The temperature and oxygen vacancy effects on the diffusion coefficient and ionic conductivity in ferroelectric BaTiO$_3$ nanowires; A molecular dynamics study

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ABSTRACT

In this work, the influence of oxygen vacancy defects on ionic conductivity and oxygen diffusion in BaTiO$_3$ (BTO) nanowires (NWs) was investigated for different temperatures ranging from 700 K to 1000 K by molecular dynamics simulation method. The BTO NWs with cubic structure and axial directions of [001] and [110] were considered for simulation. The oxygen vacancies ranging from 0 to 4% were created by random deletion of oxygen atoms from perfect BTO NWs. The results show that ionic conductivity and diffusion constant of oxygen atoms in individual BTO NWs are at least ten times higher than those of single crystalline BTO and they enhance by increasing the oxygen vacancy percentage. The pre-exponential factor of oxygen diffusion coefficient and also oxygen activation energy of NWs were evaluated from linear least square fits to Arrhenius plots. Results also show that the activation energy of oxygen atoms reduces with increasing the oxygen vacancy percentage. The Arrhenius plots show a critical point about 850 K which at this point the slop of the fitted lines to Arrhenius plots shows a sudden change.

1. Introduction

Depletion of fossil fuels, air pollution and also global warming brought about focusing on advanced methods of generation, conversion and storage of energy. Solid oxide fuel cells (SOFCs) are one of the most promising energy sources which are extremely considered due to their advantages such as high power density, low pollution and high efficiency. Despite these advantages, high operating temperature is one of the main problems of these systems which cause technological complications and economic obstacles. For this reason a great deal of research has been done on how to decrease the temperature of solid oxide fuel cells [1–3].

Among the power storage devices, the lithium ion batteries (LIBs) are wildly used in the last decade and many attempts have been made to improve efficiency of these batteries [4–6] especially at low temparature. However, reduction of ionic conductivity in low temperature often limits the performances of Li-ion batteries and also solid oxide fuel cells. Therefore many efforts have been made to create materials with higher ionic conductivity. A particular enhancement in ionic conductivity of nanostructured materials which is known as "nanoionics" is highly investigated for several applications, such as improving the efficiency of Lithium-ion batteries and lowering operating temperature of solid oxide fuel cells [7–10].

Perovskites with the chemical formula of ABO$_3$ are one of the vital key materials used in the above mentioned technologies. In the recent years, nanostructured perovskites have attracted great interest because of their special physical and chemical characteristics such as electrical, piezoelectric, mechanical, sensing and magnetic properties compared with the bulk materials [11–15].

Barium Titanate (BTO) is a famous perovskite which is used in modern electroceramics and electronic, such as nanogenerateres [16], microactuators [17], positive temperature coefficient resistors [18], multi-layer capacitors dielectric memories [19], ferroelectric memories [20] and etc.

This is also considered for employing in SOFC [21] and lithium ion batteries [22]. The catalytic properties of BTO as anode material for SOFC's were investigated by Rivera et al. [23] through DFT method. Their results show that adsorption of H atoms on the TiO$_2$-terminated surface of BTO is more stable than BaO-terminated surface. Jian-Hui et al. [21] used BTO as anode materials for H$_2$S-containing CH$_4$ fueled and they revealed that the BTO based fuel cell has better electrochemical performance, higher resistance to carbon deposition and is

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very stable during long time operations in comparison with $SrTiO_3$ and $La_2Ti_2O_7$ fuel cells. Teranishi et al. [22] showed that coating of $LiCoO_2$, particles with BTO layers considerably increases the performance of $LiCoO_2$ Lithium-ion batteries.

In the past decade, a great deal of research efforts is performed on significant behaviors and the fundamental properties resulting from oxygen vacancies in nanostructures. The response to structural imbalances and deformation toward oxygen vacancy in nanoscale systems, such as nanobelts (NBs) and nanofilms is considerable [24]. The vacancies have a prominent effect on electrical and mechanical properties especially on the transport of charge carriers. The oxygen vacancy as a general defect in BTO and related materials controls mass transport and other physical and chemical properties in permeation membranes and solid oxide fuel cell cathodes. Lian-Xing et al. [25], and Choi et al. [26] demonstrated that point defects change the ionic conductivity and thermodynamic quantities of undoped $BaTiO_{3-x}$. Recently Ching et al. [27] synthesized a new type of oxygen-deficient $BaTiO_{3-x}$ by using sol–gel method which acts as an efficient bifunctional oxygen electrocatalyst. Given the above mentioned facts, $BaTiO_{3-x}$ is a promising material which can be used in storage and reversible electrochemical energy conversion technologies such as regenerated fuel cells and metal–air batteries.

In previous study, we investigated influence of oxygen vacancies on electromechanical properties of individual $BaTiO_3$ nanowires [28], now in this work the influence of oxygen vacancy defects, temperature and crystallographic orientation on ionic conductivity and oxygen diffusion constant of BTO NWs is investigated by using a molecular dynamics method. The maximum limit of 4% vacancy fraction is assumed here, since there is still no common view of the exact limit of the vacancy fraction in the BTO structures. Up to our knowledge, although many studied have been performed on ionic conductivity of bulk oxygen-deficient BTO but no study is conducted regarding this matter at nanoscale. The scientific novelty of the work consists of considering the motion of oxygen vacancies in the nanowire $BaTiO_3$ with respect to the confined geometry (a wire instead of the isotropic bulk medium). The application of results is relevant not only due to the possibility of the application of the studied process in development of solid oxide fuel cells and energy conversion systems, but also in development of advanced nanoelectronics components.

