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Calculation of proton conductivity at the $\Sigma 3(111)/[1\bar{1}0]$ tilt grain boundary of barium zirconate using density functional theory

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ABSTRACT

We theoretically investigate proton conductivity at the $\Sigma 3(111)/[1\bar{1}0]$ tilt grain boundary of barium zirconate using density functional theory. In order to evaluate the space charge layer model and the structural disorder model, segregation energies of a +1-charged proton and a +2-charged oxygen vacancy, as well as energy barriers for proton migration, are calculated. The effect of the proton concentration on its segregation is verified and it is found that the segregation energy decreases with increases in the concentration. With consideration of this effect, the segregation energies of the proton and oxygen vacancy are in the range of −0.35 to −0.60 and −0.57 to −0.65 eV, respectively. Based on the segregation energies, an electrostatic potential of 0.51 V at 600 K is obtained through numerically solving Poisson's equation. An energy barrier range of 0.71–0.95 eV is required for the proton to migrate across the grain boundary core. The proton concentration and mobility that are obtained from the electrostatic potential and energy barrier are used to calculate the proton conductivities in the bulk and at the grain boundary. The calculated proton conductivities are consistent with the experimentally measured proton conductivities in the bulk and at the grain boundaries of barium zirconate.

1. Introduction

The origin of highly resistive grain boundaries (GBs) of barium zirconate ($BaZrO_3$), which is a promising electrolyte material for protonic ceramic fuel cells, has been widely investigated by both experimental and theoretical researchers [1–4]. Because the existence of non-conducting secondary phases at GBs has been excluded via high-resolution transmission electron microscopy (HRTEM) research [5–8], high proton resistance at the GBs (R_{GB}) of $BaZrO_3$ has been explained using the space charge layer (SCL) model [1,2,9–12]. Fig. 1 presents a schematic of a polycrystalline sample based on the SCL model. The GB is composed of the core and SCL, which is located on both sides of the core. The segregation of positively charged defects, such as anion vacancies, cation interstitials, and protons, at the core builds a positive electrostatic potential ($\Delta\varphi$), and therefore depletes the mobile protons near the core. The presence of the proton depletion region, the so-called SCL, at the GBs of $BaZrO_3$ has been proven in several experimental studies [2,10–12].

Recently conducted theoretical research has explained the resistive GBs of $BaZrO_3$ using the SCL model. Nyman et al. investigated the $\Sigma 3(112)/[\bar{1}10]$ tilt GB of $BaZrO_3$ using density functional theory (DFT) and obtained a segregation energy of −1.25 eV for an O vacancy [3]. The calculated $\Delta\varphi$ at the core was 0.45 V in a wet atmosphere at 600 K. Polfus et al. investigated the defect chemistry at the $\Sigma 3(111)$ tilt GB of $BaZrO_3$ using DFT [4]. A proton and an oxygen (O) vacancy were segregated at the core with segregation energies of −0.81 and −0.65 eV, respectively, and they built a $\Delta\varphi$ of 0.51 V at the core in a wet atmosphere at 573 K. Lindman et al. investigated the segregation of an O vacancy at the (11k) GBs (k = 3, 4, …, 8) of $BaZrO_3$ using interatomic potentials [13]. The O vacancy was segregated at the core of the GBs, and the calculated $\Delta\varphi$ values were in the range of 0.24 to 0.76 V at 600 K. Helgee et al. investigated the $(111)/[\bar{1}10]$, $(112)/[\bar{1}10]$, and (210)/[001] tilt GBs of $BaZrO_3$ using DFT [14]. Both a proton and an O vacancy were segregated at the core, and they built a $\Delta\varphi$ of approximately 0.6 V in a wet atmosphere at 600 K. Several theoretical studies investigated the effect of structural disorder at the core on the proton migration across GBs in order to explain the resistive GBs of $BaZrO_3$ without using the SCL model. van Duin et al. calculated the energy barrier (E_B) for proton migration at a twisted GB between the (111) and (110) planes of yttrium (Y)-doped $BaZrO_3$ using reactive force field molecular dynamics [15]. The calculated E_B values in the bulk and at the GB were 0.66 and 1.12 eV, respectively. Kim et al. calculated the E_B values for the proton migration at the $\Sigma 5(310)/[001]$ tilt GBs of Y- and zinc (Zn)-doped $BaZrO_3$ using DFT; they were 0.72 and 0.68 eV, respectively [16,17].

It is necessary to consider both the SCL model and the structural disorder model in order to explain the resistive GBs of $BaZrO_3$ because the

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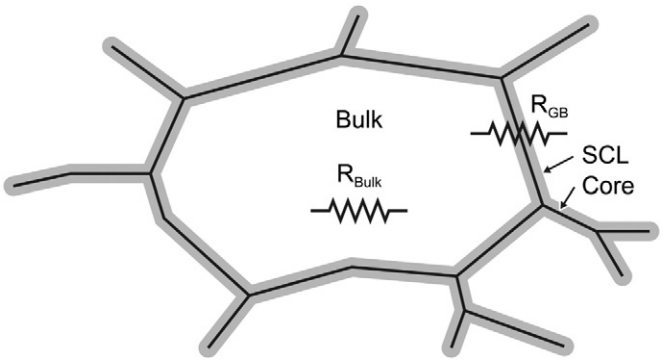

Fig. 1. Schematic of a polycrystal indicating the bulk (white zone) and GB. The GB is composed of the core (black solid line) and SCL (gray zone).

