Molecular dynamics simulations of the coke formation progress on the nickel-based anode of solid oxide fuel cells

Haibin Lu, Dong Hua, Taosif Iqabl, Xiongwen Zhang*, Guojun Li, Di Zhang

MOE Key Laboratory of Thermo-Fluid Science and Engineering, School of Energy & Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

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ABSTRACT

Coke formation on anode of solid oxide fuel cells (SOFC) can lead to SOFC performance degradation or even failure. This paper investigates transfer mechanism of carbon atoms in coke formation process on nickel-based anode using the reactive force field molecular dynamics simulation (ReaxFF-MD). The simulation results show that the transfer processes of carbon atoms in methane reforming are composed of three stages, and the alkyl makes formation of coke easier on the surface of Ni(100). The driving force of the carbon atoms diffusion into Ni (100) changes from the carbon concentration difference to the chemical potential difference, which leads to the generation of a new phase of carbon and the structural damage of the SOFC anode. The structural changes of Ni (100) during the carbon atom transport and precipitation are simulated and analyzed to reveal the chemical reaction mechanisms of coke formation, and provide theoretical foundation for optimal design in materials and operating parameters of SOFC anode.

1. Introduction

Solid oxide fuel cell is a high-temperature fuel cell (600 °C–1000 °C) with high efficiency and low emission advantages. A high operating temperature poses risk of coke formation in the catalytic reforming of hydrocarbon fuels (e.g. methane, propane and butane, etc.). Coke formation on anode can make nickel electrochemically oxidized [1]. It can also destroy the topological structure of the triple-phase-boundary (TPB) in the anode, which leads to performance degradation of SOFC and makes SOFC stack efficiency very low [2]. The key factor is to understand the issue of carbon deposition by investigating the mechanism of carbon precipitation and transport.

Current research on inhibiting coke formation mainly attaches great importance to the controls of the operating conditions and gas compositions of fuel. For example, by introducing a quantity of oxygen into hydrocarbon fuel was proved to be helpful in removing the coke [3]. Many researches also illustrated operating at higher steam to carbon ratios (S/C) can inhibit the formation of coke [4,5]. A Control-oriented Dynamic Model Adapted to Variant Steam-to-carbon Ratios for an SOFC with Exhaust Fuel Recirculation. The core concept with the aforementioned methods is to enhance the responsive reaction by diluting carbon concentration in the fuels. Choudhary and his collaborators [6,7] constructed a three-dimensional transient model, using CFD and FEM methods to study the air ratio and temperature field impact to carbon deposition.

In the recent years, researchers began to use molecular dynamics (MD) simulation method to study the process of hydrocarbons cracking into carbon clusters with nickel catalyst. Nielson and his partners used ReaxFF-MD to study the process of amorphous carbon converting to carbon nanotubes and other substance with nickel catalysis under certain conditions [8]. Using the retrained force field parameters, Somers et al. [9–11] studied the mechanism of carbon formation from hydrocarbon plasma catalyzed by different types of nickel. Their study results reveal CH₃· has high adsorption rate on all kinds of nickel surface. Different types of nickel in the process of reaction have different reactivity like the adsorption rate of free radical on Ni(100) is higher than that of Ni(111) [9–11]. Lu et al. studied the catalytic dehydrogenation reaction mechanism of aromatic compounds on Ni(111) surface in the chemical vapor deposition reactor [12]. Merinov et al. developed force field parameters to simulate ions transport and chemical reactions on the triple-phase interface (TPB) [13]. This study established the basis of nickel-based catalytic reactions, including the reaction of carbon with relevant elements, coke formation and the formation process of carbon clusters.

Accordingly, to study SOFC coke formation, the transition process of carbon atom from carbon compounds to carbon clusters should be investigated. It contains the processes of the catalytic cracking of hydrocarbon, carbon atoms diffusion in nickel and carbon atom gathering into clusters. Considering that the internal reforming of hydrocarbon fuel in SOFC is usually at high temperature and the reforming reaction

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rate is too fast to measure, it is difficult to obtain the detail thermal reforming reaction by experiments. For example, Fan et al. [16] studied the carbon deposition process of methane on Ni-YSZ surface by means of experimental thermodynamics simulation and numerical simulation. However, the physical damage of anode cannot be discussed deeply because of the limitation of the research method [14]. Molecular dynamics simulation is an effective method to study the mechanism of coke formation process. Compared to the traditional molecular dynamic simulations, ReaxFF-MD takes molecular bond order into account in the simulations. Therefore, it can reveal the course of the chemical bond breaking and formation in the chemical reaction. Meanwhile, as the computational cost of ReaxFF-MD is inexpensive, it can be used to calculate larger time scale than that of quantum chemistry and primary molecular dynamics calculation while get the same precision as quantum chemistry [15]. Therefore, ReaxFF-MD was widely used in the complex chemical reactions, such as the rapid reaction of explosions, the thermal cracking and combustion, the catalytic reactions under extreme conditions, and the structural transformation of state aggregation [16]. Merinov et al. [17] modeled chemical reactions, diffusion, and other physicochemical processes at the fuel/Ni/YSZ interface by simulating amorphization of the Ni surface, partial decohesion (delamination) at the interface, and coke forming. The products obtained by ReaxFF MD properly describes complex physicochemical processes, such as the oxide-ion diffusion, fuel conversion, water formation reaction, coking, and delamination, occurring at the TPB.

