Defect-driven anomalous transport in fast-ion conducting solid electrolytes

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Solid-state ionic conduction is a key enabler of electrochemical energy storage and conversion. The mechanistic connections between material processing, defect chemistry, transport dynamics and practical performance are of considerable importance but remain incomplete. Here, inspired by studies of fluids and biophysical systems, we re-examine anomalous diffusion in the iconic two-dimensional fast-ion conductors, the $\beta'$- and $\beta''$-aluminas. Using large-scale simulations, we reproduce the frequency dependence of alternating-current ionic conductivity data. We show how the distribution of charge-compensating defects, modulated by processing, drives static and dynamic disorder and leads to persistent subdiffusive ion transport at macroscopic timescales. We deconvolute the effects of repulsions between mobile ions, the attraction between the mobile ions and charge-compensating defects, and geometric crowding on ionic conductivity. Finally, our characterization of memory effects in transport connects atomistic defect chemistry to macroscopic performance with minimal assumptions and enables mechanism-driven ‘atoms-to-device’ optimization of fast-ion conductors.

The transport of charged ions in solid electrolytes underpins critical technologies, such as rechargeable batteries, fuel cells and electrocatalysts, which are vital to the transition to low-carbon energy systems. In the solid state, ionic diffusion and conductivity are mediated by thermally activated rapid translations or hops of mobile ions between stable lattice sites. Hops are separated by relatively long residence times, and each ion executes a random walk. Based on Fickian diffusion, in the long-time regime of such a random walk, the time-averaged mean-square displacement (tMSD) of a mobile ion is linear with time. The prediction of practical performance in the low-frequency, direct-current (d.c.) limit from atomistic simulations hinges on the key assumption of Fickian diffusion.

The prediction of macroscopic ionic conductivity and of its dependence on material processing in turn enables device design. The frequency-dependent conductivity is described by the net movement of charge, that is, the ensemble-averaged mean-square displacement (eMSD) of all ions. At picosecond to nanosecond timescales accessible to atomistic simulation, slowly evolving dynamics such as the fluctuating positions of other mobile ions and the motions of the host structure may couple to the transport of hopping ions. Phenomenological mesoscale models incorporate disorder via randomly frozen energetic barriers, dynamic relaxation or non-linear terms in the diffusion equation. However, a general frequency dispersion in conductivity highlighted by Jonscher and others is not yet explained. Here, we demonstrate a computational approach that quantitatively connects atomistic defect chemistry to macroscopic conductivity in these model ionic conductors. First, we characterize persistent subdiffusion and non-Gaussian statistics. Second, we quantify deviations from ergodicity, which complicate the prediction of a practical d.c. conductivity. Hence, we calculate the alternating-current (a.c.) ionic conductivity in excellent agreement with literature spectra. We then explain the anomalous transport and the frequency dispersion of a.c. conductivity by analysing the...
nanometre-scale defect chemistry of β/β″-aluminas. Finally, we compare distributions of defects that correspond to variations in processing conditions. Together, our mechanistic study shows how defect chemistry and disorder determine the energy landscape and practical conductivity in solid electrolytes.

Statistical descriptors of ion transport

We consider first the mean-square displacements of mobile ions, time-averaged over trajectories (tMSD, Fig. 2a) for Na β″-alumina. From short to long timescales $t$, an ion sequentially undergoes ballistic ($F_r$), bound ($F_r^b$) and diffusive dynamics. However, the expected Fickian dependence ($t^1$) is only reached at elevated temperature. At 300 K and below, the simulated transport is subdiffusive, characterized by an exponent below unity even for long timescales ($\geq 10$ ns, Fig. 2a) and average displacements substantially larger than one unit cell (Fig. 2b).

The non-Fickian long-time behaviour of the average tMSD at 300 K motivates an examination of the full distributions of ion displacements. Figure 2c shows such distributions along [100] in Na β″-alumina at 300 K, with obvious peaks at lattice sites every 2.8 Å. The same distributions, aggregated to one point per 2.8 Å lattice site, and each rescaled by its standard deviation, are shown in Fig. 2d. At short timescales, the distributions are wider than a Laplace distribution, and even for 20–30 ns remain wider than a Gaussian. While short-time deviation is expected given the activated nature of ion hopping, the persistence of a non-Gaussian distribution at long time lags suggests that deviations from normal diffusion impact the macroscopic conductivity. Of all the simulated materials, only K β″-alumina reaches a Gaussian distribution at 300 K during the simulation.

We begin to quantify hopping kinetics using the self part of the van Hove function ($G_s$), the Fourier counterpart of the experimentally observable incoherent intermediate scattering function for the mobile ions[34]. The decay of the probability of an ion remaining within 1.7 Å (<1 hop) or 4.6 Å (<2 hops) of an initial position (Fig. 2e) provides a simple proxy for hopping timescales. The probability follows stretched-exponential behaviour at short timescales, followed by power laws for long time lags (Supplementary Note 1). For simplicity, we use $1/e$ decay times (Fig. 2e, yellow circles) as proxies for the timescales for one and two diffusion events. We refer to them below as ‘1-hop relaxation time’ and ‘2-hop relaxation time’ by analogy with the structural relaxation interpretation of the van Hove function[4].

Deviations from ergodicity

The anomalous features of the statistics in Fig. 1a–d motivate a quantitative exploration of the distributions beyond their averages, that is, dynamic heterogeneity. We compare three descriptors of dynamic heterogeneity: the diffusion kernel correlation ($C_D$, Fig. 2f), the non-Gaussian parameter (NGP) (Supplementary Fig. 1) and the relative variance of the average tMSD as the ergodicity breaking parameter (EB) (Extended Data Fig. 7).