SCL model only considers the variation of the proton concentration (N_H), while the structural disorder model only considers the variation of the proton mobility (μ_H) at the GBs. Kim et al. recently calculated proton conductivity (σ_H) at a BaO-terminated (001) $BaZrO_3$ surface considering both the SCL model and the structural disorder model [18]. However, to date, there have not been theoretical studies that have considered both models in order to calculate σ_H at the GBs of $BaZrO_3$. In this study, the segregation energies of a proton and an O vacancy, as well as the E_B values, are calculated for the proton migration at a $\Sigma3(111)/[1\bar{1}0]$ tilt GB of $BaZrO_3$ using DFT in order to consider both models. Poisson's equation is numerically solved to obtain N_H from the segregation energies, and μ_H is obtained from the E_B. At the end of this paper, σ_H at the GB and in the bulk of $BaZrO_3$ are calculated based on the calculated N_H and μ_H, and the results are compared with the experimentally measured σ_H values. The conductivity calculation procedure in this study can be applied to other ionic conductors, such as zirconia (ZrO_2) and ceria (CeO_2).

2. Calculation details

All DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) code [19–21]. The DFT calculation method for GB super cells is summarized below, and further details have been provided previously [22]. The electron wave functions were described using the projector augmented wave (PAW) method of Blöchl [23], which was implemented within the code created by Kresse and Joubert [24]. The exchange correlation energy was described using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [25]. The cutoff energy was 500 eV, and the k-points mesh was $1 \times 3 \times 5$ for the GB super cells using the Monkhorst–Pack grid method [26]. The partial wave occupancies were calculated using the Gaussian smearing method; their factor was 0.05 eV. The electronic and geometric optimizations converged when the total energy differences between successive calculation steps were less than 10^{-4} and 10^{-3} eV, respectively.

Fig. 2 presents the $\Sigma3(111)/[1\bar{1}0]$ tilt GB super cell of $BaZrO_3$ modified from our previous work [22]. The super cell is composed of 120 ions, and its dimensions are 2.98 nm × 1.05 nm × 0.60 nm. The bold lines represent the GB plane that contains two Ba and six O ions. A +1-charged proton and a +2-charged O vacancy were considered as relevant defects and were introduced into the GB super cell in order to calculate the segregation energy of the defects. Other defects, such as the Ba vacancy, Zr vacancy, Ba interstitial, Zr interstitial, electron, and hole, are not considered in this study because they are not the main defects under typical operation conditions. The effective charge states of the defects were controlled through removing the corresponding number of electrons from the super cell. The E_B values for the proton migration at the GB super cell were calculated using the climbing image nudged elastic band (CI-NEB) tool implemented in the VASP code that can determine the saddle points and minimum energy paths [27]. To evaluate the size effect of the super cell on the segregation energy and E_B, some calculations were repeated with an increased dimension of the super cell by 50% perpendicular to the GB plane.

3. Space charge layer (SCL) model

The SCL model at the GB of acceptor-doped $BaZrO_3$ was evaluated based on the DFT calculation results and some experimental parameters. The GB was divided into the core and SCLs on both sides of the core. The core was defined to include the GB plane and the nearest neighboring Zr layers on both sides. The thickness of the core (w_c), which corresponds to the distance between the neighboring Zr layers, was approximately 0.3 nm. The SCL included the bulk area that was affected by $\Delta\varphi$. The experimentally measured thickness of one side of the SCL (λ) was 2–4 nm [1,2,5]. The Mott–Schottky approximation, which assumes uniform concentration of an acceptor dopant (N_A) throughout all regions, was applied. A one-dimensional GB model was applied in order to ignore the spatial charge distribution parallel to the GB plane. N_H, the O vacancy concentration (N_V), and $\Delta\varphi$ at the GB were calculated in an equilibrium condition and are expressed as a function of the distance from the GB plane (x); $x = 0$ corresponds to the GB plane. The profiles of the $\Delta\varphi(x)$ were primarily affected by the $\Delta\varphi(0)$, and they determined the variation of the N_H and N_V.

The $\Delta\varphi(0)$ can be calculated through numerically solving Poisson's equation. The iterative calculation procedure from the literature was partially adapted to solve Poisson's equation [28,29]. In order to obtain the numerical solution for $\Delta\varphi(0)$, the charge neutrality condition between the core and the SCLs was used. The charges of the core (Q_{Core})

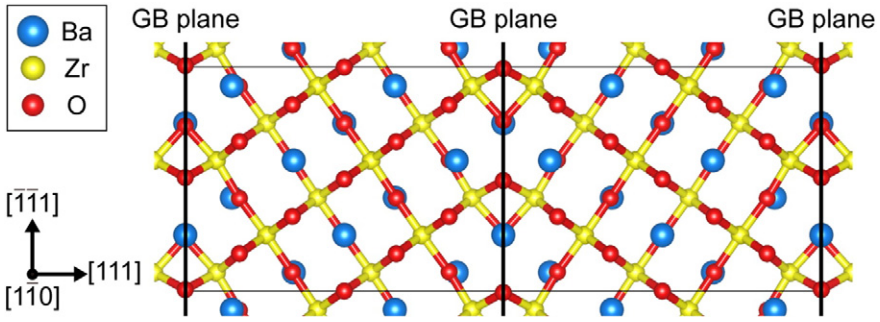

Fig. 2. A planar view of the $\Sigma3(111)/[1\bar{1}0]$ tilt GB super cell of $BaZrO_3$ depicted along the $[\bar{1}10]$ direction, partially modified from the previous work [22], where the blue, yellow, and red circles indicate the Ba, Zr, and O ions, respectively. The box indicates the GB super cell and the bold lines indicate the GB plane that contains two Ba and six O ions.