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Enhancement of ion conductivity for doped electrolytes in SOFC by MD modeling

Hsin-Yi Lai, Yen-Hsin Chan, Cha'o-Kuang Chen *

Department of Mechanical Engineering, National Cheng Kung University, No. 1, University Road, Tainan City 701, Taiwan, ROC

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ABSTRACT

The objective of this paper is to search for new electrolyte materials with high conductivity to work in a middle working temperature range between 673 K and 1073 K for SOFC in order to lower down industrials manufacturing cost (Tucker, 2010). Since Yttria-stabilized zirconia (YSZ) is known as an electrolyte material for Solid Oxide Fuel Cell (SOFC) at high temperature and is relatively low in the middle temperature range, in view of the circumstance, there is a need to search for new electrolyte materials for doping to enhance the Oxygen Ion Conductivity (OIC). In this study Molecular Dynamics (MD) simulation is employed as a tool to search for great doped electrolytes that can enhance the OIC for higher performance numerically. Several new findings are obtained and reported in the context that can be used as standards to be concurrently used for YSZ electrolytes efficiency enhancement. By employing different dopants in combination of Fe_2O_3, ZnO, MgO, CuO and BaO with YSZ to enhance the ion conductivity of YSZ electrolytes for the middle as well as full-range working temperature for the SOFC. Subsequently, this study is able to conclude with some suitable dopants of Fe_2O_3 with 8YSZ in the middle working temperature range, which the best OIC is also pointed out.

1. Introduction

Solid Oxide Fuel Cell (SOFC) is one of the most promising energy research topics. Both high power efficiency and least generation of greenhouse gases are characteristics of SOFC. SOFC needs to be operated in a temperature range above 1273 K for better power efficiency and high flexibility of sensitive fuel selection. The search for SOFC of lowing operating temperature and enhancing both operating life and stability [2] are of great importance in recent years. In view of needs to enhance the power efficiency, this research is focused on the improvement of Oxygen Ion Conductivity (OIC) in a working temperature range between 673 and 1073 K. In an attempt to enhance the performance of SOFC at middle temperature range, it is important to investigate the behavior of oxygen ions in SOFC electrolyte. Yttria-stabilized zirconia (YSZ) is one of the most commonly-used materials for SOFC's electrolyte. However, YSZ needs to be operated at temperatures above 1273 K to attain high OIC, and the cost is well-defined by the large amount of zirconia used in oxygen sensors [1]. In this research, molecular dynamics (MD) simulation is employed to examine the OIC at different working temperatures. By using MD simulation, the cost of experiments can be minimized and various physical properties not easily observed in practical experiments [3] can be estimated.

In this study, a molecular model is constructed that allows both the Oxygen Diffusion Coefficient (ODC) and Oxygen Ion Conductivity (OIC) of the SOFC electrolytes are separately estimated. Following the MD models implemented in the context, some satisfactory outcomes are achieved. The results are compared with data given in literatures to validate the feasibility of our modeling strategy. The behavior of 8YSZ (i.e. YSZ doped with8%Y_2O_3 with ZrO_2) for different dopants is also characterized to realize the change of OIC in the doped electrolyte for the SOFC.

Brinkman et al. [4] estimated the electrolyte's ODC at both 1759 K and 2057 K by using MD simulation and computing the Mean Square Displacement (MSD), the essential parameter for the estimation of ODC. The research team proved that the result of electrolyte's ODC obtained by MD simulation matched well with that of the experiment.

In order to further explore the change of electrolyte's OIC for different working temperature and doping ratio, several research teams [5–7] have paid attention to the subject in different aspects. Tarancón et al. [5] compared the ion conductivity of two different electrolyte materials (YSZ and Gadolinium-Doped Ceria, CGO) for working temperatures between 1159 K and 1959 K. The team

* Corresponding author.
E-mail address: ckchen@mail.ncku.edu.tw (C.-K. Chen).

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reported that oxygen vacancy generation and arrangement of oxygen vacancy are obviously influenced by employing different doping ratios and lattice arrangements. Chang et al. [6] reported molecular simulation results indicating that the increase of Y_2O_3 concentration in YSZ can successfully increase oxygen vacancy. However, both freedom of ion and mobility of oxygen vacancy are decreased. Huang et al. [7] indicated that ion conductivity is indeed significantly influenced by both grain boundaries and temperature, and an Y_2O_3 doping ratio of 8% yields the best Mean Square Displacement (MSD) for the YSZ. Razmkhah et al. [8] studied the diversification of SOFC's OIC by using molecular dynamic simulation and treating the working temperature and doping atom as variable parameters. The research team reported that the oxygen activation energy is significantly affected by using different dopants and working temperature, and also as working temperature lower than 1000 K, the ion conductivity of 8YSZ is relatively low.

