



The sulfur poisoning of the nickel/oxygen-enriched yttria-stabilized zirconia



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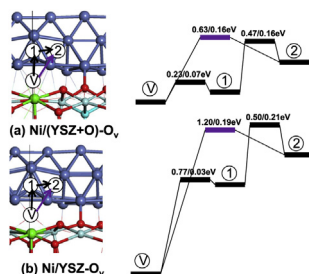
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HIGHLIGHTS

- The adsorption and diffusion properties of sulfur on the Ni/YSZ + O are studied.
- The adsorbed sulfur doesn't favor to be located at the Ni/YSZ + O interface.
- The extra O in YSZ weakens the S adsorption at the vacancy site of Ni/YSZ-O_v.
- The extra O in YSZ improves the diffusion of S out of the vacancy of Ni/YSZ-O_v.
- The Ni/YSZ + O can help to alleviate the sulfur poisoning as compared with the Ni/YSZ.

GRAPHICAL ABSTRACT



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ABSTRACT

The sulfur poisoning properties of the nickel/oxygen-enriched yttria-stabilized zirconia (denoted as Ni/YSZ + O) with or without the interface O vacancy are studied using the first-principles method based on density functional theory. The effects of the extra O atom at the subsurface vacancy of Ni/YSZ are focused. It is found that S at the Ni/YSZ + O can diffuse easily away from the interface oxygen to the top Ni layer sites. With the formation of O vacancy at the Ni/YSZ + O interface (denoted as Ni/(YSZ + O)-O_v), the adsorbed S prefers to diffuse back to the Ni/YSZ interface O vacancy. Compared with Ni/YSZ-O_v, the Ni/(YSZ + O)-O_v can effectively not only weaken the S adsorption at the interface O vacancy site, but also improve the diffusion of S out of the interface O vacancy. Therefore, the Ni/YSZ + O can help to alleviate the sulfur poisoning at the interface O vacancy site as compared with the Ni/YSZ.

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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, denoted as Ni/YSZ, is consisted of nickel and yttria-stabilized zirconia (YSZ). However, a major issue in the long-term stability and activity of the anode catalyst is its poor resistance toward poisonous compounds

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presented in the feed stream of fuels. Trace amounts of H₂S presented in biomass generated syngas streams are enough to deactivate the catalyst [3,4], which is called sulfur poisoning. Many previous experimental studies indicated that the S poisoning behavior is characterized by two stages, fast initial degradation and long term degradation [4–10].

Liu et al. [7,11] showed that S poisoning observed in the low concentration of H₂S at elevated temperatures is originated from the dissociation of sulfur-containing species and the adsorption of atomic sulfur on the anode surface. The adsorbed H₂S 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) of H₂S dissociation and a large exothermic enthalpy (ΔH). 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 [3] also suggest that the adsorbed sulfur species exist primarily in the form of atomic sulfur instead of molecular species, e.g., H₂S. In fact, the faster or sluggish kinetics is related to the barriers of reactions. The very small E_a means that the barrier for H₂S dissociation is small, but the large exothermic ΔH indicates that the barrier of the reverse reaction of the H₂S dissociation is large. The very small E_a and large exothermic ΔH further imply fast kinetics for sulfur adsorption (as a result of H₂S dissociation) and sluggish kinetics for sulfur removal, which is consistent with the experimental observation of the instant drop in performance upon exposure to H₂S 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/Sc₂O₃ [8] or Ni/Gd₂O₃-doped ZrO₂ [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 (X₂O₃ stabilized zirconia) anodes using density functional theory. The calculated sulfur adsorption energies reveal a clear correlation between the size of the cation dopant X³⁺ 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, oxygen vacancies may be created 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 S⁻ diffuses to the Ni/YSZ interface and is oxidized to S²⁻ and trapped at the oxygen vacancy. The trapped S is very difficult to be removed by the fuel (e.g., H₂) and therefore blocks the pathway for the O ion transfer. As a result, the resistance for O ion transfer would increase and the SOFC performance would drop. Trace amounts of S would block the O 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 S out of the interface oxygen vacancy site would help to enhance the resistance to S 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 H₂S. 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.

For maintaining charge neutrality of the YSZ system, the oxygen vacancies are created during the substitution of Zr⁴⁺ by Y³⁺ in the YSZ lattice. Under practical operating conditions of SOFCs, these O vacancies are mobile to give rise to oxygen ionic conductivity via vacancy diffusion mechanism, and can be filled by O²⁻ migrating through the crystal lattice of YSZ, to form an O-enriched YSZ surface, YSZ + O (111). The O²⁻ ions supplied to the intrinsic vacancy of YSZ originate from the electrochemical reaction of O₂ at an electrode, which depends on the actual SOFC fuel gas operation and polarization conditions in the anode polarization measurement [24–26]. It is found that the favored hydrogen oxidation reaction process on Ni/YSZ is water formation on an O atom at the interface and this is also the most facile hydrogen oxidation reaction process on Ni/(YSZ + O) [27].

In this work, we study the sulfur poisoning at the TPB region of the Ni/(YSZ + O) -O_v, focusing on the effects of the extra O atom at the subsurface vacancy of Ni/YSZ-O_v on the adsorption and the diffusion of S at the interface O vacancy site.

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) [28]. The exchange–correlation interactions are treated with the Perdew–Burke–Ernzerhof (PBE) functional [29]. Spin-polarized calculations are applied throughout. The electron–ion interactions are treated using the projector augmented wave (PAW) method [30,31]. 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 × 7.25 Å as that used in the Shishkin and Ziegler's work [32] is adopted as the substrate. The Ni/YSZ model with two intrinsic vacancies used in this work includes two building blocks of the 9% mol YSZ, which has 10 ZrO₂ and 1 Y₂O₃ and can be considered as an elementary building unit of YSZ with 9% mol concentration of yttria shown in Fig. 1(a). A vacuum layer of 15 Å is used to separate the periodic images in the direction perpendicular to the surface. The model has been successfully used in our previous researches [16,33–37]. 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. [38] and other researchers [39,40] 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 Monkforst-Pack [41] *k*-point mesh of 2 × 3 × 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 eV Å⁻¹. The climbing image nudged elastic band (CI-NEB) [42] method is

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