The origin of the low efficiency of carbon removal from the Nickel/Yttrium–Stabilized Zirconia triple-phase boundary by adsorbed water
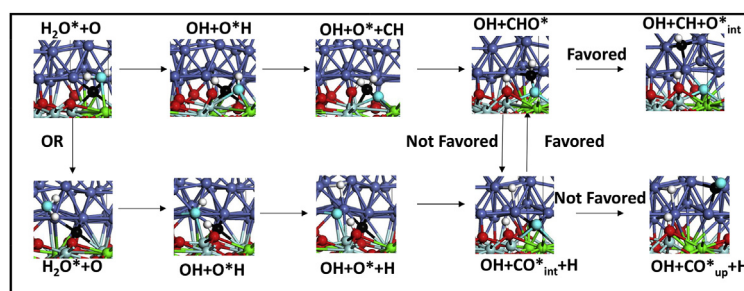
Yanxing Zhang, Zongxian Yang[*]

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

HIGHLIGHTS

- The dynamic picture of carbon removal by adsorbed water is presented.
- The adsorbed H_2O molecule can dissociate easily at the Ni/YSZ interface.
- H_2O molecule dissociates and reacts with carbon at the interface to form CHO species.
- CHO dissociates into CH + O easily at the interface.
- CH diffuses to the interface and dissociates to regenerate carbon.

GRAPHICAL ABSTRACT

ABSTRACT

Carbon removal from the anode triple-phase boundary (TPB) of solid oxide fuel cells (SOFCs) by adsorbed water molecule was studied using the density functional calculations, and a detailed dynamic picture was presented. It is found that the adsorbed H_2O molecule can dissociate easily at the Ni/YSZ interface and on the YSZ part compared with the Ni part and react with the interface carbon to form the CHO species. The dissociation process of CHO to CH and O is more favorable as compared with that of CHO to CO and H. The CH fragment can easily diffuse to the O vacancy formed in the dynamic reaction processes and dissociate into C and H, which regenerates carbon at the interface. This might be the main reasons for the low efficiency of carbon removal from the TPB of Ni/YSZ by adsorbed water.

© 2015 Elsevier B.V. All rights reserved.

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 the use of solid electrolytes, lack of moving parts, ability to circumvent precious metal use, high efficiency, low pollution, and fuel flexibility. The fuel flexibility [3–5] is achieved by the direct electrochemical oxidation of hydrocarbon fuels at the anode. The oxygen molecules are reduced in the cathode compartment and the oxygen ions are transported to the anode for fuel oxidation through the solid state electrolyte, which requires high operating temperatures (600–1000 °C). Unfortunately, the high operating temperatures of SOFC lead to a number of complications that can be detrimental for the cell performance. These include low anode stability to redox cycling, [6,7] adverse reactions between adjacent cell components, [8,9] and

* Corresponding author.
 E-mail address: yzx@henannu.edu.cn (Z. Yang).

temperature gradients in the cell parts occurring during the start-up and shut-down phase [10,11]. Moreover, the direct electro-chemical oxidation of hydrocarbon fuels in SOFCs is, in principle, possible, but has resulted in carbon deposition (coke formation) at elevated temperatures (most severely at T > 800 °C), which results in chemical deactivation of the anode [12]. The formation of coke over nickel-based catalysts during the partial oxidation or the steam and CO_2 reforming of methane or other hydrocarbons has been extensively investigated during the past decades [13—15]. Coke accumulation has been suggested to be a balance between the formation and the removal of coke which determines the degree of coking [16]. The growth of carbon on the nickel surface during a hydrocarbon reforming process has been explored experimentally in detail by Sehested [17]. Three types of carbon have been observed in a reformer: pyrolytic, encapsulating, and whisker car-bons. Ni catalyzes the formation of carbon deposition at the anode of SOFCs under reducing condition, [18,19] which would block the active sites and deactivate the Ni catalysts, ultimately destroy the catalyst completely [19—23].