Within continuous-time random walk models, the diffusion kernel yields the second moment of displacement that determines the tracer diffusion coefficient. Its correlation $C_D$ characterizes the coupling of environmental dynamics to diffusion. Two timescales are of interest. First, the times when $C_D$ peaks can be interpreted as the timescale of fluctuation modes that mediate diffusion. In Na β″-alumina, $C_D$ peaks close to the 1-hop relaxation time at $\geq 300$ K, but at a shorter time at $\geq 473$ K (Fig. 2f). By contrast, in all β-aluminas, $C_D$ peaks after the 1-hop relaxation time, and the 2-hop relaxation begins a long-time regime when $C_D$ slowly decreases (Extended Data Figs. 1, 4 and 6).

Second, the timescale at which $C_D$ reaches an asymptotic value represents the onset of a long-time regime where average values may suffice to characterize diffusion. At $\geq 473$ K for Na β″-alumina, the 2-hop relaxation time comes already after $C_D$ asymptotically approaches zero ($C_D \rightarrow 0$). By contrast, for Na β-alumina...
C_{0} approaches zero only at 1,000 K, and only at \( t \geq 1 \text{ ns} \). For Na \( \beta″ \)-alumina, the NGP (Supplementary Note 1), like \( C_{\text{sp}} \), exhibits two temperature regimes at long timescales. The low-temperature regime is consistent with persistent heterogeneity and subdiffusive transport, and is similar to that in \( \beta \)-aluminas, while the high-temperature regime remains distinct.

This difference highlights the distinct diffusion mechanisms between the \( \beta″ \) and \( \beta \) structures. Because of its two non-equivalent mobile-ion sites (Fig. 1c), single hops in Na \( \beta \)-alumina create dynamic heterogeneity, and only double hops constitute diffusion events at all temperatures. In Na \( \beta″ \)-alumina, with one type of mobile-ion site (Fig. 1b), at high temperatures, single hops suffice for diffusion, but the low-temperature regime also requires diffusion by double hops. Notably, this low-temperature regime is absent in K \( \beta″ \)-alumina (Extended Data Fig. 2). We investigate the origin of the low-temperature regime in Na \( \beta″ \)-alumina and of its absence in K \( \beta″ \)-alumina below.

Finally, the relative variance in the average tMSD for an arbitrary short timescale \( t \) (EB) should collapse with the inverse of the overall length of simulation (\( \Delta \)) for the ergodic assumption to hold\(^{16-18,42}\). However, this does not hold at \( \leq 300 \text{ K} \) for any simulated material and is only reached at elevated temperatures (Extended Data Fig. 7). Thus, at room temperature, the diffusion of mobile ions in both Na \( \beta \)- and \( \beta″ \)-alumina remains weakly non-ergodic within \( \Delta = 100 \text{ ns} \), and the trajectories of individual ions remain distinguishable to macroscopic timescales. This is consistent with experimentally

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**Fig. 2 | Ion diffusion in Na \( \beta″ \)-alumina.**  
**a.** tMSD of mobile ions.  
**b.** Exponent of tMSD versus time-averaged displacement of ions. For the same average displacements, the exponent at \( \leq 300 \text{ K} \) is lower than at \( \geq 473 \text{ K} \). In b, the horizontal guide is the Fickian limit \( t^1 \), and the vertical line is one unit cell (5.6 Å, 2 hops).  
**c.** Time slices of the distribution of ion displacements \( \Delta x \) along [100] at 300 K.  
**d.** Distributions of ion displacements \( \Delta x \) along [100], each rescaled by its standard deviation \( \sigma_{x} \). Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively.  
**e.** The probability \( G_{x} \cdot t \) of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position after a time lag \( t \). The yellow circles denote the times of decay to 1/e, where \( e \) is the base of the natural logarithm. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is \( \leq 10\% \).  
**f.** \( C_{p} \) with 1- and 2-hop relaxation times as derived from e, shown as yellow circles. In b and f, short-time checks of the ballistic limits (dashed), tMSD \( \propto t^2 \) and \( C_{p} \rightarrow 2 \), respectively, used short, 250 ps trajectories. Corresponding metrics for other simulated materials are shown in Extended Data Figs. 1–6.
Fig. 3 | In-plane ionic conductivity in $\beta^\prime$-alkaline earth metals. a–c, Simulated a.c. frequency spectra: Na $\beta^\prime$-alumina at 230 K, 300 K and 473 K (a); Na $\beta$-alumina at 300 K (b); Ag $\beta$-alumina at 300 K (c). d–f, Arrhenius relations: Na $\beta^\prime$-alumina (d); K and Ag $\beta^\prime$-alkaline earth metals (e); Ag, Na and K $\beta$-alkaline earth metals (f). Filled symbols in a–c represent literature measurements of electrical impedance. In d–f, $t = 2.5$ ns (400 MHz), and error bars denote 20th–80th percentiles of the sampled eMSD. Power-law scaling relations (grey lines in a–c) are guides to the eye, not fits.

observed non-Debye dispersion of a.c. conductivity in large single crystals$^{25–27}$. For practical applications, our key findings of subdiffusion and ergodicity breaking imply that singular, constant-valued transport coefficients in the d.c. limit at 300 K cannot be derived. For finite applied bias and finite passed currents (Supplementary Note 9), a d.c. limit exists due to the thermodynamic uncertainty relation$^{29}$, but within $\Delta = 100$ ns of unbiased simulation, this limit is not reached here. We discuss simulations with applied electric fields and the differences between our work and subdiffusive transport in semiconductors$^{46}$ in Supplementary Note 9.

