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Analysis of the Effects of Temperature and Doping on the Oxygen Ion and Proton Conduction of SOFC Electrolyte BZY

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Keywords: Solid Oxide Fuel Cell (SOFC); Molecular dynamic (MD); Diffusion coefficient (DC);

ABSTRACT

This article uses molecular simulation to investigate the effects of doping and temperature on the diffusion coefficients of oxygen ions and proton in the electrolyte of solid oxide fuel cells. By comparing different doping ratios and operating temperatures, it is found that for the intermediate temperature electrolyte BZY, doping with 13.6% Y provides the best proton and oxygen ion diffusion coefficients. In addition to affecting the transport capabilities of the electrolyte, the doping ratio also affects how temperature influences the diffusion ability of the electrolyte.

INTRODUCTION

Hydrogen energy is one of the clean energy which has been believed that could an important role for zero carbon environment in the future. Therefore, the efficiency of fuel cell system and the fabrication cost are two of the most problem that make hydrogen energy could not be commercialized. In order to solve the problem, increasing the performance of fuel cell would be the main issue for researcher in recent years.

In order to increasing the efficiency of fuel cell, using the high temperature fuel cell system to be the power generation system is one of the methods. Solid Oxide Fuel Cell (SOFC) has the highest idea efficiency in power generation and also the flexibility of fuel utilization (Seymour et al. 2012). However, traditional SOFC should be operate at high working temperatures (T>1073 K) for high power generation, the materials used are required to be stable with a suitable thermal expansion coefficient (TEC) in the associated high temperature environment (Ullmann et al. 2000). These requirements consequently limit the development of SOFC in the selection of inexpensive stable materials.

Yttria-stabilized zirconia (YSZ) is the electrolyte materials which has been used usually in SOFC system, however, YSZ needs to be operated in high temperature (above 1073K) for high oxygen ion conductivity. So as to improve the above shortcomings, finding the different electrolyte materials to decrease the manufacturing cost and increase the oxygen ion conductivity in medium temperature zone (573–1073K) would be studied in this research.

As mentioned above, the development direction of SOFC in recent years and its importance for future hydrogen energy are known. However, due to issues with the lifespan of SOFC and system costs, which are still not widely used for hydrogen production, storage, and power generation. Therefore, this project would explore the key factors affecting cell performance through various analysis and experimental techniques, with the expectation that its results could provide reference for future industry evaluations of power system performance and lifespan.

To investigate the differences in conductivity of SOFC at different temperatures, this project plans to use molecular simulation to evaluate the electrolyte and cathode materials of SOFC, with the main goal of exploring the key factors affecting single cell performance. Based on the work of Brinkman et al. (1995), who used molecular simulation to establish a SOFC electrolyte model and calculated the diffusion coefficients of oxygen ions at 1759 K and 2057 K through the mean square displacement (MSD) of oxygen ions, this team believes that molecular simulation could accurately predict the diffusion coefficients of materials and the results could be directly applied to evaluate the characteristics of SOFC materials. In addition to the establishment of the SOFC electrolyte model through molecular simulation by the aforementioned scholars and teams, this team has also evaluated the oxygen ion conductivity of

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SOFC electrolyte under different doping effects (Chan et al., 2018). According to the results of molecular simulation, the doping of different Fe_2O_3 in 8YSZ would affect the oxygen ion conductivity, and the performance at different doping ratios and operating temperatures is also different.

Based on the previous literature, it is known that using molecular simulation could effectively predict the performance of SOFC electrolyte materials. On the other hand, in recent years, scholars from various countries have conducted performance evaluations on mid-temperature SOFC using BZY (Y-doped $BaZrO_3$). The main reason is that BZY could transmit both oxygen ions and hydrogen ions simultaneously at intermediate temperatures, thereby improving the conductivity of the electrolyte and enhancing the cell performance. However, although BZY exhibits good hydrogen proton conductivity at intermediate temperatures, few teams have evaluated and verified the optimal doping ratio, and BZY requires a sintering temperature exceeding 1400℃. Therefore, how to reduce the sintering temperature through doping and maintain the material's electrochemical stability is the development goal of various countries in recent years.

