–Supporting Information–

Atomic-Scale Influence of Grain Boundaries on Li-Ion Conduction in Solid Electrolytes for All-Solid-State Batteries

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Table S1. Potential model parameters used for Li_3OCl.

Buckingham potentials ($A\exp(-\rho/r)-C/r^6$)			
Interaction	A (eV)	ρ (Å)	C (eVÅ^6)
O^{2-}–O^{2-}	22764.30	0.149	13.19
Li^+–Li^+	360.53	0.161	–
Li^+–O^{2-}	292.30	0.347	–
Li^+–Cl^-	421.04	0.334	–
Cl^-–Cl^-	1227.20	0.321	14.53
Cl^-–O^{2-}	8286.91	0.259	62.20

Table S2. Comparison of calculated and experimental lattice parameters and bond lengths for Li_3OCl.

	Lattice parameter (Å)	Li-O distance (Å)	Li-Cl distance (Å)
This work	3.919	1.960	2.771
X-ray diffraction[1]	3.907	1.954	2.763

Table S3. Li$_3$OCl GB supercell dimensions.

GB	Cell dimensions (x, y, z) (Å)	GB separation (Å)
Σ3(111)	5.88, 10.19, 57.62	28.81
Σ3(112)	5.53, 6.67 57.47	28.74
Σ5(210)	3.91, 8.74, 52.46	26.23
Σ5(310)	3.91, 12.36, 74.19	37.10

Boltzmann distribution

Since four different GBs were considered in this work, we accounted for their ideal Boltzmann distribution according to their respective formation energies, E_{fi}, as tabulated in Table S4:

$$Probability_i = \frac{e^{\frac{-E_{fi}}{kT}}}{\sum_{j=1}^{4} e^{\frac{-E_{fj}}{kT}}} \tag{1}$$
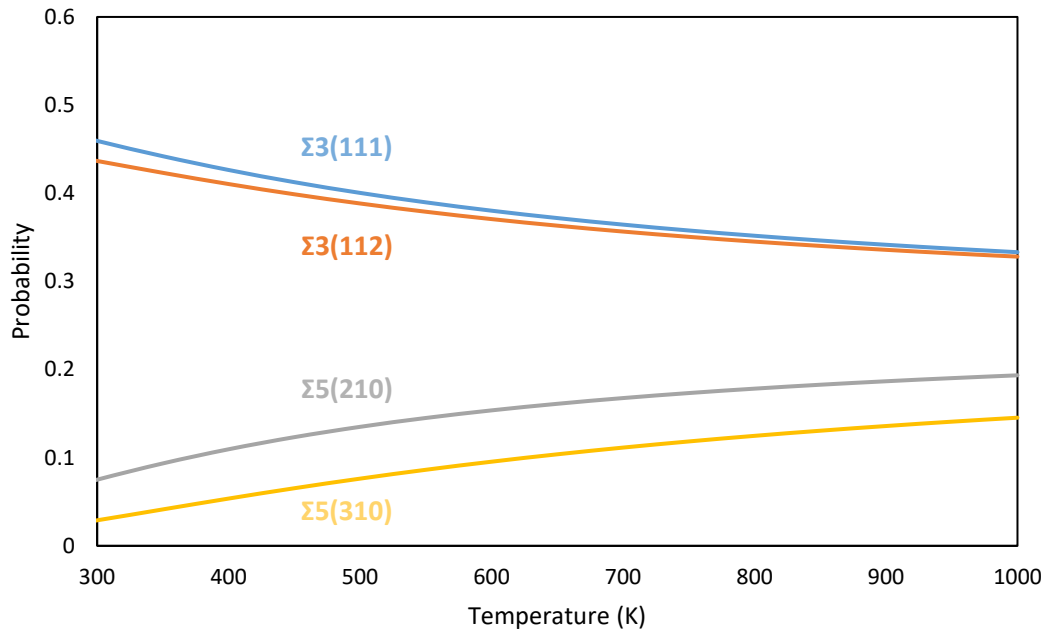

Figure S1. Probability of formation of the four GBs considered in this work according to a Boltzmann distribution.

