning effects can be prevented from the purification of fuels to some extent. However, the degradation caused by sulfur poisoning cannot be solved completely by purification techniques alone because it is very difficult to entirely remove the sulfur compounds from fuels [8]. In addition, poisoning can originate from only a small amount of sulfur [9]. Therefore, it is essential to understand the mechanism for sulfur poisoning in the SOFC anode, and design new anode materials with strong tolerance to sulfur compounds for the development of SOFCs with long-term durability.

Ni metal has been used widely as a representative SOFC anode material. However, Ni catalyst can be poisoned easily by sulfur compounds. As an example, Zha et al. reported that the cell performance of the Ni/YSZ anode decreases rapidly and concentration dependently when exposed to H_2S-containing fuel [9]. To overcome this issue, numerous studies have examined the sulfur poisoning behavior on the surface of transition metals, which may replace the Ni catalyst, including Fe [10], Co [11], Cu [12,13], Mo [14], Rh [15], Pd [16], Ag [17], W [18], Pt [19], and Au [20]. Nevertheless, considering the superior intrinsic reactivity and relatively low cost of the Ni catalyst, there is no single-component metal catalyst that can completely replace Ni [21]. Therefore, the development of Ni-based binary alloys is a practical way to enhance the sulfur tolerance while maintaining the properties of Ni metal. The possibility of this strategy to improve the sulfur tolerance has been already verified in previous studies. For example, Choi et al. examined the adsorption phenomenon of atomic sulfur on the surface of Ni, Cu-Ni alloy, and Cu catalysts based on first-principles calculations [22]. According

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to their results, Cu doping into Ni enhances the sulfur resistance by reducing the adsorption strength of the sulfur atom. However, the sulfur tolerance of Cu_xNi_{1-x} is not larger than that of pure Cu. In another case, Xu et al. reported that alloying Ni with Cu, Ag, and Au generally increases the sulfur tolerance ability on the surfaces of (111), (110) and (111) [23]. In addition, Malyi et al. examined sulfur poisoning phenomenon on Ni and metal (M)-doped Ni surfaces (M = Ag, Au, Al, Bi, Cd, Co, Cu, Fe, Sn, Sb, V, and Zn) using density functional theory (DFT) calculations. They reported that the interactions between the sulfur atom and metal surface are the weakest in Sb, Sn, and Bi-doped Ni, which can be useful information for the design of new SOFC anode materials [24]. Most theoretical studies, however, focused only on the adsorption of atomic sulfur, which is a product generated by the decomposition of sulfur compounds. Consequently, despite these studies, it is still insufficient to understand the dissociation mechanism of sulfur compounds in a variety of Ni-based alloys.

This study analyzed the H_2S decomposition mechanism in a range of Ni-based alloys to directly compare the degree of sulfur tolerance under a consistent theoretical scheme. Although sulfur compounds may exist in fuels in several forms, most are easily converted to H_2S in the reforming process due to its high stability under SOFC operating conditions [25,26]. Therefore, this study focused on the H_2S dissociation reaction to quantitatively assess the sulfur tolerance of catalysts. The mechanism of H_2S dissociation was investigated in pure Ni and 6 Ni-based bimetallic alloys (M/Ni, M = Cu, Rh, Pd, Ag, Pt, and Au). The dopant metals were selected by considering the thermodynamic data calculated by HSC Chemistry [27] and the tendency of dopant segregation in binary alloys, as described in detail later.

This paper is organized as follows. The computational modeling and simulation methods are introduced in the following section. Section 3 is divided into three specific parts. In Section 3.1, the ways to choose the candidate binary pairs are explained. The adsorption phenomena of H_2S, HS, S and H are discussed in Section 3.2. In Section 3.3, the dissociation mechanisms of H_2S and HS are examined. Furthermore, a potential anode material with a high sulfur tolerance is suggested based on the results.

2. Computational methods

All calculations were carried out using the Vienna *ab initio* simulation package (VASP) code [28–30]. The Perdew-Burke-Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA) was used to treat the exchange-correlation energies [31]. A conjugate gradient algorithm was applied to relax the geometries until the forces on all the unrestricted atoms were less than $0.03\,\mathrm{eV\,Å^{-1}}$. A plane wave expansion with a cutoff of 400 eV and spin-polarization were considered for all calculations. Dipole corrections were used to cancel out the artificial electrostatic field [32].

