Supporting Information for

Sodium Ion Diffusion in Al₂O₃: A Distinct Perspective Compared with Lithium Ion Diffusion

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Density functional theory calculations

Kohn–Sham density functional theory (DFT) calculations were carried out by employing the Vienna ab initio simulation package (VASP). The electron–electron interaction was treated by the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functionals, and the ion–electron interaction was described by the projector augmented wave (PAW) method. The electronic wave functions were expanded on a plane wave basis of 400 eV. In terms of valence electron configurations, we treated $1s^22s^1$ for Li, $2p^63s^1$ for Na, $3s^23p^1$ for Al, and $2s^22p^4$ for O. To study the lithiation and sodiation processes of the $\text{Al}_2\text{O}_3$ coating layer, we simulated amorphous $\text{A}_x\text{Al}_2\text{O}_3$ bulk structures by a periodic cubic supercell containing $20 \times x$ A atoms, 40 Al atoms, and 60 O atoms ($A = \text{Li}$ and $\text{Na}$). The $x$ values in $\text{Li}_x\text{Al}_2\text{O}_3$ were chosen to be 0.0, 0.2, 0.4, 1.0, 1.4, 2.0, 2.5, 3.0, 3.5, and 4.0 corresponding to the atomic compositions of $\text{Al}_{40}\text{O}_{60}$, $\text{Li}_4\text{Al}_{40}\text{O}_{60}$, $\text{Li}_8\text{Al}_{40}\text{O}_{60}$, $\text{Li}_{20}\text{Al}_{40}\text{O}_{60}$, $\text{Li}_{28}\text{Al}_{40}\text{O}_{60}$, $\text{Li}_{40}\text{Al}_{40}\text{O}_{60}$, $\text{Li}_{50}\text{Al}_{40}\text{O}_{60}$, $\text{Li}_{60}\text{Al}_{40}\text{O}_{60}$, $\text{Li}_{70}\text{Al}_{40}\text{O}_{60}$, and $\text{Li}_{80}\text{Al}_{40}\text{O}_{60}$, respectively. The $x$ values in $\text{Na}_x\text{Al}_2\text{O}_3$ were chosen to be 0.0, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 corresponding to the atomic compositions of $\text{Al}_{40}\text{O}_{60}$, $\text{Na}_4\text{Al}_{40}\text{O}_{60}$, $\text{Na}_{10}\text{Al}_{40}\text{O}_{60}$, $\text{Na}_{20}\text{Al}_{40}\text{O}_{60}$, $\text{Na}_{30}\text{Al}_{40}\text{O}_{60}$, $\text{Na}_{40}\text{Al}_{40}\text{O}_{60}$, $\text{Na}_{50}\text{Al}_{40}\text{O}_{60}$, and $\text{Na}_{60}\text{Al}_{40}\text{O}_{60}$, respectively. The $2 \times 2 \times 2 k$-point meshes were used for Brillouin zone integrations. The calculated density of amorphous $\text{Al}_2\text{O}_3$ is 3.12 g/cm$^3$, which enters the experimental range of 3.05–3.40 g/cm$^3$. The DFT calculations for A–O bond breaking in the $\text{A}_2\text{O}$ molecule and A–Al bond formation between the AF and $\text{AlF}_3$ molecules ($A = \text{Li}$ and $\text{Na}$) were performed by using the Gaussian 09 program package. The PBE functional and standard 6-311+G* basis sets were used.
Ab initio molecular dynamics simulations

We used ab initio molecular dynamics (AIMD) simulations in the course of generating the amorphous structures. The equations of motion were integrated with the Verlet algorithm using a time step of 1 fs, and the temperature was controlled by velocity rescaling and canonical ensemble using a Nosé-Hoover thermostat. The amorphous structures were generated by using a “liquid-quench” technique in which heating, equilibration, and cooling were done in series by the AIMD simulations. A $1 \times 1 \times 1$ $k$-point mesh was used to save computational time during the AIMD simulations.