**Ionic conductivity**

Due to non-Fickian diffusion and deviations from ergodicity in our simulations, we adopt a stochastic diffusion framework to calculate the a.c. ionic conductivities directly from the mean-square charge displacement via the eMSD. The values of eMSD sampled from the simulated 100-ns trajectories for any given time lag $t$ in the ps–ns range are distributed exponentially, with one parameter sufficient to describe both the mean and variance at each $t$ (Extended Data Fig. 8). We compare the conductivities calculated using the means of eMSD distributions with literature experimental a.c. conductivity spectra of $\beta^\prime$-$\beta^\prime$-alkaline earth metals at frequencies $\nu = 1/t$ (Fig. 3a–c) and $\sigma \propto \nu^{\alpha}$ for Na and Ag $\beta$-alkaline earth metals at 300 K (Fig. 3a–c) and $\sigma \propto \nu^{\alpha}$ for Na and Ag $\beta$-alkaline earth metals at 300 K (Fig. 3a–c). More importantly, our simulations reproduce the weaker dispersion $\sigma \propto \nu^{\alpha}$ that extends to lower frequencies at room temperature, in agreement with measurements of centimetre-size single crystals$^{25–27}$ (Fig. 3a–c). In our simulations, this additional dispersion disappears at elevated temperature, concurrent with the disappearance of anomalous diffusion. This is consistent with the power-law form of hopping relaxation at long time lags extending beyond a stretched exponential (Fig. 2e and Supplementary Note 1): the conductivity extrapolated towards the d.c. limit using the relaxation converges only if the asymptotic limit of $\nu \to 0$ is sampled. These results suggest that the long-time dispersion of a.c. conductivity extending to macroscopic timescales is a consequence of the anomalous diffusion, and the decay of $\sigma_0$ towards zero characterizes its timescale.

For the longest time lag used, $t = 2.5$ ns, we also compare our results to previous experimental measurements in the low-frequency limit$^{26,30,33,48–50}$ (Fig. 3d–f) while acknowledging that at low temperatures, the simulated conductivities overestimate experimental ones because of the remaining frequency dispersion. The agreement of simulated a.c. and low-frequency conductivities with experiment for Na and K $\beta^\prime$-alkaline earth metals is better than within a factor of 2 at $\geq 300$ K. This provides further validity that our simulations successfully model the macroscopic performance of $\beta^\prime$-alkaline earth metals at room temperature.

For $\beta^\prime$-alkaline earth metals, except for Ag, simulated conductivities underestimate experiments (Fig. 3b,c,f). However, the discrepancy propagates...
from the fastest, vibrational timescales and does not arise from long-time behaviour discussed here. The good agreement for Ag β'-alumina (Fig. 3c) most likely comes from using two-coordinate Ag, for example, in Ag₂O, as a model for the Ag–O interaction; no natural analogues for Na/K exist. The ability of Ag to effectively shrink in a two-coordinate configuration underpins fast ionic conduction in Ag β'-alumina, while Ag β''-alumina is instead the slowest of its family. It is likely that our simulation underestimates the success rates of hops into the high-energy anti-Beevers–Ross (aBR) sites in Ag (b). K (c) and Na (d) β''-aluminas at 600 K. All colour scales are normalized to the noted maximum rates (yellow). For example, the highlighted square in b corresponds to a rate of 71 ± 1.3 diffusion events per edge per nanosecond from sites located next to four Mg₆Al defects to sites located next to three Mg₆Al defects. The uncertainty value is a standard error over the edges that fit this criterion. e–g. Distributions of relative Helmholtz free energies for all conduction-plane sites in Ag (e), K (f) and Na (g) β''-aluminas at 600 K, when ergodicity is shown to hold, aggregated by whether each site has one ‘direct’ Mg₆Al defect neighbour (blue) or none (orange) as defined in a. Boxes, first and third quartiles; centre line, median; limits, minimum and maximum.

**Fig. 4 | Site energetics in β''-aluminas.** a. Schematic of two types of Mg₆Al defect positions relative to conduction-plane sites: directly in the centre (bottom) and offset to a corner (top). The example conduction-plane site shown in a is counted as having two Mg₆Al neighbours. Both distances are ≈6 Å. b–d. Rates of diffusion, in units of hops per edge and per nanosecond, classified by their sites of origin (horizontal axes) and destination (vertical axes), in Ag (b), K (c) and Na (d) β''-aluminas at 600 K. All colour scales are normalized to the noted maximum rates (yellow). For example, the highlighted square in b corresponds to a rate of 71 ± 1.3 diffusion events per edge per nanosecond from sites located next to four Mg₆Al defects to sites located next to three Mg₆Al defects. The uncertainty value is a standard error over the edges that fit this criterion. e–g. Distributions of relative Helmholtz free energies for all conduction-plane sites in Ag (e), K (f) and Na (g) β''-aluminas at 600 K, when ergodicity is shown to hold, aggregated by whether each site has one ‘direct’ Mg₆Al defect neighbour (blue) or none (orange) as defined in a. Boxes, first and third quartiles; centre line, median; limits, minimum and maximum.
the lattice, sites with more defect neighbours are attractors of mobile ions and are on average more fully occupied (with lower average Helmholtz free energies by \(\sim 25–30\) meV per neighbour).

