

# Ionic dynamics at porous alumina surfaces

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## INTRODUCTION

Anodic porous alumina has broad applications in self-assembled nanostructures for various devices such as nanowire solar cells [1] and resistive random access memory [2, 3], and atomistic understanding of ionic transport at pore surfaces is indispensable for the control of the nanostructures. In this study, we perform molecular dynamics (MD) simulation to study ionic transport under an electric field in amorphous alumina with a cylindrical pore. The simulation results reveal novel ionic transport phenomena, including enhanced oxygen transport and inverted aluminum transport at pore alumina surface.

## METHOD

Schematic of simulation setup is shown in Fig. 1. System size is  $270 \text{ \AA} \times 270 \text{ \AA} \times 160 \text{ \AA}$  with periodic boundary conditions in the x-, y- and z-axis. Melt-quench procedure is used to prepare bulk amorphous alumina with a density of 3.0 g/cc, and subsequently atoms within a radius of 20 Å are removed to produce a cylindrical pore with its axis parallel to the z-axis. The interatomic potential incorporates ionic and covalent effects through a combination of two- and three-body terms [4]. The system is heated up 700 K during which the radius of the pore changes to about 50 Å. After thermalization at temperature 700 K for 10 ns, an electric field of 0.1 V/Å is applied in the z direction.

## RESULTS

To study the ion drift mobility of Al and O, Fig. 2 plots the displacements of Al and O averaged in the z direction. Figure 3 plots the displacements of Al and O averaged in surface

and bulk regions as a function of time. Here, the surface region is within 10 Å from the cylindrical pore center (see Fig. 1). In the bulk, we observe ordinary drift mobility, *i.e.*, Al and O move along and opposite to the electric field, respectively. Since Al has the larger charge ( $\text{Al}^{3+}$  as opposed to  $\text{O}^{2-}$ ) and the smaller ionic radius, it is more mobile than O. The most striking feature is the inverted Al transport at the surface. Another notable feature is that O is more mobile at the surface. To understand the unusual Al transport at the surface, we calculate the radial profile of the stoichiometry (Fig. 4). The local stoichiometry is calculated as an average in a shell of thickness  $\sim 10 \text{ \AA}$ . Structural analysis reveals an oxygen-rich stoichiometry,  $\text{O/Al} \sim 3/1$  at the surface as compared to the bulk value of 3/2. The negatively charged Al-O network at the surface explains the apparent inverse drift mobility of Al at the surface.

## CONCLUSION

In summary, our MD simulation has revealed a novel ionic transport phenomenon under an electric field at anodic porous alumina surfaces. This phenomenon is expected to play an important role in nanoionics-based porous alumina growth mechanisms.

## ACKNOWLEDGEMENT

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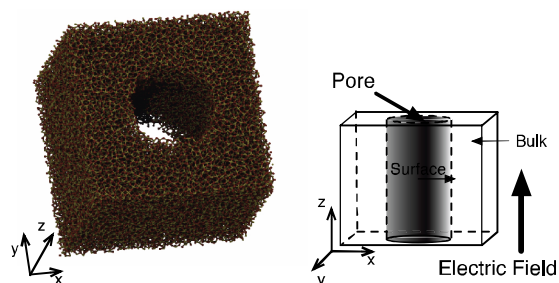


Fig. 1. (Left) Snapshot of the amorphous alumina structure with pore, where the yellow and red balls indicate Al and O atoms, respectively. (Right) Schematic of the simulated system.

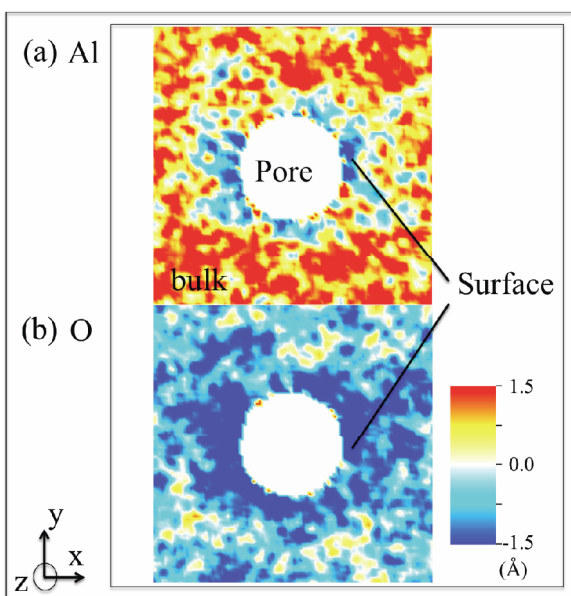


Fig. 2. Spatial distribution of atomic displacement on an xy-plane for (a) aluminum and (b) oxygen atoms. Red and blue regions indicate parallel and antiparallel motion to the direction of the applied electric field, respectively.

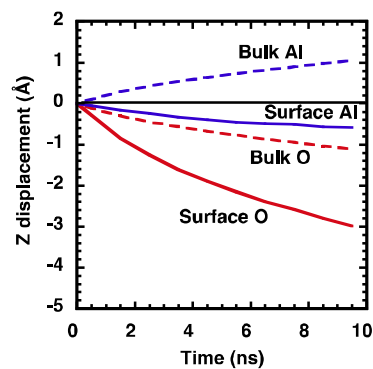


Fig. 3. Atomic displacement in the z direction in the surface (solid lines) and bulk (dashed lines) regions. The red and blue lines are for O and Al atom, respectively.

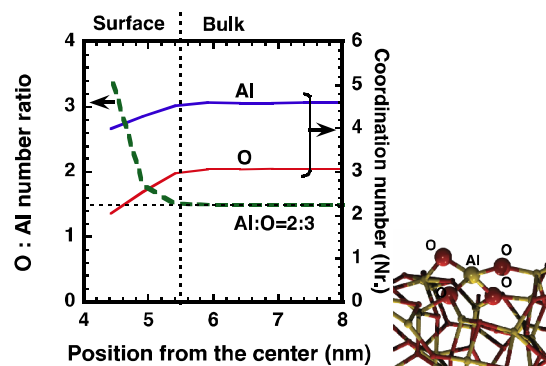


Fig. 4. Local stoichiometry (*i.e.* the ratio between the numbers of O and Al atoms) and the coordination number as a function of the distance from the cylindrical center.