We first determined the volume of $A_x\text{Al}_2\text{O}_3$ ($A = \text{Li}$ and $\text{Na}$). Initially, for each $x$, $20 \times x$ $A$ atoms, 40 Al atoms, and 60 O atoms were distributed at random in a cubic supercell of $L \times L \times L$ Å$^3$ size ($L = 10–14$). The system was heated from 0 K to 3000 K at a heating rate of 1 K/fs, equilibrated for 3–5 ps at 3000 K, and quenched from 3000 K to 300 K at a cooling rate of 1 K/fs. The resulting system was again equilibrated for 5 ps at 300K. Three structures were selected during the last 5 ps AIMD run and then fully optimized with respect to the atomic position, cell shape, and cell volume using static DFT calculations. A 30% larger plane-wave energy cutoff of 520 eV was used during the optimization to avoid the Pulay stress problem$^9$ caused by cell shape/volume changes. The average value of the volumes of the optimized three structures was used as the volume of $A_x\text{Al}_2\text{O}_3$. We next determined the total energy of $A_x\text{Al}_2\text{O}_3$. The $A_x\text{Al}_2\text{O}_3$ system with the determined volume was equilibrated for 5 ps at 300 K using the AIMD simulations. We selected three structures during the simulations and then calculated their total energies using static DFT calculations. The average value of the three total energies was used as the total energy of $A_x\text{Al}_2\text{O}_3$. Similar schemes to construct the amorphous structures and to determine the volume and total energy were successfully employed in our previous studies.$^{10,11,12}$
**Coordination numbers**

The coordination numbers (CN) were analysed using the RINGS code. The analyses were done for the equilibrium Li$_x$Al$_2$O$_3$ and Na$_x$Al$_2$O$_3$ structures, i.e., the room-temperature simulation structures during the final AIMD simulations in the procedure for constructing the amorphous phases.

![Coordination numbers](image)

**Figure S1.** Partial CN of Li, Al, and O in Li$_x$Al$_2$O$_3$ and Na, Al, and O in Na$_x$Al$_2$O$_3$. In Li$_x$Al$_2$O$_3$, the bond cutoff distances are 3.4, 3.2, 2.6, 2.8, 2.4, and 2.8 Å for the Li–Li, Li–Al, Li–O, Al–Al, Al–O, and O–O bonds, respectively. The data were taken from Ref. 11. In Na$_x$Al$_2$O$_3$, the bond cutoff distances are 3.8, 3.6, 3.0, 2.8, 2.4, and 2.8 Å for the Na–Na, Na–Al, Na–O, Al–Al, Al–O, and O–O bonds, respectively.
Bulk moduli

The bulk modulus $B$ is given by

$$B = V_0 \frac{\partial^2 E}{\partial V^2},$$

where $E$ is the total energy, $V$ is the volume, and $V_0$ is the equilibrium volume. The total energy values of Na$_x$Al$_2$O$_3$ were calculated as a function of volume and were fitted to Murnaghan’s equation of state to determine the bulk modulus.

Figure S2. Total energies of Na$_x$Al$_2$O$_3$ as a function of the volume of unit cell.
Molecular calculations

We examined the dissociation of molecule $A_2O$ into $AO + A$ ($A = Li$ and $Na$) to compare the $Li–O$ and $Na–O$ bond strengths. While the energy needed to break one $Li–O$ bond in $Li_2O$ was calculated to be $3.84 \text{ eV}$, the energy needed to break one $Na–O$ bond in $Na_2O$ was calculated to be only $2.30 \text{ eV}$, as shown in Figure S3. The $A–Al(III)$ repulsive interaction between the $AF$ and $AlF_3$ molecules ($A = Li$ and $Na$) was also examined to compare the $Li–Al(III)$ and $Na–Al(III)$ repulsive strengths. The calculated energy curve for the $Na–Al(III)$ repulsion between $NaF$ and $AlF_3$ is similar to that for the $Li–Al(III)$ repulsion between $LiF$ and $AlF_3$, as shown in Figure S3. In particular, the two energy curves are nearly the same in the $A–Al$ distance range of 2.5–3.5 Å (see the box), which include the equilibrium $Li–Al$ and $Na–Al$ bond lengths in $Li_3Al_2O_3$ and $Na_3Al_2O_3$, respectively (see Figures S4 and S5).