The more interesting comparison is between sites of different types (`direct' or `offset') for an equal total number of \(\text{Mg}_\text{Al}\) defect neighbours. In Ag and Na \(\beta''\)-aluminas, the sites with a `direct' neighbouring defect (Fig. 4e–g, blue) are more attractive than sites without them (Fig. 4e–g, orange), by \(\sim 60\) and \(\sim 40\) meV, respectively. This energetic difference causes `offset' sites to anchor the mobile-ion vacancy ordering at low temperatures (Supplementary Note 2) and is responsible for the increased low-temperature activation energy. In K \(\beta''\)-alumina, the sites with and without `direct' \(\text{Mg}_\text{Al}\) defect neighbours are energetically indistinguishable, and the activation energy remains almost constant with temperature (Fig. 3e).

The site-specific diffusion rates and free energies for \(\beta''\)-aluminas, corresponding to Fig. 4, calculated for 1,000 K (Supplementary Fig. 6), show average free energy differences between BR and aBR sites higher than the simulated activation energy for conduction, as in previous studies\(^4\). This result suggests that an interstitiality-like knock-on mechanism where the repulsion between mobile ions transiently comprising an interstitial pair on neighbouring BR and aBR sites lowers the energy barrier for hopping.

**Defects drive heterogeneity in transport dynamics**

Static energetics predict vacancy ordering but do not explain why diffusion proceeds via distinct sites among the three \(\beta''\)-aluminas (Fig. 4b–d). Hence, we quantify the location-dependent kinetics of diffusion events. The memory of a hop's origin is characterized by the residence-time-dependent deviation from unity of the correlation factor \(f = (1 + (\cos \theta)) / (1 - (\cos \theta))\), where \(\theta\) is the angle between consecutive hops. In \(\beta''\)-aluminas, \(f\) is near-zero at short residence times and increases for longer residence times towards the random value of 1 (Fig. 5). At 300 K, the timescales for this randomization are longer than 2-hop relaxation times (Fig. 5, yellow circles). Instead, the timescale of \(\theta = 0\) is the best descriptor of the kinetics of memory loss. This is consistent with the derivation of \(\theta\) from the evolution of a random-walker's environment\(^6,4\) and with Funke's dynamic relaxation model\(^1\). At 300 K, all diffusion events are non-random. This is consistent with a simple mechanism for dynamic relaxation: an ion randomizes following a hop only as fast as other ions also hop around it. Additionally, a waiting-time memory is present, as for a continuous-time random walk, at short residence times (Supplementary Note 3).

The shading around the average curves in Fig. 5 shows the location dependence of \(f\) or relaxation kinetics for sites with different numbers of neighbouring \(\text{Mg}_\text{Al}\) defects. This defect-induced heterogeneity of relaxation kinetics is largest for Ag (wide shaded regions in Fig. 5a), smaller for Na (Fig. 5c) and negligible for K (Fig. 5b).

For Na and Ag \(\beta''\)-aluminas, hops to sites with fewest neighbouring defects are fastest to randomize (Fig. 5a,c, top/left edges of the shaded regions), explaining the fact that these emptier sites contribute most to diffusion (Fig. 4b,d). By contrast, slower relaxation at sites with more neighbouring defects (Fig. 5a,c, bottom/right edges of the shaded regions) impedes diffusion at those sites. The overall diffusivity of ions in Na and Ag \(\beta''\)-aluminas is location-dependent on the nanometre scale, determined by the distribution of charge-compensating defects, despite the defects being \(\approx 6\) Å away within rigid spinel blocks. By contrast, in K \(\beta''\)-alumina, the memory timescale is independent of location (the location-resolved curves in Extended Data Fig. 9, corresponding to the shading in Fig. 5b, coincide), and a site's contribution to diffusion tracks its time-average occupancy (Fig. 4c,f). This is consistent with repulsions between the K ions dominating the attraction between K ions and static defects. We conclude that repulsion between mobile ions drives conductivity in K \(\beta''\)-alumina.

The location dependence of dynamic relaxation is exacerbated in \(\beta''\)-aluminas (Extended Data Fig. 9): the charge-compensating oxygen interstitial is doubly charged and located immediately adjacent to mobile ions. The interstitial associates or binds mobile ions in a defect cluster\(^7,26\). In \(\beta''\)-aluminas, the slow (\(\geq 10\) ns at 600 K) exchange of mobile ions between free and defect-bound states determines the timescale of reaching ergodicity. We propose that this slow exchange and the resulting location dependence of ion mobility drive the dispersion of conductivity (\(\sigma \propto \nu^{-1}\) regime in Fig. 3a–c) at 300 K, the same way the ordering of mobile-ion vacancies does in \(\beta^-\)-aluminas.

**Tuning disorder and conductivity with processing**

Finally, we consider tuning the relative positions of defects, as they may be engineered with processing\(^1,5,4\). Our simulation shows that sites without `direct' \(\text{Mg}_\text{Al}\) neighbours anchor the ordering
of mobile-ion vacancies in Na \( \beta'' \)-alumina. Whereas in a slowly cooled material the ‘direct’-neighbour sites belong to half of the six possible \( \sqrt{3} \times \sqrt{3} \) conduction-plane sublattices, and vacancy ordering proceeds on the other sublattices, quenching distributes ‘direct’-neighbour sites randomly between the sublattices (Supplementary Note 2). This makes all sublattices equivalent, destabilizes the ordering of mobile-ion vacancies and increases room-temperature conductivity to match the high-temperature regime. The effect is absent in K \( \beta'' \)-alumina (Supplementary Fig. 3), where repulsions between mobile ions control conductivity.

