



# Resistance to sulfur poisoning of the gold doped nickel/yttria-stabilized zirconia with interface oxygen vacancy



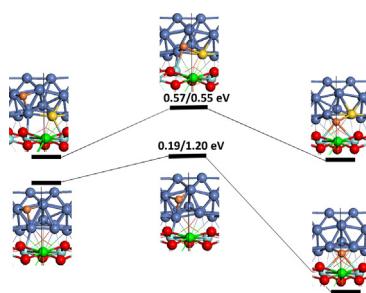
Yanxing Zhang, Zongxian Yang\*

College of Physics and Electronic Engineering, Henan Normal University, Xinxiang, Henan 453007, People's Republic of China

## HIGHLIGHTS

- Au dopant prefers to be at the neighbor of the oxygen vacancy site.
- The adsorption and diffusion properties of sulfur on the NiAu-d/YSZ-Ov are studied.
- NiAu-d/YSZ-Ov can weaken the sulfur adsorption at the interface oxygen vacancy.
- NiAu-d/YSZ-Ov can restrain the diffusion of sulfur to the interface oxygen vacancy.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The effects of IB metal (Gold, Silver, and Copper) dopants at the triple phase boundary (TPB) on the resistance to sulfur poisoning of the Nickel/Yttria-Stabilized Zirconia (YSZ) with interface oxygen vacancy (denoted as Ni/YSZ-Ov) are studied using the first-principles method based on density functional theory. Models with Au, Ag, Cu dopants at the TPB of Ni/YSZ-Ov are proposed. It is found that the Au dopant prefers to be at the neighbor of the oxygen vacancy site (denoted as NiAu-d/YSZ-Ov) while the Ag, Cu dopants tend to be located at the top Ni layer, which have little effects on the sulfur adsorption at the interface oxygen vacancy site. Compared with Ni/YSZ-Ov, the NiAu-d/YSZ-Ov can not only weaken the sulfur adsorption at the interface oxygen vacancy site, but also restrain the diffusion of sulfur to the interface oxygen vacancy. Instead, the adsorbed S at the oxygen vacancy is more easily to diffuse out of the interface oxygen vacancy site. So we propose that doping Au in Ni at the neighbor of the interface oxygen vacancy site would be good way to increase the resistance to sulfur poisoning of the Ni/YSZ-Ov anode.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are expected to be a crucial technology in the future power generation [1,2]. SOFCs offer many desirable advantages compared to other types of fuel cells and conversion devices due to their use of solid electrolytes, lack of

moving parts, ability to circumvent precious metal use, high efficiency, low pollution, and fuel flexibility.

The conventional anode for a SOFC is consisted of nickel and yttria-stabilized zirconia (YSZ) (denoted as Ni/YSZ). However, a major issue in the long-term stability and activity of the anode catalyst is its poor resistance toward poisonous compounds presented in the feed stream. Trace amounts of H<sub>2</sub>S presented in biomass generated syngas streams are enough to deactivate the catalyst [3,4], which is called sulfur poisoning. Many previous experimental studies indicate that sulfur poisoning behavior is

\* Corresponding author.

E-mail addresses: [zongxian.yang@163.com](mailto:zongxian.yang@163.com), [yzx@henannu.edu.cn](mailto:yzx@henannu.edu.cn), [yzx@htu.cn](mailto:yzx@htu.cn) (Z. Yang).

characterized by two stages (fast initial degradation and long term degradation) [4–10].