In principle, the coke formation can be avoided thermodynami-cally through the introduction of a sufficient amount of steam or other oxygen-containing oxidant(s) into the fuel system. Sasaki and Teraoka [24] have studied the equilibrium diagrams of methane within the temperature range of 100—1000 °C. The temperature region associated with the carbon deposition became narrower when the steam was added into the system with steam-to-carbon (S/C) molar ratio of 1.0, whereas almost no solid carbon formed at an S/C ratio of 1.5. The Ni—YSZ cermet has been popularly used as the anode in most of the research and development of SOFCs. The reaction gas composed of high steam/carbon (S/C) ratios, typically over 2, was used to suppress carbon deposition; however, it is unattractive for fuel cells since steam dilution of the fuel lowers the conversion ef-ficiency. In fact, the efficiency of carbon removal by water is low [24—27], and coke resistance in the respective anodes is usually achieved at the expense of losing electrochemical activity, which emphasizes the need for the development of a coke-tolerant anode that does not suffer from loss of power generation. In this regard, the $Ni/BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$ anodes, studied by Yang et al., [27] fall into the category of anodes, characterized by a long operational time (>100 h), when using propane as a fuel, and high output power densities. The resistance to coke formation of these anodes heavily relies on supply of water (~ 3 vol % steam), indicating that adsorbed water molecules affect the removal of carbon from the anode triple phase boundary (TPB). For the $Ni/BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$, the small amount of water (~ 3 vol % steam) can help to entirely resistant the carbon formation, while ~ 3 vol % steam can not help to resistant the carbon deposition on the Ni/YSZ anode. In their more recent study, Yang et al. have proposed to cover the Ni surface of Ni/YSZ anode with BaO nanoislands, achieving a similar effect of carbon removal from the metal surface (hydrocarbon fuel was used in this case as well) when a small amount of water (~ 3 vol % steam) is added to the fuel feed [26]. The most likely pathway in SRM (steam reforming of Methane) on many transition metal surfaces was depicted by two steps: CHO species is formed through the direct reaction of adsorbed CH fragments with adsorbed O, which then dissociates to yield adsorbed H and CO [25—28]. Inderwildi et al. [26] also pointed out that, in the oxidation of hydrocarbons on Rh(111), the dissociation of CH into its components (C and H atoms) prior to oxidation can be neglected according to the DFT-based micro-kinetic simulations. And the main reaction pathway is that CH is oxidized to CHO, which subsequently dissociates to CO and H. Hecht et al. [27] reported experimental and modeling (by solving differ-ential—algebraic equations) investigations of thermal methane reforming chemistry within porous Ni—YSZ anode materials and got the same reaction mechanisms that CH is oxidized to CHO, which

subsequently dissociates to CO and H. Blaylock et al. [28] performed computational investigation of thermo-chemistry and kinetics of steam methane reforming on Ni(111) under realistic conditions and predicted that 56% of the total reaction flux was involved in the re-action of CHO formation by CH bonding to O and then the decom-position of CHO to CO and H. In our previous work [29], the processes of CH diffusion to the vacancy site at the Ni/YSZ interface and the dehydrogenation of CH at the vacancy site were studied. Therefore, the carbon deposition may form easily at the interface oxygen va-cancy of TPB as compared with that on the pure Ni (111) surface. Many key details still need to be clarified: (1) How doses the H_2O molecule dissociate and react with the C at the Ni/YSZ interface? (2) Does the CHO form in the reaction? (3) If the CHO forms, which is the preferred pathway for CHO dissociation, to CH and O or to CO and H?

In this work the adsorption and dissociation of H_2O at the TPB of Ni/YSZ with an interfacial carbon atom, denoted $Ni/YSZ-C_{int}$, are studied and the origin of the low efficiency of Carbon removal from the TPB by adsorbed water is proposed. It is found that the adsorbed H_2O molecule can dissociate at the Ni/YSZ interface and on the YSZ part with small barriers and react with the interface carbon to form the CHO species. The dissociation process of CHO to CH and O is more favorable as compared with that of CHO to CO and H.

2. Computational details

2.1. Computational 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 Per-dew—Burke—Ernzerhof (PBE) functional [29]. Spin-polarized cal-culations 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 Monkhorst-Pack 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 eV Å^{-1}. The climbing image nudged elastic band (CI-NEB) [32] method is employed to calculate the transition states and migration barriers. The adsorption energy of an atom or mo-lecular fragment (e.g. H_2O) is defined by

$$E_{ads} = E_{H2O} + E_{Ni/YSZ-Cint} - E_{H2O-Ni/YSZ-Cint} \qquad (1)$$

where E_{H2O} is the energy of a single H_2O simulated in a $8 \times 8 \times 8$ Å box; $E_{Ni/YSZ-Cint}$ and $E_{H2O-Ni/YSZ-Cint}$ are the total energies of Ni/YSZ-C_{int} with and without the H_2O adsorbate, respectively. The $1s^2$ of H, $2s^2 2p^2$ of C, $2s^2 2p^4$ of O, $3d^8 4s^2$ of Ni, $4s^2 4p^6 5s^2 4d^2$ of Zr and $4s^2 4p^6 5s^2 4d^1$ of Y are treated as valence electrons in the DFT cal-culations. The Bader charge [33] 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) [34], GW approximation [35], and hybride functionals (HSE06, PBE0, B3LYP) [36,37], 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 international system of units (SI) in this paper. However, we keep some of the popular units used in the micro world and give their equivalent in SI for clarity,