In the \( \beta \)-aluminas, mobile ions screen the Coulomb field of oxygen interstitials at the expense of forming defect clusters (Supplementary Note 4) that directly block diffusion pathways. This could further hinder diffusion by isolating a fraction of mobile ions in tortuous landscapes between the stationary clusters and is termed ‘geometric crowding’\(^{17,19}\). If present, crowding would be expected to manifest as increased dispersion when tMSD of mobile ions becomes comparable to the distances between defects. We simulate two quasi-random distributions of interstitials in Na \( \beta \)-alumina (Supplementary Note 5): located \( \geq 1 \) site apart (more disordered), and located \( \geq 4 \) sites apart (more ordered). The simulation with the higher disorder exhibits lower conductivities at long time lags, but not at short ones, and higher heterogeneity of dynamics (Supplementary Fig. 8). In our simulation, disorder among interstitials decreases conductivity by \( \approx 50\% \) at 1 ns. All features are consistent with increased geometric crowding when interstitials are disordered. Due to the different effects of the Coulomb field of charge-compensating defects in \( \beta'' \)-aluminas versus \( \beta \)-aluminas (extended vacancy ordering versus formation of blocking clusters), processing that yields a kinetically controlled (quenched, disordered) distribution of defects improves the former, but thermodynamic control (ordered, well-separated defects) improves the latter.

Towards multiscale modelling of ion conduction

Here, we have investigated how charge-compensating defects drive subdiffusive transport dynamics in model solid-state ion conductors. By accounting for anomalous diffusion using an effective stochastic approach, we reproduce the frequency dispersion of a.c. conductivity in the Jonscher regime (\( \sigma(\nu) \propto \nu^{0.6} \)), and at lower frequencies (\( \sigma(\nu) \propto \nu^{-2} \)). The latter is caused by the slow kinetics of exchange of mobile ions between lattice sites and immobilized within defect clusters (\( \beta \)-aluminas), or within a mobile-ion/vacancy superlattice (\( \beta'' \)-aluminas). Our new approach quantitatively predicts macroscopic ionic conductivity even with subdiffusive dynamics.

\( C_0 \) characterizes the location-dependent dynamic relaxation that accompanies diffusion events and the influence of hidden degrees of freedom on diffusion. The decay of this object to zero, that is, the loss of both waiting-time (Supplementary Figs. 1, 5 and 6) and orientational (Fig. 5) memory, corresponds to the production of entropy in the Jonscher regime (\( \sigma(\nu) \propto \nu^{0.6} \)), and at lower frequencies (\( \sigma(\nu) \propto \nu^{-2} \)). The latter is caused by the slow kinetics of exchange of mobile ions between lattice sites and immobilized within defect clusters (\( \beta \)-aluminas), or within a mobile-ion/vacancy superlattice (\( \beta'' \)-aluminas). Our new approach quantitatively predicts macroscopic ionic conductivity even with subdiffusive dynamics.

Furthermore, comparing the timescales at which \( C_0 \) peaks with 1-hop and 2-hop relaxation timescales yields the mechanism of diffusion. In \( \beta'' \)-aluminas, a switch from diffusion via double hops at the edges of ordered domains at low temperature to unimpeded diffusion via single hops at high temperature is consistent with the decrease of the activation energy upon heating. However, since the spatial distribution of charge-compensating defects anchor the local energetic disorder and room-temperature ordering of mobile ions, we conclude that the room-temperature subdiffusive transport and the switch of dynamic regimes upon heating are both ultimately driven by defect chemistry. Finally, using quenching in \( \beta'' \)-aluminas\(^{13}\) and geometric crowding by interstitials in \( \beta \)-aluminas as examples, we demonstrate new mechanistic insights into processing–disorder–performance relationships of solid electrolytes. In both cases, a redistribution of charge-compensating defects modulates practical ionic conductivity. Our approach highlights the mechanisms by which thermodynamic versus kinetic control of defect distributions during processing controls performance.

In general, we present a quantitative framework for ionic conduction between the atomistic and macroscopic timescales, which is a key enabler of ‘atoms-to-devices’ multiscale modelling. We show that information about atomistic quantities is necessarily lost in order for the system to reach an ergodic regime. Our statistical-mechanics approach, benchmarked to experimental a.c. conductivity, offers pathways for the understanding and optimization of contemporary ion conducting electrolytes for many energy-related applications. Our study informs further investigations of mechanistic descriptors of collective and non-equilibrium transport phenomena.

Online content

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Methods

General methods. The python packages pandas, tensorflow and networkx were used extensively to generate the quasi-random structures. The perceptually uniform barlow colour scheme was adapted for many visualizations.

MD simulations. Buckingham (exponent + sixth power) pairwise potentials were used with a long-range Coulombic cutoff at 12 Å. These were first developed for Na β-alumina and have been used extensively since. All simulations were carried out using the LAMMPS simulation package using a Nose-Hoover thermostat. All ionic charges were integral, that is, +1 for all mobile ions, etc. Every simulation was started with the same random seed. The simulation volume was annealed at 1,000 K for 20 ps at constant pressure (NPT ensemble), cooled to simulation temperature over 6 ps and simulated at fixed volume (NVT ensemble) for (for ensemble controls, see Supplementary Note 8) run of length $\Delta = 100$ ns with a timestep of 1 fs to accumulate hopping events and average statistical descriptors for long time lags. The only simulation executed for $\Delta = 300$ ns was Na β-alumina at 230 K. The simulations of ‘quenched’ K and Ag β-alumina were executed for $\Delta = 10$ ns.

