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Density functional theory study of the effects of alloying additions on sulfur adsorption on nickel surfaces

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ABSTRACT

Reactions of hydrogen sulfide (H_2S) with Nickel/Yttria-doped zirconia (Ni/YDZ) anode materials might cause degradation of the performance of solid oxide fuel cells when S containing fuels are used. In this paper, we employ density functional theory to investigate S adsorption on metal (M)-doped and undoped Ni(001) and Ni(111) surfaces. Based on the performed calculations, we analyze the effects of 12 alloying additions (Ag, Au, Al, Bi, Cd, Co, Cu, Fe, Sn, Sb, V, and Zn) on the temperature of transition between clean (S atoms do not adsorb on the surfaces) and contaminated (S atoms can adsorb on the surfaces spontaneously) M-doped Ni surfaces for different concentrations of H_2S in the fuel. Predicted results are consistent with many experimental studies relevant to S poisoning of both Ni/YDZ and M-doped Ni/YDZ anode materials. This study is important to understand S poisoning phenomena and to develop new S tolerant anode materials.

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1. Introduction

In modern surface science, a gas–surface interaction is one of the main fields of interest. This is because adsorption and dissociation processes are the main steps behind chemical reactions at a surface. Consequently, the knowledge in this field is the basis not only for understanding of complicated reactions but also for a prediction of device performance. For instance, interaction of sulfur (S) with nickel (Ni) surface has significant importance for modern anode materials of solid oxide fuel cells (SOFCs). So, at low concentrations of S impurity in fuel, S atoms might adsorb on Ni surfaces leading to a reduction of the area for catalytic reactions [1–5]. While at high S content, the impurity might induce formation of Ni–S compounds (Ni_3S_2 , Ni_7S_6 , and NiS) and, as a result, may reduce the catalytic activity of SOFC anode for hydrogen oxidation [1–6]. These reactions and the effects of S impurity on the properties of yttria-doped zirconia (YDZ) [7] and its interfaces with metals [8] determine degradation of SOFC performance (S poisoning) when S containing fuels are used. Herewith, since S atoms affect the ionic conductivity of zirconia only at high S partial pressures [7] and agglomeration of particles is usually a slow process, it becomes

apparent that the initial cell voltage drop of SOFC is caused by the Ni–S reactions.

It is well known that the rapid initial degradation of SOFC performance might be observed directly after switching from H_2 to S containing fuels. Herewith, it was shown that time needed for the S poisoning is almost independent of the impurity concentration, whereas degradation rate is sensitive not only to the concentration but also to the operating temperature [9]. For instance, it was found that under typical operating temperature (1073 K) the S poisoning can be observed at ppm levels of H_2S . However, increasing the operating temperature to 1250 K can provide stable SOFC performance under the same S partial pressure [10]. Later, Zha et al. summarized effects of operating temperature and S partial pressure on initial cell performance drop [11]. Thus, it was shown that the rapid initial degradation is reversible process, in other words, switching from S containing fuels to hydrogen fuel might induce recovering SOFC performance [5,10,11]. The recovering process can be protracted but the anode performance can be recovered to the initial state or some steady state (when long-term degradation takes place). In the most of reported studies the rapid initial degradation (for low concentrations (ppm levels) of S impurity) was explained by S adsorption on Ni surfaces. The fact is that experimental studies of S poisoning using in situ Raman spectroscopy at elevated temperatures ($\sim 500^\circ C$) in fuels with $P_{H_2S}/P_{H_2} = 100$ ppm showed that formation of both bulk or surface Ni–S compounds cannot be obtained under these conditions, while

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S adsorption is thermodynamically favorable [12]. Further studies of Liu's group confirmed the above observations [4,10,13,14]. It also should be noted that such approach was used as a basis for investigation of S poisoning of SOFC nickel anodes by a Temkin isotherm, which explained relation between S area coverage and loss of SOFC performance [15]. Therefore, during last decades, several experimental and theoretical studies of the interactions of H_2S , HS, and atomic S with metal surfaces have been reported [1,10,16–26]. These studies formed the basis for an initial thermodynamics model of the competitive adsorption of H_2 and H_2S on Ni surfaces [27], understanding of S poisoning of different materials, etc. Nevertheless, it is obvious that the design of new anode materials for SOFCs requires not only understanding of the process of S adsorption but also, more importantly, development of ways to control and avoid it. In the last couple years, the search of materials that can replace Ni in classical Ni/YDZ anode materials became important. Several works discussed the possibility of using Cu as alternative to Ni, since it has been shown that Cu has good carbon and S tolerances [24,28–30] as well as addition of CeO_2 to Cu/YDZ can significantly increase catalytic activity of the anode materials for hydrogen oxidation [29,31]. However, low thermal stability of the anode materials, caused by Cu sintering, is the key issue for Cu/ CeO_2 /YDZ systems [29]. Many researches were focused on the modifications of Ni/YDZ by different alloying additions [5,13,32–34]. For instance, it has been demonstrated that M (M = Cu, Sn, and Sb)–Ni/YDZ and M–Ni/ CeO_2 /YDZ anode materials have better carbon and S tolerances than Ni/YDZ [5,13,32,33]. Despite these studies, the understanding of the above experimental observations is weak and requires detailed theoretical analysis. Therefore, based on density functional theory (DFT), we investigate the effect of alloying additions on S adsorption on Ni surfaces. Through this study, we try to explain some experimental studies and even make suggestions for the design of new S tolerant anode materials.