The aforementioned literature mainly emphasizes the importance of the electrolyte in SOFC. However, the energy changes of gas adsorption and desorption in cathode materials also need to be considered. Scholars P. Priya and N.R. Aluru (Pikee Priya et al., 2021.) calculated the energy transfer and adsorption/desorption energy changes of hydrogen protons of SOEC. In order to calculate for different energy levels, they established molecular models of electrolytes and cathode/anode, such as BZY and Pt/AG. The scholars believe that molecular models are helpful in predicting material performance and could be in line with performance curves in experiments. Furthermore, the arrangement of materials is a crucial factor affecting the cell's transport properties. According to the conclusion of the literature, in addition to the electrolyte conductivity, the catalytic reaction in both poles is also an important factor. Therefore, this project would focus on the cathode part, establishing a molecular model of gas adsorption/ desorption to observe the changes in gas adsorption/ desorption energy under different operating conditions.

In this study, molecular dynamics would be used and its theory would be described in subsequent chapters. However, as described in the literature review, most researchers currently refer to the molecular model and atomic potential parameters proposed by the Brinkman et al. (1995) when simulating SOFC electrolytes. However, the parameters of the Buckingham Potential used by this team must be adjusted based on empirical values obtained from actual experiments. Therefore, under different doping conditions, the atomic potential parameters must be considered. In addition, the potential field could not consider the quantum mechanics of the system and is computationally intensive. Therefore, in this study, the ReaxFF would be used for molecular simulations of SOFC electrolytes based on the research results of the A.C.T.V. Duin (Senftle et al., 2016.). The research results of this team have shown that the ReaxFF could be used for molecular simulations of YSZ and is in the range between quantum mechanics and traditional molecular dynamics. Additionally, the Merinov et al. (2014.) applied the ReaxFF force field to the Ni/YSZ anode end of SOFC, and their research showed that the ReaxFF could simulate the oxygen ion transport phenomenon in the three-phase boundary layer between the anode end and the electrolyte. By comparing the literature mentioned above, this study aims to investigate the impact of doping and temperature effects on the diffusion coefficients of hydrogen protons and oxygen ions in BZY. Additionally, we would compare the changes in electrolyte performance caused by different effects to identify the key factors that affect performance.

Modeling Methodology

The primary aim of using Molecular Dynamics (MD) modeling, which is based on Newton's theory, is to calculate the trajectory of atomic motion in a molecular scale and analyze the physical properties associated with the collective behavior of atoms. Following the approach presented in Gale et al. (1997.), this study focuses on characterizing the mechanism of oxygen ion transport in SOFC. This is achieved by analyzing the motion trajectory and velocity field of atoms in each time step using the potential function (Li and Hafskjold, 1995)) of Reactive Force Field (BMB). The material properties are subsequently evaluated using the statistical thermodynamics method (Haile, 1997.).

Potential Function

Choosing the correct potential function is crucial for accurately simulating the motion between different atoms. In this paper, the Reactive Force Field (ReaxFF) potential function (Senftle et al., 2016.) is used to characterize the oxygen ion transport mechanism in SOFC. To estimate the material properties, the method of statistical thermodynamics is applied. It should be noted that selecting a suitable force field for simulating materials requires careful consideration. Typically, the Born-Meyer-Buckingham (BMB) potential (Lewis and Catlow, 1985) is used to describe the potential of SOFC electrolytes in molecular dynamics simulations, which is expressed by the following equation:

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

where r_{ij} is distance between the atoms i and j and A,

ρ, and C are potential parameters specific to each ion pair.