Quasi-random placement of charge-compensating defects. Little is known about the precise locations of the oxygen interstitials $O_i^\prime$ in β-aluminas relative to one another. Here, we make an assumption of thermodynamic control over their relative distribution. Since they carry a $\pm 2$ charge each, they should repel each other, but we are aware of no evidence for a defect superlattice in β-aluminas. We assumed that during crystal synthesis, typically multiple days above 1,500°C and slow cooling, the $O_i^\prime$ defects are relatively mobile and settle to a thermodynamically favourable arrangement, that is, far away from one another. For simulation, the interstitials were placed quasi-randomly within the conduction planes starting with a defect-free material, with a minimum distance of five lattice planes (Beevers–Ross or ABR) between closest defects. This was the maximum distance attainable with an otherwise-random placements of defects. From 30 randomly generated configurations of defects, one was picked with the lowest $z$ score for the distribution of the number of defects versus distance from nearest defect to ensure the structure could be considered representative for the given set of constraints. Similar algorithms were used to simulate a more random distribution of defects. A representative configuration was chosen with a less restrictive constraint, minimum distance of two sites between nearest defects. This example modification is one possible response to processing conditions in β-aluminas, but not the only one.

For β-aluminas, MgAl′ defects were substituted onto Al(2) sites according to experiments of crystallographic studies: only one half of Al(2) sites was used to approximate the ‘un-symmetric’ distribution. Each Mg defect is ‘directly’ above or below one conduction-plane site, and ‘offset’ from sites— but in a second conduction plane. Each conduction-plane site is affected by the defects on both sides of the conduction plane. Within the ‘un-symmetric’ distribution of defects, any conduction-plane site has at most one ‘direct’ Mg defect associated with it, and at most three ‘offset’ ones. For comparison, a quenched distribution of defects (Supplementary Fig. 10) was simulated by placing the Mg substituents randomly on any Al(2) sites enforcing a minimum separation of one Al(2) between them as above for β-aluminas. Up to two ‘direct’ defect neighbours are possible for a conduction-plane site in this case, one above and one below.

Multiple-starts sampling and statistical quantities. The NPG and $C_d$ were computed as follows. The 100-ns trajectory of each ion was subdivided into 50-ns chunks starting at 0 simulation time, and spaced 70 ps apart, until 50 ns, approximately 700 starts for each ion. From all these, taken together for all mobile ions, etc. Every simulation was started at 0 time lag $t$ and $\Delta = 20$ ps and varying subsets of the overall simulation length (starting at the beginning of the simulation) as: $C_d (t, \Delta) = \frac{t}{2 \langle \Delta^2 (t) \rangle}$

Song et al. proposed that the relaxation of dynamic heterogeneity $C_d \rightarrow 0$ necessarily precedes EB.$\Delta^4$. This holds for all simulated materials, and most clearly in Ag β-alumina (Extended Data Fig. 4), where at 600 K, the former occurs at $t = 10$ ns, and the latter at $\Delta = 20$ ns. We propose that tests for $C_d \rightarrow 0$ and EB.$\Delta^4$ can serve as benchmarks for the extraction of constant-valued transport coefficients and d.c.-limit conductivities from large-scale simulations of ion conductors.

Centre-of-mass diffusion coefficient and conductivity. The centre-of-mass displacement of the mobile ions is recorded directly in LAMMPS. It is referenced to the rest frame of the host lattice by subtracting the lattice centre-of-mass displacement, which is especially important for simulations with an electric field. Here, we denote the corrected displacement of the centre-of-mass of mobile ions within the simulation volume $V$: $\sigma(t) = \frac{1}{V} \frac{q N_i^2}{k_B T} D_{\mathrm{C-M}}(t)$

This is plotted in Fig. 3 but sampled with the independence of sampled trajectories enforced, versus inverse time lag $t$, which corresponds to a frequency. Given that $D_{\mathrm{C-M}}(t)$ is distributed exponentially for all time lags used (Extended Data Fig. 8), the expectation value of $D_{\mathrm{C-M}}(t)$ also characterizes the standard error. If the distribution were to have a different shape, the standard errors would need to be noted individually for each time lag.

Hopping statistics. Coordinates within the simulated conduction planes are assigned to Beever-Ross and ABF sites based on a 2D Voronoi tessellation using O(5) of the Voronoi polygons. For the trajectory of a mobile ion, a hopping event is recorded every time the site whose centre is closest to the ion changes. This is a simpler hop detection algorithm than others, and in principal, it could overlook ‘incomplete’ hops with subpicosecond residence times. Since we focus on the behaviour at longer timescales, ‘incomplete’ hops do not affect the hopping statistics.
not affect any results or conclusions. This approach also simplifies the recording of back-hops for the analysis of dynamic relaxation (Fig. 5 and Extended Data Fig. 9). Within a series of hopping events by an ion, diffusion events are hops that are followed by another hop to a new (third) site, while hops that are immediately reversed do not directly contribute to diffusion.

Hopping locations. As with the placement of defects, each conduction-plane mobile-ion site (that is, the Voronoi polygon) is referenced by its distance to the nearest defect (for β) or by the number of defects adjacent to it above and below the conduction plane (for β'). Each hop is mapped to an origin site and a destination site. The non-returning hops, that is, a hop from site A to site B followed by a hop to site C, are diffusion events. The last hop for each ion within a simulation was discarded, as its outcome is indeterminate. The 2D matrices in Fig. 4b–d and Supplementary Fig. 7a–d show the rates of diffusion events by their origin (horizontal axis) and destination (vertical axis) for β–aluminas at 600 K and β–aluminas at 1,000 K, respectively.