2. Methodology

All calculations were carried out within the framework of the generalized gradient approximation (GGA) to DFT using the Plane-Wave Self-Consistent Field (PWSCF) computational code and the Perdew–Burke–Ernzerhof (PBE) [35] functional as implemented in the Quantum Espresso package [36]. The ultrasoft pseudopotentials [37] were used for a description of the electron–ion interactions (see Table S1). Before any geometry relaxation or property calculation, the converging tests were performed from which the plane-wave kinetic energy and charge density cutoffs were set as

40 Ry and 400 Ry, respectively. With the selected modeling parameters, the predicted lattice constant of bulk Ni (3.52 Å) agrees well with the experimental data (3.49 Å) [38]. Ni(111) and Ni(001) surfaces were modeled using a periodic slab with 5 atomic layers of Ni separated by a vacuum region (12 Å in this work). One single S atom, H_2 , and H_2S molecules were stored in a 20 Å cubic boxes as the reference states of S, H_2 , and H_2S , respectively. To avoid an image interaction between adsorbate and its periodic images a 4×4 surface supercell was used (sixteen metal atoms in each layer). It also should be noted that we performed spin-polarized calculations for all considered systems.

Based on the previously reported models for adsorption of single atoms on metal surfaces [16,18,19,21,24,27], calculations for the S adsorption were performed by placing the adsorbate at one of the high symmetry sites on the Ni surfaces (see Fig. 1, more details are given in our recent paper [24]). All atoms in the considered systems were relaxed by using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method until the maximum force on each atom was less than 0.01 eV/Å. It also should be noted that for investigation of adsorption on Ni surfaces we also considered possibility of a fixation of bottom surface layers; however, its effect was negligible for the considered surfaces. A $3 \times 3 \times 1$ Monkhorst–Pack k-point grid was used for the Brillouin zone integrations. The binding energy (E_{bind} , calculated from Eq. (1), in some papers it is also called adsorption energy) was chosen as a criterion for the study of S adsorption on M-doped and undoped Ni surfaces.

$$E_{\text{bind}} = E_{\text{adsorbate+slab}}^{\text{DFT}} - (E_{\text{adsorbate}}^{\text{DFT}} + E_{\text{slab}}^{\text{DFT}}) \quad (1)$$

where $E_{\text{adsorbate+slab}}^{\text{DFT}}$ and $E_{\text{slab}}^{\text{DFT}}$ refer to the total energies of the relaxed adsorbate–surface system and relaxed pure surface, respectively; $E_{\text{adsorbate}}^{\text{DFT}}$ refers to the total energy of gas phase adsorbate (S in this study). In our calculations we did not include zero point energy for calculations of the binding energy, since the effect of such correction is small [27] and therefore was neglected in the most of recent papers. The positive binding energy indicates that adsorption of gas phase (S in this study) is unfavorable, whereas negative E_{bind} suggests the possibility of adsorption of the adsorbate on a surface. It also should be noted that due to the reasons discussed in our recent paper [24] we have neglected the interactions between the adsorbate and its periodic images during calculations of binding energies.

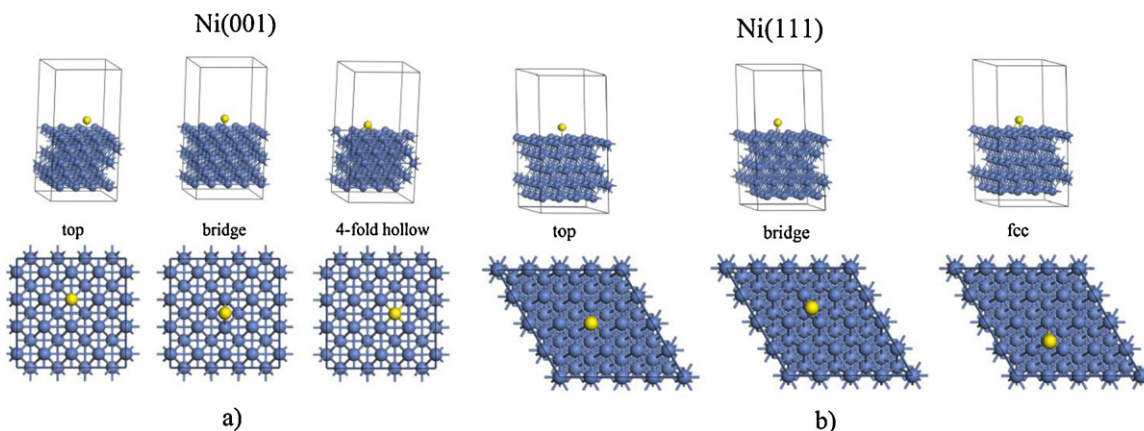


Fig. 1. Adsorption sites of atomic S on pure Ni(001) (a) and Ni(111) (b) surfaces. Ni atoms are blue circles, S atoms are yellow circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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