Duin et al. [18,19] applied the ReaxFF to describe the proton diffusion in crystalline and across grain boundaries of BYZ. Their research results validated the use of ReaxFF to study transport properties of the membranes. They also validated it for fuel cell applications to predict the oxygen ion diffusion coefficient in yattria-stabilized zirconia as a function of temperature. It was proved the usefulness of ReaxFF to model the transport of oxygen ions through the YSZ electrolyte for SOFC.

In this paper, we utilize the ReaxFF-MD to develop the model of chemical reaction to investigate the precipitation and diffusion process of carbon atoms on Ni(100). By examining the carbon atoms migration process, tracing the structural evolutions, we were able to investigate the mechanism of the occurrence and growth of coke on the anode. The simulation results are in agreement with the experimental results and provide theoretical support for the improvement in operating parameters of SOFC anode.

2. Simulation methodology

2.1. Models construction

Three Ni(100) models so-called Model-1, 2, and 3 with 125 nickel atoms are defined for the simulations. A vacuum layer filled by hydrocarbon molecules was built on the surface of Ni(100). Different types and numbers of hydrocarbon molecules in the vacuum layer are simulated to investigate the influence of hydrocarbon molecule structures on the coke formation. Therein, Model-1 contains 54 methane molecules surrounding Ni(100) models (see Fig. 1a). Model-2 includes 30 methane molecules and 24 methanol molecules (see Fig. 1b) and model-3 contains 30 methane molecules and 12 ethanol molecules (see Fig. 1c). In the case study of Model-1, the hydrogen generated from the chemical reactions are removed after 250 ps of simulation, thus avoiding the hydrogen interference to the carbon cluster forming process and therefore being able to reveal the mechanism of the carbon cluster formation [20]. Additionally, another model (Model-4) containing 400 nickel atoms of Ni(100) with 200 methane molecules is defined to show the details of the carbon atoms diffusion progress in Ni (100).
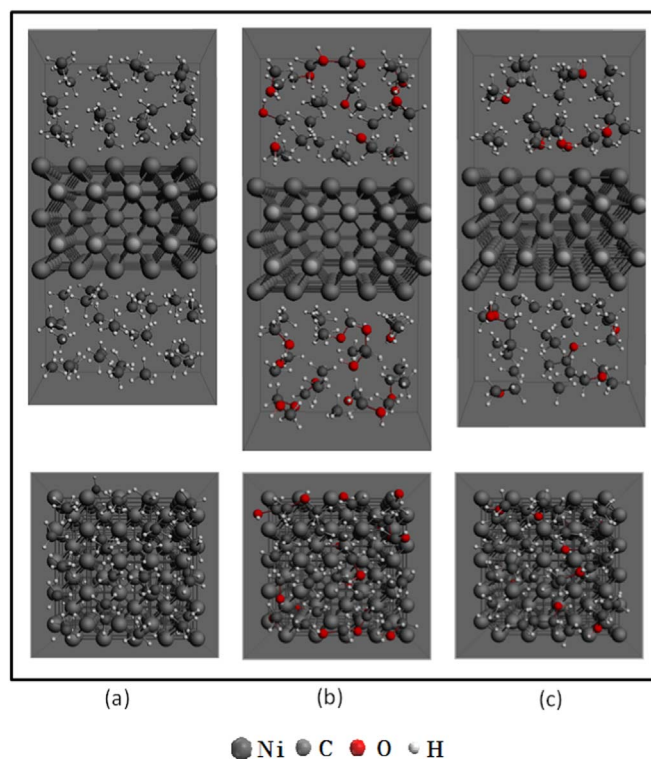

Fig. 1. The side view and top view of (a) Model-1, (b) Model-2, (c) Model-3.

2.2. Simulation details of ReaxFF MD

ReaxFF-MD considers the system energy composed of various partial energy contributions, such as bond angle, dihedral angle, conjugate, Coulomb, van der Waals and adjustments. They are similar to empirical nonreactive force fields (Eq. (1)). ReaxFF-MD takes bond order as the core, and transforms the chemical bonds ($BO_{ij}\delta$, $BO_{ij}\pi$, $BO_{ij}\pi\pi$) as function of r_{ij} (Eq. (2)) [15]. According to the bond orders of any two atoms in the simulation progress, ReaxFF-MD determines the connectivity between atoms and simulates the bond formation and cleavage of chemical reactions. The molecule structures are modified on the basis of the atomic valence change, interatomic bonding method, conjugate and non-conjugate structure change, intermolecular forces and nonbonding effort. The model of ReaxFF-MD is a close simulation to the real situation.

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{triple}$$
$$+ E_{tors} + E_{conj} + E_{H-bond} + E_{vdw} + E_{coulomb} \tag{1}$$

$$BO'_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} = \exp\left[p_{bo1}\cdot\left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{bo2}}\right] + \exp\left[p_{bo3}\cdot\left(\frac{r_{ij}}{r_o^{\pi}}\right)^{p_{bo4}}\right]$$
$$+ \exp\left[p_{bo5}\cdot\left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo5}}\right] \tag{2}$$

A ReaxFF program package referred to [15,21] is used to conduct the ReaxFF-MD simulations in this work. The sets of the ReaxFF force field parameters for hydrocarbon were taken from the study of Merinov et al. [13]. This study focuses on the methane catalytic decomposition mechanism in the high temperature. According to the reaction thermodynamics can promote methane reforming in the positive direction if the temperature is increased but Sørensen's work of temperature accelerating kinetics based on harmonic transitional state theory demonstrate higher temperature can accelerate coke formation without a accuracy. Qualitatively, the mechanism of coke formation does not change with the increase of simulation temperature. Thus, we set the