Many scientists have employed the Born-Meyer-Buckingham (BMB) potential to simulate SOFC electrolytes. However, this force field couldnot accurately describe quantum mechanical motion. To achieve a smooth simulation, the Reactive Force Field (ReaxFF) (Senftle et al., 2016; Duin, 2008.) would be used in this project. The ReaxFF potential is capable of incorporating both force field and quantum mechanics, making it a more suitable choice for simulation. The ReaxFF potential is described by the following equation:

$$\begin{aligned} E_{system} &= E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} \\ &+ E_{pen} + E_{coa} + E_{C2} + E_{tors} + E_{H-bond} \\ &+ E_{vdWaals} + E_{Coulomb} \end{aligned} \quad (2)$$

where E_{bond} is energy related bound, E_{lp} is energy related lone pair, E_{over} and E_{under} are the energies related to overcoordination and undercoordinatio, E_{val}, and E_{coa} are the energies related to valence and conjugation, E_{pen} is the energy penalties that used to enforce the correct bond order, E_{C2} is the energy related to the correction of erroneously predicting a strong triple bond in C2, $E_{vdWaals}$ is the energy related to van der Waals interactions, $E_{H\text{-}bond}$ is the energy related to hydrogen bonding, E_{tors} is the energy related to torsion angles, $E_{Coulomb}$ is the energy related to Coulomb interactions.

Mean Square Displacement (MSD)

The initial and crucial step in the Molecular Dynamic (MD) modeling process for SOFC is to determine the atomic motion trajectory within the system's electrolyte. This trajectory could be quantified by the Mean Square Displacement (MSD), which is defined as follows:

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

where N_i stands for the number of atoms, $r_i(t)$ is the position of atom i, and t stands for time.
During the MD simulation process, the Mean Square Displacement (MSD) curves of different electrolytes would be calculated and compared under various conditions. By analyzing these MSD curves, the motion trajectories of atoms under different conditions could be estimated and characterized.

Diffusion Coefficient (DC)

To estimate the essential capability of the electrolyte, the diffusion coefficient (DC) would be analyzed. The DC estimation would provide insight into the transmission ability of oxygen ions within the SOFC electrolyte. To obtain the DC, the relationship between the diffusion coefficient and MSD needs to be established, which could be expressed as follows:

$$MSD = 6Dt + B \quad (4)$$

where D is the oxygen diffusion coefficient, t is simulation time, B is a constant. Moreover, Equation (3) could be rewritten as the time approach infinity, and the equation of DC (K. Suzuki et al., 1998.) could be described as

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

To ensure consistency and completeness in the MD simulation process, the following assumptions would be adopted: (1) the General Utility Lattice Program (GULP) (Gale, 1997) would be used for the entire process, (2) a 5 x 5 x 5 supercell would be used as the molecular model, (3) the N.V.T. ensemble would be employed to maintain a fixed system during the simulation, (4) the Reactive Force Field (ReaxFF) potential model would be used with associated parameters given in Table 1, (5) the simulation time for each case would be set to 200 ps, (6) the time step for the simulation would be 0.5 fs, (7) three different doping ratios of BZY would be studied to characterize the mechanism and chemical reaction of the ODC in the electrolyte. The molecular modeling structure is depicted in Fig. 1.

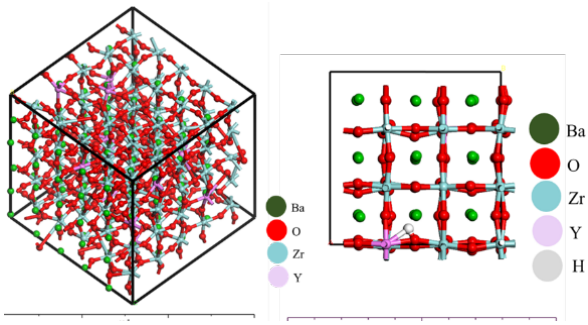

Figure 1. The molecular model of BZY

Results and discussion

This study used the previously introduced molecular dynamics method and used BZY as the electrolyte material for SOFC to discuss the effects of doping and temperature on the oxygen and hydrogen ion mobility of BZY. Finally, this study would also explore the effects of different doping materials and doping ratios on the diffusion coefficients of BZY oxygen ions and hydrogen protons. At the beginning of the study, calculations would be performed according to the simulation conditions mentioned earlier for undoped BZY. The results are shown in Figure 2. By comparing with previous literature (Bansal, 2009.), it could be seen that the DC calculated using the ReaxFF could match the literature. This result shows that the ReaxFF could indeed be used for BYZ research. In addition, through Figure 2, it could be found that when the ambient temperature increases, the amplitude of DC also increases. This result shows that temperature effects do affect diffusion coefficients, and the higher the temperature, the greater the impact.

