

Oxide Ionic Conduction at Y_2O_3 -Segregated ZrO_2 Grain Boundaries by Atomistic Simulation: Roles of Oxide Ion Vacancy

Masato YOSHIYA¹, Keisuke SHIMIZU¹, and Takashi OYAMA²

¹Department of Adaptive Machine Systems, Osaka University, Osaka 565-0871, Japan

²Murata Manufacturing Co. Ltd., Kyoto 617-8555, Japan

As grain size gets finer to increase the number density of electrode-electrolyte interfaces in solid oxide fuel cell applications, grain boundary (GB) plays more crucial roles in oxide ion transport and governs overall ionic conductivity. Compared with grain interior, the potential to reside foreign elements or defects are altered not only at adjoining planes but also in the vicinity of GBs due to lattice discontinuity at GB plane. This results in so-called grain boundary segregation which accompanies enrichment or depletion of foreign species in the vicinity of GB. The grain boundary segregation further modifies oxide ion conduction along or across the GB in Y_2O_3 -doped ZrO_2 , in addition to those by lattice discontinuity itself. Origins of the change in ionic conductivity across the GB, often reduction compared with grain interior, is still unclear, which is an impediment for optimizing the ionic transport for polycrystalline materials. Besides, it is extremely difficult to monitor foreign species that are segregated at GB in Y_2O_3 -doped ZrO_2 by experiment since difference in atomic number between Y and Zr is only one and oxide ions are mobile. Therefore, it is rational to analyze GB segregation and its effect on ionic conduction at GB using atomistic simulations which enable us to monitor states of each constituting element and vacancies.

Atomic configuration of matrix elements and foreign species in the vicinity of tilt GBs reported by authors [1,2] were employed in this study and configuration of oxide ion vacancies were further optimized by molecular dynamics simulation at 2000 K, followed by relaxation at desired temperature, 1273 K. Then, with optimized lattice constant at the desired temperature, molecular dynamics simulation has been carried out to obtain coordinates of all the constituting species as a function of time, followed by calculations of mean square displacement from which diffusivity and ionic conductivity can be calculated by Einstein equation and Nernst equation, respectively. By summing only over GB region, which is defined by the potential change mentioned above, and about a component along an axis of three dimensional space at a time, local directional diffusivity and ionic conductivity across or along the GB were obtained. Although whether ionic conduction in polycrystalline materials takes place across grains and GBs or along GB region is determined by cross section of each region through which oxide vacancies diffuse and ionic conductivity across or along the GB region, since preliminary study showed that transgranular ionic conduction is preferable in these symmetric tilt GB, we focused on ionic conductivity across the GB in order to discuss atomistic mechanism that restrain ionic conduction in the GB region.

Figure 1 shows local diffusivity across $\Sigma 5$ (310)/[001] symmetric tilt GB for 1 Å wide slices. Since three-dimensional periodic boundary conditions are applied to supercells, two GB appear in a supercell, on the right and the left in the figure. Fitted curves are only for eyes aid. As it is easily seen in the figure, though values are scattered due to modest simulation time for this spatial resolution, diffusivity significantly dropped in the vicinity of GB. This corresponds to the GB resistance. Comparing this result obtained from segregated models with that obtained from the same GB model with random Y_2O_3 substitution, it is found that origins of the GB resistance can be classified into three: (1) Lattice discontinuity and resulting local strain around GB, (2) local chemistry change in the vicinity of GB, and (3) partial ordering of Y ions that occupy specific sites to be accommodated at GB. Of these, the partial ordering of Y showed little effect on ionic conductivity across GB. The lattice discontinuity is inevitable at GB unless any foreign atoms, possibly small atoms, occupy interstitial sites on GB plane. Since the resulting local strain in the vicinity of GB, actually expansion of lattice perpendicularly to the GB plane, should have positive effect on the ionic conductivity, as manifested by independent calculation of single crystal with various lattice expansion, this is not an origin of the resistance. A remaining factor, local

chemistry change in the vicinity of GB, is also responsible for the GB resistance and is controllable, in contrast to lattice discontinuity.