Site occupancy. The occupancies of every site are calculated by summing the residence times of all the hops into that site, plus the initial occupancy starting at time zero and ending with the first hop out of the site, and dividing by the total duration of the simulation (Δt). For simulations where ergodicity is verified using Cβ→0 and EB→0 (600 K for β–alumina, and 1,000 K for β–aluminas), the occupancies can be assumed to have reached a thermal steady state. In that case, the occupancies of each site reflect a Maxwell–Boltzmann distribution of Helmholtz free energies, with each site as a distinct state with degeneracy 1. This includes both ion–host and ion–ion interactions. This quantity is plotted in Fig. 6e–g, disaggregated by the ‘geographic’ site descriptor (the count of neighbouring defects) for β–aluminas at 600 K. For β–aluminas, the corresponding calculation is performed at 1,000 K (Supplementary Fig. 7) given that the distributions of trapping times near defects extend throughout the simulation at lower temperatures (Supplementary Fig. 8) and ergodicity cannot be assumed to be reached at 600 K and 300 K. If the calculation is attempted when ergodicity does not hold (simulation length too short for the temperature), the difference in energies between, for example, aBR and BR sites is underestimated.

Simulations with applied d.c. and a.c. fields. We also simulate the response of mobile ions in β– and β–aluminas to d.c. and a.c. electrical fields of strength 10–100 kV cm⁻¹ applied along the [100] crystal direction. The application of such strong fields dissipates large amounts of heat, and we apply aggressive cooling to the host lattice by maintaining separate thermostats for the mobile ions, AlO₄ blocks and the in-plane and interstitial oxygens, all set to the same temperature. The time constant of the NVT thermostat does not make an appreciable difference (within 10 fs to 1 ps) and is left at 10 fs as for the unbiased simulations. The electric field is applied to the entire simulation. To avoid the ‘flying ice cube’ effect, we account for net currents, that is, the net translation of mobile ions past the host lattice, by exempting the centre-of-mass motions from thermostatting, which suffices to yield stable temperatures. The present method allows for an easy accounting of net currents through the simulation.

Data availability

The scripts and templates to generate simulation structures and to run simulations and analyses are available at https://github.com/apoletayev/anomalous_ion_conduction. Source data are provided with this paper.

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Author contributions

A.D.P. initiated the application of anomalous–transport concepts and conceptualized the study with advice and support from A.M.L. A.D.P. carried out simulations with instruction and help from I.A.D. and advice from M.S.I. A.D.P. carried out analysis. A.M.L. advised and supervised the work. All authors contributed to the writing of the manuscript.

Competing interests

The authors declare no competing interests.