Liu et al. [7,11] showed that sulfur poisoning observed in the low concentration of  $\text{H}_2\text{S}$  at elevated temperatures is originated from the dissociation of sulfur-containing species and the adsorption of atomic sulfur on the anode surface. The adsorbed  $\text{H}_2\text{S}$  on Ni surfaces has been shown to dissociate above 300 K [12], with only S remaining on the surface. These studies clearly suggest that the elemental sulfur strongly adsorbs on the Ni surfaces with a small activation barrier ( $E_a$ ) and a large exothermic enthalpy ( $\Delta H$ ). The strongly adsorbed S species block the active sites on the anode surface and thus increase the resistance to electrochemical oxidation of the fuel. The calculations also suggest that the adsorbed sulfur species exist primarily in the form of atomic sulfur instead of molecular species, e.g.,  $\text{H}_2\text{S}$ . In fact, the faster or sluggish kinetics is related to the barriers of reactions. The very small  $E_a$  means that the barrier for  $\text{H}_2\text{S}$  dissociation is small, but the large exothermic  $\Delta H$  indicates that the barrier of the reverse reaction of the  $\text{H}_2\text{S}$  dissociation is large. The very small  $E_a$  and large exothermic  $\Delta H$  further imply fast kinetics for sulfur adsorption (as a result of  $\text{H}_2\text{S}$  dissociation) and sluggish kinetics for sulfur removal, which is consistent with the experimental observation of the instant drop in performance upon exposure to  $\text{H}_2\text{S}$  and a very slow recovery in performance after clean hydrogen is switched back. However, experimental results indicated that sulfur tolerance was in fact improved by using Ni/ $\text{Sc}_2\text{O}_3$  [8] or Ni/ $\text{Gd}_2\text{O}_3$ -doped  $\text{ZrO}_2$  [13] anodes, which suggest at least, that sulfur tolerance depends strongly on anode and electrolyte materials besides nickel itself. Zeng et al. [14] have studied the mechanisms governing the sulfur poisoning of the triple-phase boundary (TPB) of Ni/XSZ ( $\text{X}_2\text{O}_3$  stabilized zirconia) anodes using density functional theory. The calculated sulfur adsorption energies reveal a clear correlation between the size of the cation dopant  $\text{X}^{3+}$  and the sulfur tolerance of the Ni/XSZ anode. Malyi et al. [15] found that S addition to zirconia, either by doping or through gas diffusion, increases both the formation energy and migration barrier of the oxygen vacancies.

Since the fuel oxidation is believed to take place at the TPB made of Ni, YSZ and fuel gas, which would create oxygen vacancy at the Ni/YSZ interface. As known, the anode of SOFC is the Ni/YSZ composite, instead of the Ni itself. The ideal Ni (111) only represents the anode region beyond the TPB. Therefore, people should give special attention to the Ni/YSZ system and the effects of the interface O vacancy. In our recent work [16], we studied the sulfur poisoning at the TPB region of the Ni/YSZ. We found that the adsorbed sulfur does not favor to be located at the stoichiometric Ni/YSZ interface. With O vacancy at the Ni/YSZ interface, the adsorbed  $\text{S}^-$  diffuses to the Ni/YSZ interface and is oxidized to  $\text{S}^{2-}$  and trapped at the oxygen vacancy. The trapped sulfur is very difficult to be removed by the fuel (e.g.,  $\text{H}_2$ ) and therefore blocks the pathway for the oxygen ion transfer. As a result, the resistance for oxygen ion transfer would increase and the SOFC performance would drop. Trace amounts of sulfur would block the oxygen vacancy sites at the interface and induce the instant and significant drop in performance of SOFC. To alleviate the sulfur adsorption at the O vacancy site and/or enhance the diffusion of sulfur out of the interface oxygen vacancy site would help to enhance the resistance to sulfur poisoning at the oxygen vacancy site.

To improve the sulfur tolerance of SOFCs, alternative anode compositions have been proposed. Copper/ceria/zirconia [17] anodes were reported to be stable in fuel gases containing up to 450 ppm  $\text{H}_2\text{S}$ . Other anode compositions showing good sulfur tolerance include a lanthanum doped strontium titanate [18], Pd-impregnated titanate/cerate composition [19], lanthanum molybdate [20], gold/molybdenum disulfide [21], Ni/YSZ modified with niobia [22], and lanthanum vanadium oxide [23]. For

considerations including cost, processability, and stability, minor modifications to the widely used Ni/YSZ anode may be preferred to the more exotic compositions and forms.