In order to select the electrolyte materials that present high OIC, several research teams that worked on characterization of OIC for different electrolyte materials. Razmkhah et al. [9] studied the effect of OIC by using different electrolyte materials ($Nd_{2-x}Gd_xZr_2O_7$) and doping ratios (x = 0.8, 1.0 and 1.2) for a working temperature range between 1273 K and 1873 K. Several other research groups that were also working on estimation of OIC using different materials. Liu and Lao [10] have reported that by doping few ZnO into YSZ both oxygen activation energy and oxygen vacancy can be changed to increase the ion conductivity. Gao et al. [11] have successfully doped Fe atom (2% and 4%) into 8YSZ and proved that doping Fe atom into 8YSZ can improve cell performance by measuring I-V curve. Khan et al. [12] have doped CaO, Y_2O_3, Gd_2O_3, and Sc_2O_3 into ZrO_2, and observed the electrolyte's OIC.

Based upon the investigation reported above, the employment of molecular dynamics (MD) modeling for SOFC study has emerged as a trend for researchers in recent years. However, most of the reported research have relied on the use of Born-Meyer-Buckingham (BMB) potential for simulation, several parameters in which must be obtain experimentally. Furthermore, the BMB potential is not suitable for use in solving problems on scales at which quantum effects are significant.

For this study, the Reactive Force Field (ReaxFF) model proposed by Duin et al. [13] is adopted as the potential energy for MD modeling. ReaxFF performs simulations on scales between traditional molecular dynamics and quantum mechanics, and allows for more accurate simulation of the interaction between electrons. Furthermore, ReaxFF provides a means to enable such long-term MD on the large-scale complex systems relevant to YSZ.

Based upon the results presented above, different doping concentration that alter the amount of oxygen vacancy so as to influence the performance of OIC. Since different working temperatures can effectively affect the motion of oxygen ions in SOFC electrolyte. The focus of this study is placed upon the characterization of OIC in SOFC electrolytes at medium working temperature range of 673–1073 K, rather than the high working temperature range above 1000 K commonly considered now for most research teams.

Based upon the literature present above, dopants can change the concentration of oxygen vacancy, because of different type for valence bond. In this study, the dopants with double-valence bond and triple-valence bond, BaO, CuO, ZnO, MgO and Fe_2O_3, are doped into 8YSZ, and investigate the characteristics of ODC and OIC in different conditions. By estimating the result of ODC and OIC, the influence of oxygen vacancy and activation energy to electrolytes is discussed in depth at working temperature ranging from 673 K to 1073 K.

2. Modeling methodology

Molecular Dynamics (MD) is a modeling technique based upon Newton's theory. The main objective is to calculate the trajectory of atoms on a molecular scale, and study physical properties by analyzing the gross behavior [3].

2.1. Potential function

A function commonly selected for MD simulations modeling SOFC electrolytes is the Born-Meyer-Buckingham (BMB) potential [14], which can be described as

$$u(r_{ij}) = A\exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6} \tag{1}$$

where r_{ij} is the distance between atoms i and j, and A, ρ, and C are potential parameters specific to each ion pair. Based upon literature above, BMB potential does not adequately describe phenomena at quantum level. The Reactive Force Field (ReaxFF) [15,16] is more suitable for this purpose, and is therefore adopted in this study. Here, the function of ReaxFF is given as

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{tors} + E_{H-bond} + E_{vdWaals} + E_{Coulomb} \tag{2}$$

where E_{bond} is the energy associated with bonds, E_{lp} is the energy associated with lone pair, E_{over} and E_{under} are the energies that are associated with overcoordination and undercoordination, E_{val}, and E_{coa} are the energies associated with valence and conjugation, E_{pen} is the energy penalties that can be used to correct the bond order, E_{C2} is the energy that is associated with the correction of erroneous prediction to a strong triple bond in C_2, $E_{vdWaals}$ is the energy that is associated with van der Waals interactions, $E_{H\text{-}bond}$ is the energy that is associated with hydrogen bonding, E_{tors} is the energy that is associated with torsional angles, and $E_{Coulomb}$ is the energy that is associated with Coulomb interactions.

2.2. Mean square displacement

The atom's motion with time is well described by the Mean Square Displacement, and it is also the basic property for the calculation of Diffusion Coefficient and Ion Conductivity. Here, the Mean Square Displacement (MSD) is defined as

$$MSD = \sum N_i[r_i(t) - r_i(0)]^2/N \tag{3}$$

where N_i stands for the number of atoms, $r_i(t)$ is the position of atom i, and t stands for time.

2.3. Diffusion coefficient

The MSD data can then be used to estimate the atoms' diffusion in terms of Diffusion Coefficient. By using Eq. (3) to plot MSD versus time, one can easily compute the coefficient of diffusion [17] to give

$$MSD = 6Dt + B \tag{4}$$

$$D = \lim_{t\to\infty}\frac{MSD(t)}{6t} \tag{5}$$

where D is the diffusion coefficient and B is a constant.

2.4. Ion conductivity

Based upon the derivation and diffusion coefficient presented above, the ion transport capacity of the electrolyte can now be esti-