2. Simulation method

Molecular dynamics method is employed to study oxygen vacancy effects in BTO NWs, which is based on the interatomic potential and periodic boundary conditions in z direction. It is assumed that the BTO samples have some random oxygen vacancies. The choice of potential function is an important option, which determinates accuracy of the calculation in MD simulation.

In the present study, the shell model [29,30], which phenomenologically characterizes deformation of an atom due to the interactions with other atoms, is applied to describe the BTO NWs properties. In shell model, each ion-core is connected to the ion-shell by a harmonic spring with the potential of $V(r) = \frac{1}{2} k_2 r^2$, where r, and k_2 are the relative core-shell distance and on-site core–shell force constant, respectively. For O ions, fourth order core shell interaction potential $V(r) = \frac{1}{2} k_2 r^2 + \frac{1}{24} k_4 r^4$ along the O^{-2}-Ti^{+4} bond is applied. There are long range Coulombic interactions $\Phi_{LR}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$ between the cores and shells of different atoms, except the core and shell of the same atom. The short range Buckingham potential: $\Phi_{SR}(r_{ij}) = A \exp(-r_{ij}/\rho) - B r_{ij}^{-6}$ that interacts only with shells of atoms, is used for the Ba–O, Ti–O and O–O interactions. The detailed comment of the shell model can be found in [29]. The parameters of the shell model for $BaTiO_3$ used in this study are given in [30].

It is clear that the existence of oxygen vacancies in BTO NWs modifies the charges of the BTO ions. The modifications strongly relate

to the neighboring atoms of the oxygen vacancy. Although some charge compensation mechanisms [31,32] are developed for defected BTO systems but in the classical MD (And especially in the LAMMPS code) it is very hard to follow these changes and consider them in the simulation. In this study for simplicity, the additional positive charge which is resulted from the oxygen vacancies is divided to a number of cations and then the resulting value is subtracted from the charge of each cation to ensure neutrality condition. The exact solution of this problem may be possible with advanced simulation methods such as quantum molecular dynamics but usually these methods have a huge computational cost in comparison with classical MD.

The simulations are performed on oxygen-deficient BTO NWs at pressure of 1 atm and different temperatures ranging from 700 K to 1000 K. All of the simulations were carried out using LAMMPS code [33]. The equations of motion were integrated via the velocity Verlet algorithm with time steps of 1 fs [34].

During the simulation, the neighboring ions around the vacancies were perturbed and it was tried to modify their positions for new equilibrium locations. In solid nanostructures diffusion can take place by a number of various procedures. Vacancy diffusion may be the most fundamental of these procedures which includes the exchange of an atom at an ordered location with a vacancy. In this diffusion type, the atoms and vacancies exchange their positions [35]. The rate in which a single point defect moves can be expressed by an Arrhenius law [36]:

$$D = D_0 \exp\left(\frac{-E^{act}}{k_B T}\right), \tag{1}$$

where D is the diffusion coefficient, D_0 is the pre-exponential factor depending on parameters such as hop length and vibrational frequency and E^{act} is the activation energy.

In this work mean square displacement (MSD) is used to evaluate D. The MSD of oxygen atoms can be obtained at each temperature as follows [37]:

$$MSD(t) = \frac{1}{N_i} \sum_{n=1}^{N_i} \langle r_n(t+dt) - r_n(t) \rangle^2, \tag{2}$$

where, N_i represents the total number of particles and r_n is the position of the geometric center of an atom at certain time t. In this simulation in absence of the electric field, we computed the diffusion coefficient from the derivative of MSD with respect to the time:

$$D = \frac{1}{6} \frac{\partial}{\partial t} MSD(t) \tag{3}$$

where D is the diffusion coefficient. The ionic conductivity was calculated by a collective version of the ionic MSD [38,39]:

$$\sigma = \lim_{t \to \infty} \frac{e^2}{6k_B t T V} \sum_{ij}^{N} Z_i Z_j \langle [\vec{r_i}(t) - \vec{r_i}(0)] \cdot [\vec{r_j}(t) - \vec{r_j}(0)] \rangle, \tag{4}$$

where, V, e, Z_i, k_B and T are the volume, electron charge, charge of ion i, Boltzmann constant and temperature respectively.

To perform the simulation the original cubic structure of NWs with [001] and [110] longitudinal directions were created by repeating the conventional unit cell (with lattice constants, a = 0.4030 nm) 8-fold in the x-direction, 8-fold in the y-direction and 37-fold in the z-direction and oxygen vacancies were uniformly generated by random deletion of O atoms. The NWs were relaxed under Isobaric–Isothermal ensemble (NPT) for 1000 ps to liberate internal stresses and then relaxed under canonical ensemble (NVT) for another 5000 ps to reach the minimum value of energy. The sketch of the atomic configuration in the BTO unit cell and a perfect NW with [001] direction are shown in Fig. 1(a–c). Fig. 1(d) compares the lattice constant during relation time with initial data for NWs.