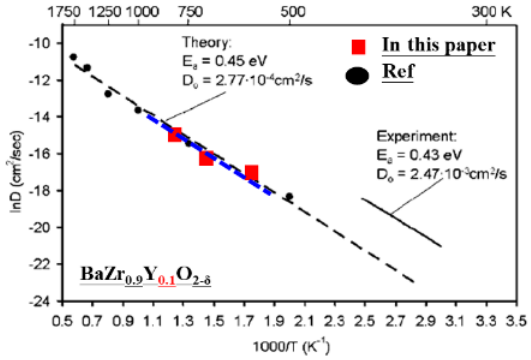

Figure 2. Comparing the diffusion coefficient of BZY between previous work and this paper

Influence of the doping effect of on the Proton Mobility Capability for Hydrogen

From Figure 2, it could be concluded that the DC of BZY increases with increasing temperature, and the feasibility of the ReaxFF is also confirmed. Therefore, in this stage, the effect of doping ratio on the MSD of hydrogen protons in BZY would be compared, and the results are shown in Figure 3. From Figures 3 and 4, it could be seen that doping 10%-16% Y at 773K would significouldtly change the size of MSD. This also indicates that doping could indeed change the proton transport capacity of the electrolyte. In addition, from Figure 3, it could be seen that at an operating temperature of 773K, the electrolyte doped with 13.6% Y in BZY has the highest MSD, indicating that the electrolyte has the best oxygen ion transport capacity at this moment. It is speculated here that although doping could increase oxygen vacouldcies and affect the bonding force between electrolytes, the overall transport capacity may decrease when doping exceeds a certain proportion. This conclusion is consistent with the discussion results of previous literature on traditional 8YSZ, which indicates that when doping new materials, the doping ratio must be considered to obtain the best electrolyte transport performance.

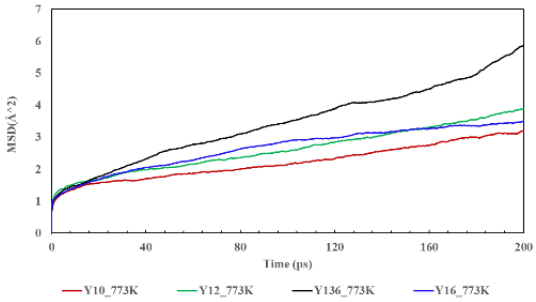

Figure 3. Comparing the Hydrogen MSD with different doping ratio of Y

Analysis of the temperature effect for MSD between hydrogen protons and oxygen ions in BZY.

Although the previous study has investigated the effect of doping on the MSD of BZY at 773K, further exploration is needed to accurately compare the transport capabilities of electrolytes. As previously mentioned, BZY could transport both oxygen ions and hydrogen protons. In order to compare the effect of temperature on the performance of BZY, this study would explore the effect of temperature on the movement ability of hydrogen protons and oxygen ions in Y-doped BZY at the optimal doping ratio of 13.6%. The overall results are shown in Figures 4 and 5.

Observing Figure 4, it could be seen that when the operating temperature is 973K and the time is 200ps, the maximum MSD of hydrogen protons is 12.89 Å^2, while at 573K, the MSD is 2.78. This result indicates that the displacement ability of hydrogen protons increases by 4.64 times when the operating temperature is increased from 573K to 973K.