The surface segregation energy (E_{segr}) of a dopant metal was calculated to simply screen out the alloys that would have surface alloying effects on H_2S dissociation. Here, E_{segr} represents the tendency of a dopant to segregate towards the host surface, which was calculated by the total energy differences between the slabs with a dopant at the topmost layer and a dopant in the bottommost layer except for two fixed bottom layers, similar to a previous study [33]. By definition, a negative E_{segr} indicates that a dopant metal in the bulk phase would tend to segregate thermodynamically to the uppermost layer.

The H_2S dissociation reaction was evaluated in Ni and Ni-based alloy surfaces. The surface calculations were conducted using the (111) surface, which is thermodynamically the most stable. The slab was constructed by a (3 × 3) surface unit cell with five layers and a vacuum of 15 Å in the direction of the surface normal. The DFT-optimized lattice constant of bulk Ni was used to describe pure Ni and the bimetallic surfaces. Four adsorption sites were investigated in Ni(111), as shown in Fig. 1(a). To construct the Ni-based alloy surfaces, host (Ni) atoms at the topmost surface were replaced with solute atoms (Cu, Rh, Pd, Ag, Pt, and Au). The solute coverage of 1/3 ML was chosen as a representative of the surface alloy composition [34,35]. To determine the rational configuration of solute atoms, the thermodynamic stability of two surface patterns was considered. Fig. 1(b) and (c) show the most stable surface configurations of M/Ni(111) (M = Rh, Pd, Ag, Pt, and Au) and Cu/Ni(111) obtained from our previous DFT calculations, respectively [35]. Six types of adsorption sites in the bimetallic alloys are produced by alloying Rh, Pd, Ag, Pt, and Au into the Ni surface (Fig. 1(b)), while there are eleven types of adsorption sites in Cu/Ni (Fig. 1(c)). More detailed information on the modeling of Ni-based bimetallic alloy surfaces is included in our previous research [35]. All calculations were performed using a Monkhorst-Pack grid of 3 × 3 × 1 *k*-points [36].

To examine the mechanism of sulfur poisoning on the metal surface, the process of H_2S dissociation was assumed to occur in two sequential steps: (1) $H_2S^* \rightarrow HS^* + H$ and (2) $HS^* + H \rightarrow S^* + H^* + H^*$ [37]. The adsorption energy, E_{ads}, was calculated by

$$E_{ads} = E_{adsorbate+slab} - E_{slab} - E_{adsorbate}, \tag{1}$$

where $E_{adsorbate+slab}$ is the total energy of the metal surface containing the adsorbed species, E_{slab} is the total energy of the metal surface, and $E_{adsorbate}$ is the total energy for the adsorbate in the gas phase. The energy of the gas molecule was obtained in a large periodically repeated cubic box (approximately 20 Å in a side). In this study, E_{ads} of H and S and the d-band center (ε_d) were imported from our previous papers [35,38] for computational efficiency and consistency with the studies. The dispersion force were considered using a semi-empirical DFT-D2 method [39] in all calculations except for E_{segr} calculations. Although the dispersion correction was not necessarily required for this study, it was considered to match the simulation conditions with several data extracted from previous papers. Moreover, the effects of the dispersion force were not significant enough to alter the trends in E_{ads} [35]. 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 [40].

3. Results and discussion

3.1. Screening of candidate binary pairs

Before examining the H_2S dissociation mechanism, dopant metals were screened out by two criteria for the rational selection of candidate bimetallic alloys. As a first standard, the thermodynamic stability of the Ni-based alloys was investigated. Sasaki et al. examined the thermodynamic stability of 25 M/Ni alloys (M = 3d, 4d, and 5d transition metal) at 800 °C in H_2 gas containing 5% H_2O and 20 ppm H_2S using a thermochemical calculation program [27]. According to their results, 14 binary pairs shown in Table 1 are stable as metals, but the others are stable as metal oxides. In this study, the latter cases were excluded from the potential bimetallic alloys while we focused only on the former cases because a study of the decomposition reactions on metal oxide surfaces was beyond the scope of this work.

Next, the degree of surface segregation of dopant metals was assessed in the 14 pairs of bimetallic alloys. If a dopant metal stays in the bulk in the alloy systems, it may not have alloying effects on the surface reactions [41]. Table 1 shows that Fe, Co, Mo, Ru, W, Re, Os, and Ir energetically prefer the bulk site to the surface site