Journal of Power Sources 254 (2014) 209–217

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Coarse-grained molecular dynamics investigation of nanostructures and thermal properties of porous anode for solid oxide fuel cell

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HIGHLIGHTS

- An AA-CG-MD method is developed to simulate the fabrication process of the porous anode of SOFC.
- This method is employed to reconstruct the microstructure of the porous anode vividly.
- Relevant thermal properties are calculated in a rapid and accurate manner on the basis of the method.
- Analyses and predictions are proceeded to capture the good performance for the porous anode of SOFC.

ARTICLE INFO

Article history:
Received 29 July 2013
Received in revised form
16 December 2013
Accepted 17 December 2013
Available online 4 January 2014

Keywords:
Ni/YSZ cermet
AA-CG-MD method
LAMMPS
Thermal properties
Solid oxide fuel cell

ABSTRACT

Incorporation of nanoscale catalysts into porous structures of SOFC has been proven highly successful in increasing active sites and catalyst utilization. In addition, electrochemical reactions as well as heat transfer process in porous anode are strongly affected by complex porous structures. It is believed that study of anode thermal properties are critical for SOFC design and operation. In this work, an AA model is developed for nickel and YSZ components via ASE, and a CG technique is further applied to represent Ni and YSZ beads by VMD, which are then self-assembled to capture the anode nanostructure via GROMACS. LAMMPS is then employed to evaluate average thermal properties of the porous anode. It is found that, at low Ni content (≤30 vol%), thermal conductivity increases with increasing temperature due to lattice vibrations. Instead, the anode exhibits metallic behavior due to rich nickel phase. Thermal expansion of the anode increases with increasing nickel content. Average thermal properties of the anode are validated by open literature data with good agreement. This approach is considered to be applied to analyze nanostructures, heat transfer and temperature distribution in the porous anode, and is also useful to capture thermal performance of SOFC and stack.

1. Introduction

Solid oxide fuel cell (SOFC) is an attracting energy-converting device due to its high energy efficiency [1,2] and fuel flexibility [3,4], as well as low pollutant emissions [5]. SOFC employs multi-layered electrodes which comprise ceramic and metallic materials with different thermal properties. All components, e.g., anode, cathode, electrolyte, etc., have to provide a well-adjusted heat diffusion, thermal expansion, mechanical strength and so on, both at material interfaces and inside materials. The performance of SOFC is not only determined by intrinsic material properties, but also subject to the fabrication technology of functional layers. Basically, that can be improved by the application of modified materials using appropriate technologies. It is well known that the higher operating temperatures in SOFC improve its performance in comparison with low-temperature fuel cells, e.g., PEMFC, DMFC, PAFC, etc. In addition, high operating temperatures make it feasible to carry out electrochemical reactions in the active sites of the porous anode with cheap catalysts. On the other hand, the internal reforming reactions of hydrocarbon fuels, e.g., methane, are contributing to keep a good balance of heat generation and consumption. Heat is mainly produced in the exothermically electrochemical reactions. However, it is noticed that too much cooling caused by the endothermic steam reforming reactions has a negative effect on the output performance of SOFC [6], which is remarkably opposed to desired thermal management in the porous anode for SOFC. Thus, studying heat transfer in order to effectively

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http://dx.doi.org/10.1016/j.jpowsour.2013.12.079

enhance the thermal management inside the porous anode has been attracting significant attention in the recent years. This means that to correctly predict the thermal properties of the porous anode of SOFC is important in developing high-performance SOFCs.

In order to generate high power density and achieve reaction-related efficiency as high as possible, abundant triple-phase boundaries (TPBs) [7,8], where the electrochemical reactions take place, should be available in the porous electrodes. This explicitly represents a principle that to sinter high porosity in the functional anode seems extremely important for the extensive distribution of so-called TPBs. Unfortunately, for the well-dispersed porous anode from nanoscale particles, e.g., Ni and yttria-stabilized zirconia (YSZ) [9,10], etc., significant reduction of the thermal conductivity is expected due to discontinuities inside mediated materials, which is described adequately by effective medium theory (EMT) [11]. The mechanical strength of the porous anode is also prone to be lowered to a certain extent. It is thus extremely important to keep a good balance among high porosity, considerable thermal diffusion and acceptable mechanical strength in the porous anode of SOFC. In addition, high temperature gradients will easily take place along and normal to the direction of fuel flow due to mass diffusion or concentration drop of the fuel gas. This will be mainly attributed to the unreasonable cooling effect due to the high supply rate of the air flow in the cathode. It is found that a sharp temperature gradient or thermal stress is primarily responsible for cracking in the porous anode, even in the electrolyte. The temperature gradient or the thermal stress accounted for by heat transfer inside the SOFC can be computed numerically but really depends on specific heat capacity as well as heat flow rate and thermal conductivity (TC), etc.