To generalize the matter and obtain physical insight on the relationship between GB chemistry and resulting ionic conductivity, oxide ion diffusivities across GB for five symmetric tilt GBs both for the GBs with random Y_2O_3 substitution and the GBs with segregation were examined in terms of oxide vacancy concentration in the GB region. For all of the GBs whether segregated or not, ionic conductivity showed drastic decrease in ionic conductivity compared with that in grain interior, as seen in Fig. 1, which includes effects of both lattice discontinuity and local chemistry change. Then, the difference in ionic conductivity between the GB with random substitution and the GB with segregation eliminates the former effect and shows how GB segregation modifies the grain boundary resistance. A horizontal line in the figure shows mean oxide ion concentration in grain interior. As shown in the figure, there is a correlation between oxide vacancy concentration in the GB region and ionic conductivity across the GB: With the increase of oxide ion vacancies, ionic conductivity across GB was decreased. This is a manifestation of the role of oxide ion vacancy upon ionic conductivity: It is necessary for the ionic conduction which is realized by vacancy mechanism, but large population of the vacancy scatters ionic conduction, resulting in the decrease in ionic conductivity, as it is confirmed by independent calculation for single crystal with various amounts of oxide ion vacancies. It should be noted that elimination of GB segregation did not improve the ionic conductivity across the GB: It resulted enrichment of mobile oxide ion vacancies at GB to compensate the potential change in the vicinity of GB and the increased oxide ion vacancies resulted in further decrease in the ionic conductivity.

In summary, atomistic simulations have been carried out to investigate so-called GB resistance for oxide ionic conduction. It is found that ionic conductivity was significantly decreased in the vicinity of GB and segregation of oxide ion vacancies is also responsible for the decrease as well as lattice discontinuity. This suggests that controlling oxide vacancy content would improve GB resistance through the control of GB segregation.

References

- [1] T. Oyama, M. Yoshiya, K. Matsunaga, and H. Matsubara, *Phys. Rev. B*, **71** 224105 (2005).
- [2] M. Yoshiya, and T. Oyama, in preparation.

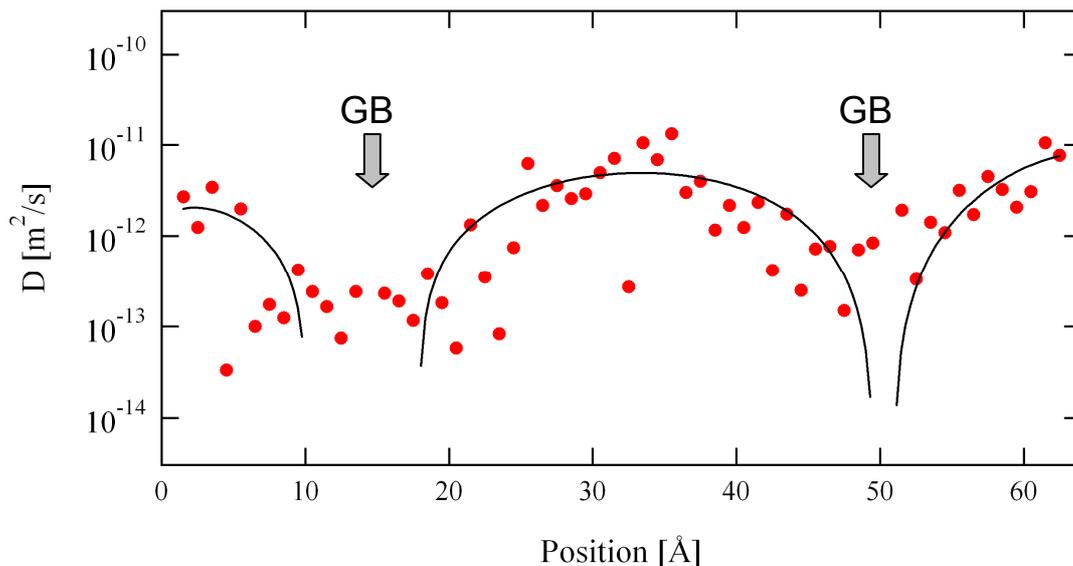


Figure 1. Spatial distribution of local diffusivity perpendicular to GB plane.