In this work, we focus on the effects of IB metal (Au, Ag, Cu) dopants at the TPB of Ni/YSZ-Ov on the adsorption and the diffusion of sulfur at the interface O vacancy site. We propose that doping Au in Ni at the neighbor of the interface oxygen vacancy site would be good a way to enhance the resistance to sulfur poisoning of the Ni/YSZ-Ov anode.

## 2. Model and computation method

All calculations presented in this work are performed employing the periodic density functional theory (DFT) method implemented in the Vienna Ab-Initio Simulation Package (VASP) [24]. The exchange–correlation interactions are treated with the Perdew–Burke–Ernzerhof (PBE) functional [25]. Spin-polarized calculations are applied throughout. The electron-ion interactions are treated using the projector augmented wave (PAW) method. [26,27] The wave functions are expanded in plane waves with a cut off energy of 408 eV. The model of the Ni/YSZ cermet with the horizontal dimensions of  $12.56 \times 7.25 \text{ \AA}$  as that used in the Shishkin and Ziegler's work [28] is adopted as the substrate. A vacuum layer of 15  $\text{\AA}$  is used to separate the periodic images in the direction perpendicular to the surface. The model has been successfully used in our previous researches. [16,29,30] In the proposed structure, both Ni and YSZ face each other by the (111) crystallographic planes, with a small lattice mismatch of 3% in the direction with sustained translational symmetry. Experimentally, Abe et al. [31] and other researchers [32,33] fabricated and characterized the Ni/YSZ anode cermet, which has the structure with the (111) planes of the Ni part parallel to the (111) planes of YSZ. Using the transmission electron microscopy technique (TEM), the authors have shown a clear absence of amorphous phases at the interface with a (111)/(111) orientation relationship between Ni and YSZ. The Monkhorst-Pack [34]  $k$ -point mesh of  $2 \times 3 \times 1$  is used for the Brillouin zone (BZ) sampling. The atoms in the bottom multilayer are kept fixed for all calculations. Structural optimization of all systems is performed until the atomic forces drop below  $0.02 \text{ eV \AA}^{-1}$ . The climbing image nudged elastic band (CI-NEB) [35] method is employed to calculate the transition states and migration barriers. The adsorption energy of a sulfur atom is defined by.

$$E_{\text{ads}} = E_{\text{S}} + E_{\text{NiAu-d/YSZ-Ov or Ni/YSZ-Ov}} - E_{\text{S-NiAu-d/YSZ-Ov or S-Ni/YSZ-Ov}} \quad (1)$$

where  $E_{\text{S}}$  is the energy of a single S atom simulated in the  $8 \times 8 \times 8 \text{ \AA}$  box;  $E_{\text{S-NiAu-d/YSZ-Ov or S-Ni/YSZ-Ov}}$  and  $E_{\text{NiAu-d/YSZ-Ov or Ni/YSZ-Ov}}$  are the total energies of NiAu-d/YSZ-Ov or the Ni/YSZ-Ov with and without the S adsorbate, respectively. The  $3s^2 3p^4$  of S,  $2s^2 2p^4$  of O,  $3d^8 4s^2$  of Ni,  $5d^{10} 6s^1$  of Au,  $4d^{10} 5s^1$  of Ag,  $3d^{10} 4s^1$  of Cu,  $4d^2 5s^2$  of Zr and  $4s^2 4p^6 5s^2 4d^1$  of Y are treated as valence electrons in the DFT calculations. The Bader charge [36] analysis scheme is applied to determine the atomic charges and charge transfer. Pure GGA functionals underestimate the band gap and, as a consequence, may affect the other properties. This drawback can be remedied in higher levels of theory, e.g. the weighted density approximation (WDA), screened exchange (sX) [37], GW approximation [38], and hybrid functionals (HSE06, PBE0, B3LYP) [39,40], etc. However, these methods demand greater computational effort and are not always feasible for large models and extensive sampling. For this reason, in our work we apply the GGA approximation, which is known to give good energetics, and the qualitative description of the electronic structure. We try to use the

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