According to the probabilities of formation shown in Figure S1, the GB with the lower energies of formation are expected to be present in higher concentrations compared to the higher energy ones.
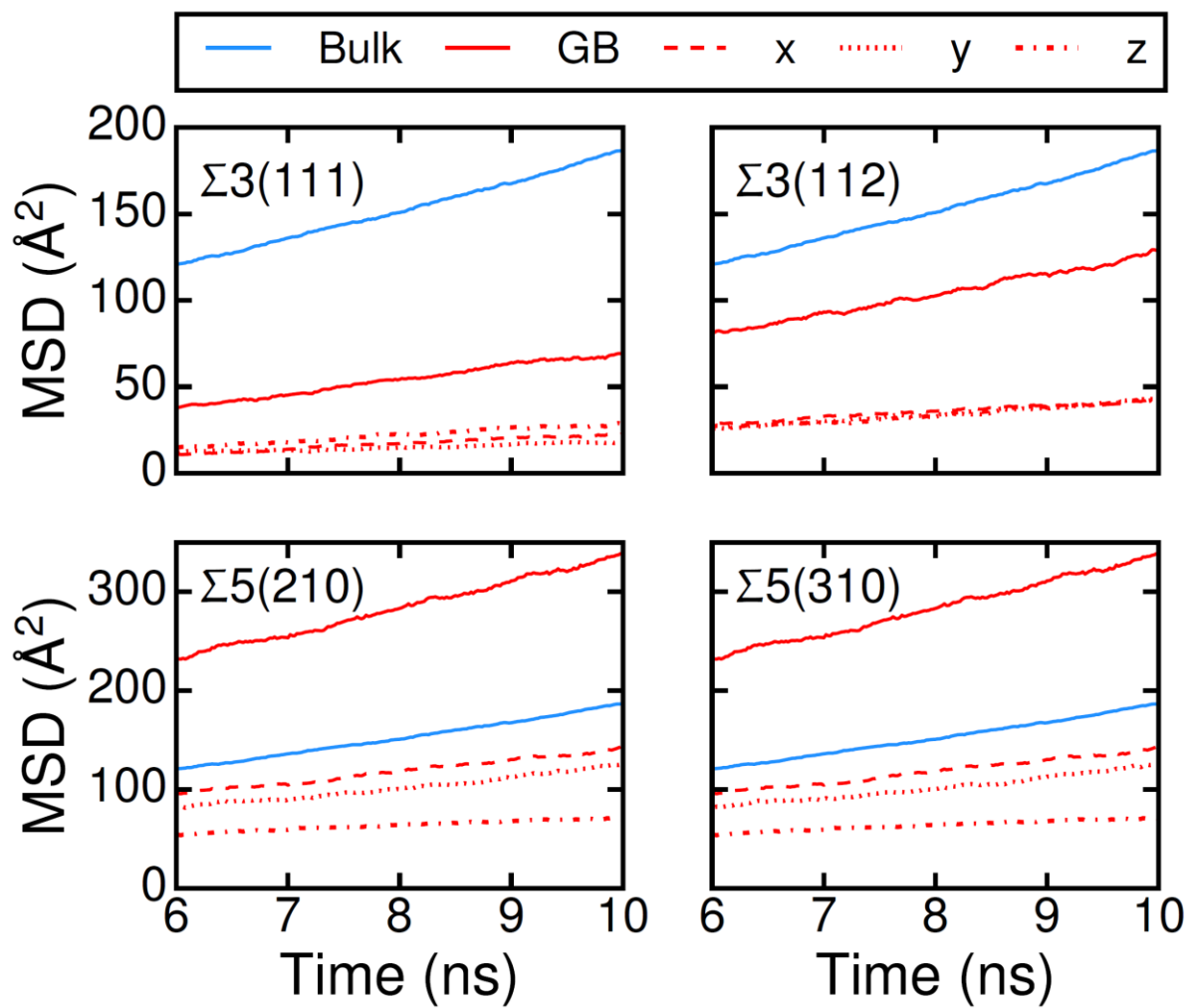
Figure S2. MSD plots of Li$^+$ diffusion in bulk Li$_3$OCl and the four GBs at 700 K. Only the time range from 6 to 10 ns has been displayed for clarity.
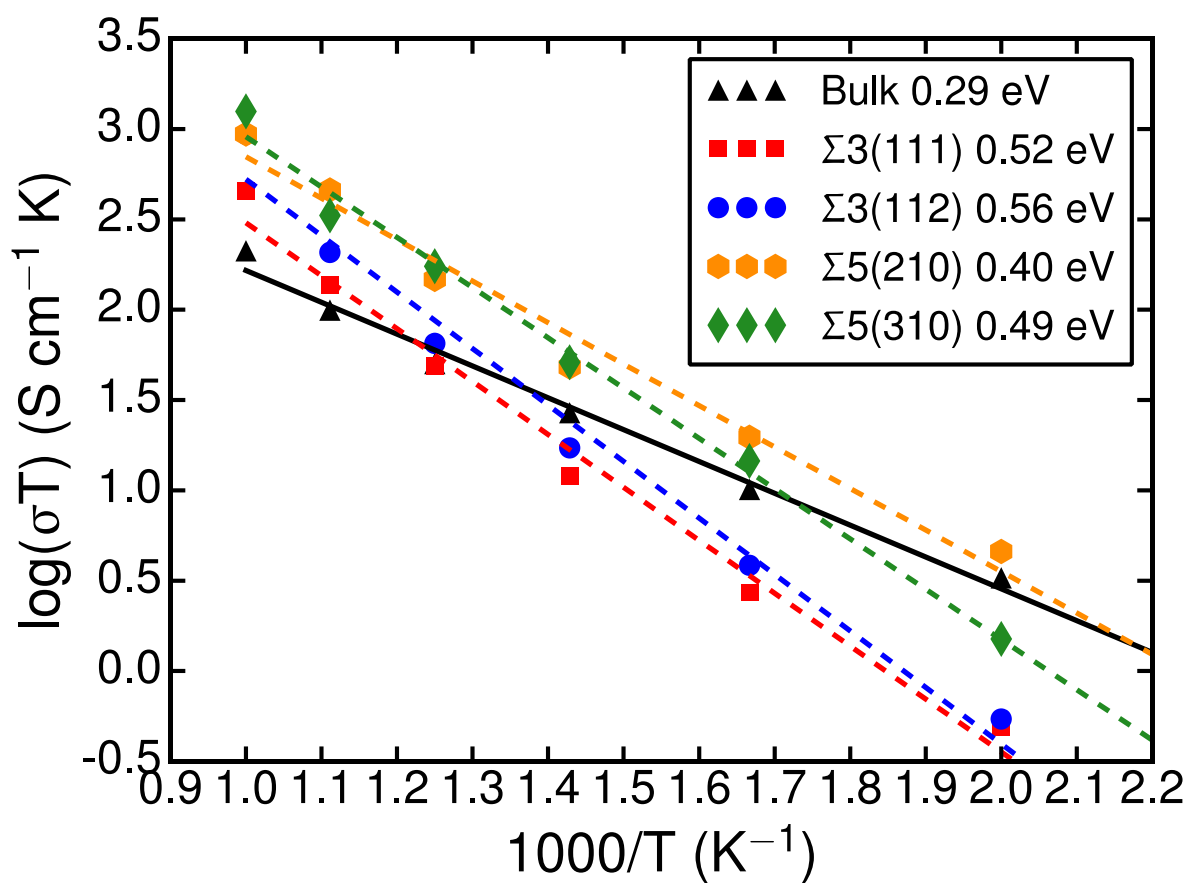
Figure S3. (a) Arrhenius plots of Li$^+$ temperature-dependent conductivity (σT) for bulk Li$_3$OCl and the four GBs.