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Extended Data Fig. 1 | Ion diffusion in Na\(\beta\)-alumina. \(\textbf{a}\), tMSD of mobile ions. \(\textbf{b}\), exponent of tMSD vs time lag, plotted against the time-averaged displacement. The exponent does not reach unity until displacements are \(\geq\) distances between defects. In \(\textbf{b}\), the horizontal guide is the Fickian limit \(t^1\), and the vertical line is one unit cell (5.6 Å, 2 hops). \(\textbf{c}\), Time slices of the distribution of ion displacements \(\Delta x\) along [100] at 300 K. \(\textbf{d}\), Distributions of ion displacements \(\Delta x\) along [100], each rescaled by its variance \(\sigma_{\Delta x}\). Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively. \(\textbf{e}\), The probability of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is \(\leq\)10%. \(\textbf{f}\), Diffusion kernel correlation \(C_D\). \(C_D\) peaks between one-hop and two-hop relaxation times at all simulated temperatures. In \(\textbf{b}\) and \(\textbf{f}\), short-time checks of the ballistic limits (dashed), tMSD \(\propto t^2\) and \(C_D \to 2\), respectively, used 100-ps trajectories recorded every 1 fs.
**Extended Data Fig. 2 | Ion diffusion in K β”-alumina.** a, tMSD of mobile ions. b, exponent of tMSD vs. time lag, plotted against the time-averaged displacement. In b, the horizontal guide is the Fickian limit $t^f$, and the vertical line is one unit cell (5.6 Å, 2 hops). c, Time slices of the distribution of ion displacements $\Delta x$ along [100] at 300 K. d, Distributions of ion displacements $\Delta x$ along [100], each rescaled by its variance $\sigma_{\Delta x}$. Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively. e, The probability of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is ≤10%. f, Diffusion kernel correlation $C_D$. Notably, unlike in Na β”-alumina (Fig. 2), $C_D$ has multiple peaks. In b and f, short-time checks of the ballistic limits (dashed), tMSD $\propto t^2$ and $C_D \to 2$, respectively, used 100-ps trajectories recorded every 1 fs.
Extended Data Fig. 3 | Ion diffusion in Na β″-alumina with a quenched distribution of Mg′Al defects. **a**, tMSD of mobile ions. **b**, exponent of tMSD vs. time lag, plotted against the time-averaged displacement. In **b**, the horizontal guide is the Fickian limit t1, and the vertical line is one unit cell (5.6 Å, 2 hops). The diffusion is Fickian (**a**, **b**) by contrast with Na β″-alumina without quenching (Fig. 2). **c**, Time slices of the distribution of ion displacements Δx along [100] at 300 K. **d**, Distributions of ion displacements Δx along [100], each rescaled by its variance σΔx. Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively. **e**, The probability of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is ≤10%. **f**, Diffusion kernel correlation C(t). Unlike the non-Gaussian parameter, C(t) has multiple peaks at 300 K. In **b** and **f**, short-time checks of the ballistic limits (dashed), τMSD ∝ t and C(t) → 2, respectively, used 100-ps trajectories recorded every 1 fs.
Extended Data Fig. 4 | Ion diffusion in Ag β-alumina. a, tMSD of mobile ions. b, exponent of tMSD vs. time lag, plotted against the time-averaged displacement. As for Na β-alumina, the exponent does not reach unity until displacements are ≥ distances between defects. In b, the horizontal guide is the Fickian limit $t^1$, and the vertical line is one unit cell (5.6 Å, 2 hops). c, Time slices of the distribution of ion displacements $\Delta x$ along [100] at 300 K. d, Distributions of ion displacements $\Delta x$ along [100], each rescaled by its variance $\sigma_{\Delta x}$. Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively. e, The probability of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is ≤10%. f, Diffusion kernel correlation $C_D$. As for Na β-alumina, $C_D$ peaks between one-hop and two-hop relaxation times at all simulated temperatures. In b and f, short-time checks of the ballistic limits (dashed), $tMSD \propto t^2$ and $C_D \to 2$, respectively, used 100-ps trajectories recorded every 1 fs.
Extended Data Fig. 5 | Ion diffusion in Ag β″-alumina. a, tMSD of mobile ions. b, exponent of tMSD vs. time lag, plotted against the time-averaged displacement. In b, the horizontal guide is the Fickian limit $t^1$, and the vertical line is one unit cell (5.6 Å, 2 hops). c, Time slices of the distribution of ion displacements $\Delta x$ along [100] at 300 K. d, Distributions of ion displacements $\Delta x$ along [100], each rescaled by its variance $\sigma_{\Delta x}$. Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively. e, The probability of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is ≤10%. f, Diffusion kernel correlation $C_D$. In b and f, short-time checks of the ballistic limits (dashed), tMSD $\propto t^2$ and $C_D \rightarrow 2$, respectively, used 100-ps trajectories recorded every 1 fs.
Extended Data Fig. 6 | Ion diffusion in Kβ-alumina. a, tMSD of mobile ions. b, exponent of tMSD vs. time lag, plotted against the time-averaged displacement. As for Naβ-alumina, the exponent does not reach unity until displacements are ≥ distances between defects. In b, the horizontal guide is the Fickian limit t1, and the vertical line is one unit cell (5.6 Å, 2 hops). c, Time slices of the distribution of ion displacements Δx along [100] at 300 K. d, Distributions of ion displacements Δx along [100], each rescaled by its variance σΔx. Laplace and Gaussian distributions are shown as black and grey dotted lines, respectively. e, The probability of an ion remaining within 1.7 Å (<1 hop, dashed) or 4.6 Å (<2 hops, solid) of an initial position. The relative change in the timescale due to varying the distance cutoff by 0.1 Å is ≤10%. f, Diffusion kernel correlation C0. In b and f, short-time checks of the ballistic limits (dashed), tMSD ∝ t² and C₀ → 2, respectively, used 100-ps trajectories recorded every 1 fs.
Extended Data Fig. 7 | Ergodicity breaking parameter (EB) versus simulation length \( \Delta \). a–c, \( \beta'' \)-aluminas. d–f, \( \beta'' \)-aluminas with a simulated distribution of defects corresponding to quenching. g–i, \( \beta \)-aluminas. The time lag used in all cases was \( t = 20 \) ps, but the asymptotic dependences at long simulation lengths are not sensitive to the precise value of \( t \) for \( \Delta \gg t \). The noted power-law relations are guides to the eye, not quantitative fits. In all simulations where \( EB \propto \Delta^{-1} \), \( C_{\alpha} \to 0 \) precedes it. This is seen most clearly in Ag \( \beta \)-alumina at 600 K (g), where \( C_{\alpha} \to 0 \) for \( t \approx 10 \) ns (Extended Data Fig. 4), and \( EB \propto \Delta^{-1} \) starting at \( \Delta \approx 20 \) ns.
Extended Data Fig. 8 | Distributions of the centre-of-mass diffusion coefficient $D_{\text{COM}}$ in Na$^{+}$-alumina. 

(a–d) Absolute values, rescaled by the standard error at each time lag. 

(a,e) 230 K, (b,f) 300 K, (c,g) 473 K, (d,h) 600 K. The rescaled distributions (e–h) are exponential. Notably, at 230 K, the distribution becomes wider rather than narrower with increasing time lag, suggesting the possibility of further glass-like collective dynamics at long timescales. At 230 K, the ordering of the mobile ions extends across the entire simulation cell within each conduction plane (Supplementary Fig. 2).
Extended Data Fig. 9 | Correlation factor $f$ for hops, disaggregated by location relative to defects, versus hop residence times. a–c, $\beta$'-aluminas. d–f, $\beta$-aluminas. For $\beta$-aluminas, hops starting in the low-energy Beevers-Ross sites are considered here. The sites with the most neighbouring defects (for $\beta$') or those closest to defects (for $\beta$) have the lowest correlation factor for a given residence time. Yellow symbols: two-hop relaxation time from $G_s$. Black horizontal ranges: $C_0 \to 0$ at 600 K. At 300 K, $C_0 \to 0$ only for K $\beta$'-alumina.