On the other hand, Figure 5 shows the movement ability of oxygen ions in BZY at temperatures ranging from 573K to 973K. From the MSD results in Figure 5, it could be seen that when the operating temperature is 973K, the MSD is 2.56 Å^2, while at 573K, the MSD is only 0.63 Å2. This indicates that the displacement ability of oxygen ions increases by 4.06 times when the operating temperature is increased from 573K to 973K.

By comparing the MSD changes of oxygen ions and hydrogen protons at different operating temperatures, it could be concluded that the operating temperature is an important parameter for both oxygen ions and hydrogen protons. However, the effect of temperature on hydrogen protons is more significouldt, and it could be found through MSD comparison that when hydrogen protons are used as the main transport method for SOFCs, their transport capability is faster than that of oxygen ions.

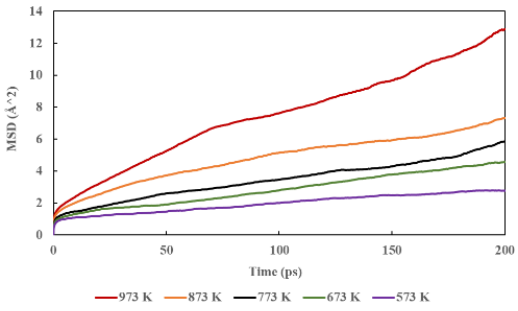

Figure 4. Comparing the Hydrogen MSD with different working temperature

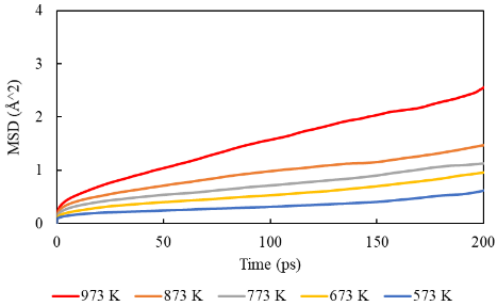

Figure 5. Comparing the Oxygen MSD with different working temperature

Analysis of the doping effect for diffusion coefficient in BZY.

The diffusion coefficient is an indicator of the electrolyte's transport ability, and its main purpose is to observe the transport characteristics of the electrolyte. Therefore, it is more convincing in analysis than the MSD discussed earlier. In this study, in order to compare the transport abilities of hydrogen protons and oxygen ions, as well as the effects of doping and temperature, the relevant results are shown in Figure 6. Through formula 5 and Figure 6, it could be seen that when BZY is used as the primary mode of transport for hydrogen protons, it has the highest DC value. On the other hand, under the optimal doping ratio, when the operating temperature is increased from 573K to 773K, the diffusion coefficient of hydrogen protons increases from the original 3.25 (10^{-7} cm^2/s) to 4.48 (10^{-7} cm^2/s), an increase of 1.38 times. On the other hand, when using oxygen ions as the mode of transport, increasing the operating temperature from 573K to 773K, the diffusion ability of oxygen ions increases from 0.43 (10^{-7} cm^2/s) to 0.68 (10^{-7} cm^2/s), an increase of approximately 1.58 times. By comparing the diffusion coefficients of hydrogen protons and oxygen ions, it could be seen that temperature does affect the diffusion ability of electrolytes. However, the diffusion ability of hydrogen protons is 6.59 times higher than that of oxygen ions, indicating that using hydrogen protons as the mode of transport for electrolytes gives the SOFC the best operating performance.

On the other hand, it could be seen from Figure 6 that doping has a direct impact on the DC value of hydrogen protons. Moreover, the doping ratio would change the effect of temperature on the electrolyte diffusion coefficient. For example, when the doping ratio reaches 16%, the diffusion coefficient increases by only 1.7 times from 573K to 773K. When the doping ratio is 10%, the diffusion coefficient increases by 8.47 times, indicating that doping not only affects the diffusion coefficient's ability but also affects the influence of temperature on the electrolyte's diffusion ability.