![Dissociation of $A_2O$ into $AO + A$ and $A–Al(III)$ repulsion between $AF$ and $AlF_3$](image)

**Figure S3.** Energy diagrams for the dissociation of $A_2O$ into $AO + A$ and the $A–Al(III)$ repulsion between $AF$ and $AlF_3$ ($A = Li$ and $Na$).
Radial distribution functions

The radial distribution functions (RDF) were analysed using the RINGS code. The analyses were done for the equilibrium Li$_x$Al$_2$O$_3$ and Na$_x$Al$_2$O$_3$ structures.

![Graphs showing radial distribution functions for Li$_x$Al$_2$O$_3$](image)

**Figure S4.** Partial RDF for the Al–O, Al–Al, O–O, Li–Al, Li–O, and Li–Li pairs in Li$_x$Al$_2$O$_3$.

The data were taken from Ref. 11.
Figure S5. Partial RDF for the Al–O, Al–Al, O–O, Na–Al, Na–O, and Na–Na pairs in Na$_x$Al$_2$O$_3$. 
**Bader populations**

The Bader charge analyses were performed using the code developed by Henkelman group.\textsuperscript{14} The atomic charges were determined as average values of the calculated charges for 3–5 structures selected in the equilibrium \( \text{Li}_x\text{Al}_2\text{O}_3 \) and \( \text{Na}_x\text{Al}_2\text{O}_3 \) structures (see Figure S6).

![Bader populations](image)

**Figure S6.** Average Bader populations of Li, Al, and O in \( \text{Li}_x\text{Al}_2\text{O}_3 \) and Na, Al, and O in \( \text{Na}_x\text{Al}_2\text{O}_3 \). The data for \( \text{Li}_i\text{Al}_2\text{O}_3 \) were taken from Ref. 11.
**Diffusivities**

The self-diffusion coefficients $D$ of A, Al, and O atoms in $A_xAl_2O_3$ ($A =$ Li and Na) at $T =$ 300 K were obtained from the Einstein relation $\langle r^2(t) \rangle = 6Dt$ where $\langle r^2 \rangle$ is the mean square displacement. We calculated the $\langle r^2 \rangle$ values of A, Al, and O atoms ($A =$ Li and Na) for AIMD simulations of 10–30 ps at $T =$ 1200, 1600, 2000, and 2400 K and determined the $D$ values at each temperature (see Figures S7 and S8).

![Graphs showing temperature dependence of Na, Al, and O diffusivities in Na$_x$Al$_2$O$_3$.](image)

**Figure S7.** Temperature dependence of Na, Al, and O diffusivities in Na$_x$Al$_2$O$_3$. 
Figure S8. Temperature dependence of Li, Al, and O diffusivities in Li₅Al₃O₉. The data for Li₀.₂Al₂O₃ and Li₃.₅Al₂O₉ were taken from Ref. 11.
The determined $D$ values at these high temperatures were used to extrapolate the $D$ value at $T = 300$ K using the Arrhenius law $D = D_0 \exp(-E_D/k_B T)$ where $D_0$ is the pre-exponential factor, $E_D$ is the activation energy for diffusion, and $k$ is the Boltzman constant. The calculated diffusion properties for Li$_x$Al$_2$O$_3$ are presented in Table S1.

**Table S1.** Diffusion properties of Li$_x$Al$_2$O$_3$. The data for Li$_{0.2}$Al$_2$O$_3$ and Li$_{3.5}$Al$_2$O$_3$ were taken from Ref. 11.

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**Atomic structures**

Snapshots of the amorphous Na$_x$Al$_2$O$_3$ structures obtained from the AIMD simulations at 300 K are displayed in Figure S9.

**Figure S9.** Atomic structures of amorphous Na$_x$Al$_2$O$_3$. Yellow, white, and red balls represent the Na, Al, and O atoms, respectively.
References


