Compared is (a) the calculated $B_1$, $B_3$, and $B_4$ diffusion coefficients with (b) the average rates of calculated diffusion events.

**Fig. S1.** (a) $\text{Ag}^+$ diffusion coefficients, $D(\text{Ag}^+)$; (b) Calculated rates of diffusion events, $\nu$(diffusion events).

**Assignment of Diffusion Events and the Construction of Chains**

Fig. S2 illustrates schematically the process of identifying diffusion events from simulation trajectories, and combining these into chains. (a) Lattice sites and ions are distinguishable throughout the simulation trajectory. (b) During the simulation trajectory, if an ion moves from one lattice site to a second, this is classified as a diffusion event, characterised by the initial and final lattice site labels, and the label of the participating ion. (c) Identifying diffusion events with common pairs of initial and final sites allows the construction of a chain of diffusion events.

**Fig. S2.** Schematic of the process of identifying diffusion events, and combining these into chains.
Effect of time window length on stoichiometric PMFs

Fig. S3 shows PMFs for k diffusion events observed in time Δt for stoichiometric B4 AgI at 550 K, for Δt between 2500 timesteps (∼ 12.1 ps) and 62500 timesteps (∼ 307.5 ps). For each time window the calculated diffusion event PMF differs qualitatively from the corresponding exact Poisson distribution.

Cramér–von Mises goodness-of-fit statistics

The goodness-of-fit between an empirical statistical population and a reference distribution can be quantified using Cramér–von Mises statistics, which have been described for discrete distributions by Choulakian et al [1, 2]. For a discrete time distribution, the probability of counting k events in time window Δt is p_k. For n independent observations, the number of observations of k events is o_k, and the expected number of observations with k events is e_k = np_k. The Cramér–von Mises W² statistic is given by

\[ W^2 = \frac{1}{n} \sum_{j=0}^{\infty} Z_j^2 p_j, \]

where

\[ Z_j = \sum_{k=0}^{j} (o_k - e_k). \]

W² is a weighted sum of squared differences between observed and expected cumulative frequency distributions, and smaller values indicate better fit between the observed frequencies and the reference probability distribution.

The “Poissonicity” of the ion-hopping statistics from each simulation can therefore be quantified by calculating W² using p_k values for the Poisson distribution with equal mean (main paper; Eqn. 2). The non-stoichiometric systems, which can be considered reference simulations of conventional hopping transport, have low W² values in the range ~ 1–4 (Table I), with the exception of the B3 excess interstitial simulation (W²_B3-int = 19.35). For the stoichiometric systems W² is much greater—of the order of 1000—showing a significant deviation from exact Poisson behaviour in these simulations.

<table>
<thead>
<tr>
<th></th>
<th>B1</th>
<th>B3</th>
<th>B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>excess interstitials</td>
<td>0.975</td>
<td>19.35</td>
<td>1.731</td>
</tr>
<tr>
<td>excess vacancies</td>
<td>1.322</td>
<td>1.781</td>
<td>3.792</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>1178.0</td>
<td>1155.0</td>
<td>834.2</td>
</tr>
</tbody>
</table>

Table I. Cramér–von Mises W² statistics.

We must still consider the possibility that ion transport in stoichiometric AgI does in fact follow Poisson statistics, and the calculated large W² values are simply an artefact of poor hopping statistics, due to the limited time and length-scales of our atomistic simulations. We assert a null hypothesis: that ion hops in stoichiometric AgI are independent; and use numerical Monte-Carlo simulation to calculate hopping frequencies consistent with this hypothesis. A Poisson process with

FIG. S3. PMFs for k diffusion events observed in time Δt for stoichiometric B4 AgI at 550 K. Filled circles (solid lines) are simulation data. Open circles (dashed lines) show exact Poisson distributions with equivalent values of ⟨k⟩.
FIG. S4. Cumulative distribution functions of Cramér–von Mises $W^2$ statistics; calculated from $10^5$ Monte-Carlo simulated trajectories with Poisson distributed events and equal length and average event rates as the stoichiometric molecular dynamics simulations.

$n$ events observed in $t$ timesteps can be simulated by randomly selecting $n$ integers in the range $0 \rightarrow t$. Each random integer gives a simulated “event” at the corresponding timestep. For each stoichiometric system we consider $10^5$ numerical Monte-Carlo “trajectories”, with lengths and numbers of diffusion events equal to the calculated molecular dynamics trajectories. Every Monte-Carlo trajectory consists of randomly distributed events, and sufficiently long trajectories therefore will have PMFs that converge to exact Poisson distributions. In practice, however, each Monte-Carlo trajectory has non-ideal statistics, and the corresponding PMF differs from an exact Poisson distribution. This deviation can be quantified for every trajectory using the Cramér–von Mises $W^2$ statistic.

The cumulative distribution function for these simulated $W^2$ values gives probabilities $p(W^2 > X)$ that a single molecular dynamics simulation of equal length and average diffusion rate to our real simulations, but where ion hopping is known to occur as a Poisson process, gives an observed frequency distribution with $W^2$ greater than some value $X$. For a simulated Poisson process with the same average rate and total simulation time as our stoichiometric simulations, $p(W^2 > X)$ falls to 0.001 by $X = 10.1$, for $B1$, $X = 10.1$ for $B3$, and $X = 8.88$ for $B4$. The calculated $W^2$ values for the stoichiometric simulations are much larger than these values, and we can reject the null hypothesis that the observed non-Poisson behaviour is an artefact of poorly sampled Poisson behaviour.

Interestingly, the $W^2$ value calculated for the $B3$ interstitial simulation (19.35) is relatively large for pure independent hopping transport; although it is significantly closer to the other non-stoichiometric values than to those of the strongly non-Poisson stoichiometric simulations. This suggests that although Poisson statistics do give a good approximation for hopping rates of interstitials in $B3$ AgI (main paper, Fig. 2), in this case al-}

ternative diffusion mechanisms involving the correlated motion of more than one mobile ion might be competitive with conventional independent hopping, even under non-stoichiometric conditions.

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