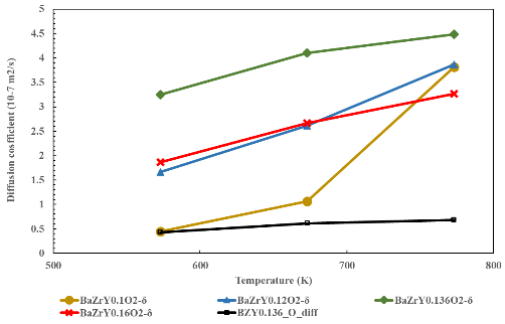

Figure 6. Comparing the diffusion coefficient of BZY with temperature effect and doping effect

Analysis of the doping materials for MSD in BZY.

As explained above, doping materials could alter the oxygen vacouldcies and proton displacement ability of electrolytes. However, the effects of different doping materials on the electrolyte vary. According to previous studies, the atomic size of the dopant is a key factor affecting MSD. In order to enhance the oxygen ion MSD of the material, this study evaluated the effect of doping materials on the oxygen ion transport ability of BZY by doping with two different oxides, Mg2O3 and Fe2O3. The results are shown in Figure 7. It could be seen from Figure 7 that when the operating temperature is 673K, doping with Mg2O3 and Fe2O3 does not significouldtly change the oxygen ion MSD in BZY. However, the doping ratio in this study was only 10%, and future studies could explore the effects of different doping materials and ratios. On the other hand, this study mainly focuses on enhancing the transport ability of oxygen ions and exploring the doping effect on diffusion ability under different doping materials for hydrogen ions could be considered in the future.

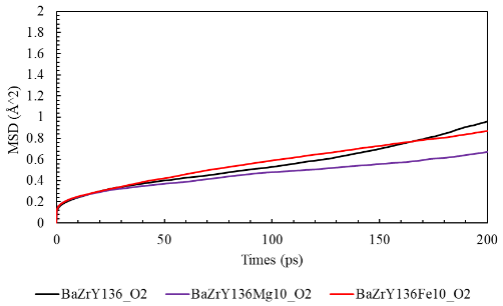

Figure 7. Comparing the Oxygen MSD with doping materials

Conclusion

Through the simulation results mentioned above, it could be clearly observed that temperature and doping effects both affect the transport properties of BZY. Furthermore, by comparing the effects of different doping ratios and operating temperatures, the following conclusions could be drawn:

1. Using BZY as the substrate for SOFC electrolytes, a doping ratio of 13.6% for Y could get highest hydrogen proton transport ability in the intermediate temperature range.
2. By comparing the temperature effects, it could be found that when the temperature rises from 573K to 973K, the MSD of hydrogen protons increases by 4.64 times and the MSD of oxygen ions increases by 4.06 times, indicating that temperature effects could simultaneously affect the transport abilities of hydrogen protons and oxygen ions.
3. By comparing the diffusion coefficients, it is known that the doping ratio affects the diffusion coefficients of hydrogen protons and oxygen ions in the BZY electrolyte, and also affects the temperature effects on the electrolyte diffusion ability. When the temperature rises from 573K to

773K, the hydrogen proton diffusion coefficient of BZY increases by 1.38 times.

4. Finally, it is known that doping different materials would affect the MSD of oxygen ions in the electrolyte. However, not every doping material could effectively enhance the transport properties of the electrolyte, and the doping ratio and operating temperature must be considered in the doping process to obtain the optimal doping coefficient.

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溫度效應與摻雜效應對於 SOFC 電解質 BZY 之氧離子傳導與氫質子傳導影響分析

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摘 要

本文以分子模擬法的方式，探討摻雜效應與溫度效應對於固態氧化物燃料電池中電解質之氧離子擴散與氫質子擴散係數的影響。藉由比較不同摻雜比例與操作溫度後發現，對於中溫型電解質BZY而言，13.6%的Y摻雜於BZY之中可以擁有最佳的氫質子與氧離子擴散係數，另外，摻雜比例除了影響電解質的傳輸能力外，亦會影響溫度效應對於電解質擴散能力的改變。