In this work, an all-atom coarse-grained molecular dynamics (also named AA-CG-MD) method is employed. In brief, a target domain with cubic 50 nm (typically limited by GROMACS, the code used to reconstruct the nanostructures of the porous anode, especially the TPB region) will be implemented from the ab initio stage, e.g., atoms, molecules, lattices, etc. The box will be filled with beads, also named “pseudo atoms”, representing groups of atoms/molecules to be computed in the MD approach. The model may be developed for the reforming and electrochemical reactions, mass and charge transfer, and heat diffusion. The predicted material properties in this study based on the open literature data [12–16] are linked to the compositions and nanostructures of the materials. Some basic principles govern the choices of SOFC materials. For example, the electrodes should have high electrical conductivity for the charge transport, high catalytic activity for the involved reforming and electrochemical reactions, adequate porosity for the gas/vapor diffusion, good physical/chemical compatibility with the electrolyte and interconnect for the long-term stability.

As experimental measurements tend to be more costly and difficult to carry out compared with the simulation work, which is speedy and relatively easy once the model is programmed and validated, their ability to investigate the effects of different material parameters and operating conditions on the performance of SOFC is critically limited. Numerical modeling and simulations incorporating the known physical and chemical phenomena occurring inside SOFC to predict its performance are quite important for the understanding and technological improvement of SOFC. Though there is no shortage of research on the numerical modeling for SOFC, the analysis focusing on the effects of nanostructures in the porous anode on thermal properties is relatively rare in the open literature. Therefore, it seems that such a research effort is quite essential for improving the performance of SOFC. In this case, the thermal properties, electrochemical performance and their interplay are supposed to be taken into account to properly extract the best performance for SOFC to practical applications. This work describes a detailed nanoscale model for the numerical simulations in the porous anode of SOFC with a representative Ni/YSZ–YSZ–LSM/YSZ setup [17,18]. The thermal properties of the porous anode are determined and evaluated against the open literature data [19–22]. Anodic nanostructure, as well as effects of Ni contents, and sintering conditions of the anode on its thermal properties are systematically investigated. Finally, the desired material compositions and anodic nanostructures are deduced.

2. Modeling development

In this study, the AA-CG-MD approach is firstly implemented to reconstruct microscopic structures for the porous anodes at the nanoscale, and the obtained structures are further applied to calculate thermal properties of the porous anodes, e.g., average TC, thermal expansion coefficient (TEC), volumetric heat capacity (VHC), etc. The size effect on TC is also evaluated. These contribute to further predict the probability of thermal failure and evaluate the overall performance of the porous anode of SOFC [23–25] by the MD modeling [26]. The precise details of the method are presented in the following three steps.

2.1. All-atom modeling

In classical MD modeling, a single potential energy surface is represented in the force-field, which is a consequence of Born–Oppenheimer (BO) approximation [27,28]. Therefore, it is possible to compute the wave-function and the energy of an atom/molecule in finite and less complicated steps.

$$\Psi_{\text{total}} = \chi_{\text{electronic}} \times \phi_{\text{nuclear}} \tag{1}$$

where Ψ referring to Equation (1), allows the wave-function of an atom/molecule to be broken into its electronic and nuclear components.

In excited states, when electrochemical reactions or a more accurate representation are needed, electronic behavior can be obtained from first principles [29] by using a quantum mechanical method, such as Density Functional Theory (DFT) [9,20]. This is known as the AA modeling [30]. Due to treating electronic degrees of freedom, the computational cost of this method is much higher than classical MD, which implies that the AA modeling is limited to smaller systems and shorter periods of time. In general, this modeling is usually made in the close neighborhood of the atom/molecule-based systems. Although various approximations may be used, these are based on theoretical considerations instead of empirical fitting. The AA calculations generate a huge amount of information that is not available from empirical methods, such as density of electronic states or other electronic properties. A significant advantage of using the AA modeling is the ability to study nanostructures, even interactions that involve breaking or formation of covalent bonds, which correspond to multiple electronic states and potential energy. In this study, the AA modeling is mainly applied to generate the nanocrystals for sintering powders at the atom-scale, i.e., Ni and YSZ particles. The face-centered cubic (FCC) nickel nanocrystals are generated according to the AA modeling, and partially stabilized tetragonal YSZ nanocrystals are also produced very well by the same technique, and then both of them compose the so-called “green body” (GB) [31] for sintering the porous anodes. Although no open literature data supports that the crystalline nanostructure shows higher oxygen-ion conductivity than the amorphous nanostructure in the porous anode, extensive research work has been focused on this over the past decades. It has been found that the crystalline nanostructure is more stable energetically compared to the amorphous nanostructure in the porous