Total conductivity model

Development of total conductivity equation

Any resistance can be written as the product of conductivity (σ) and geometric parameters length (l) and area (A):

$$R = \frac{l}{\sigma A} \qquad (2)$$

The calculations of the total conductivity stem from the two-mechanism model schematically depicted in Figure 7 and its associated direct current circuit, given in Figure S4:
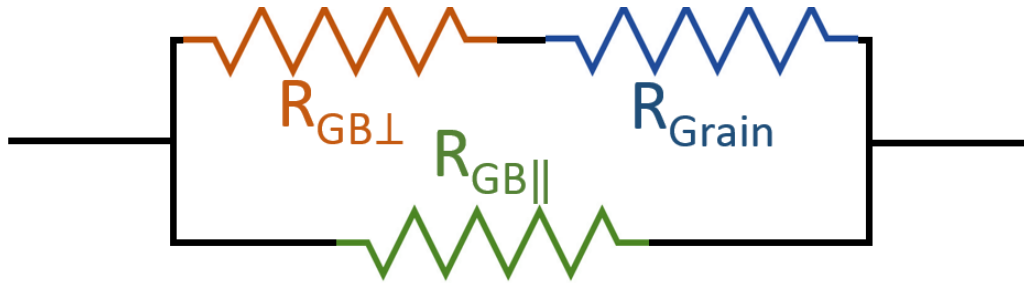

Figure S4. Direct current circuit for the two competing mechanisms of Figure 7.

The total resistance, R_{Total} related to the ionic conductivity is equal to:

$$R_{Total} = \left(\frac{1}{R_{GB\perp} + R_{Bulk}} + \frac{1}{R_{GB\|}}\right)^{-1} \qquad (3)$$

As such, Eq. (3) becomes:

$$\frac{l_{Total}}{\sigma_{Total}A_{Total}} = \left(\frac{1}{\frac{l_{GB\perp}}{\sigma_{GB\perp}A_{GB\perp}} + \frac{l_{Bulk}}{\sigma_{Bulk}A_{Bulk}}} + \frac{1}{\frac{l_{GB\|}}{\sigma_{GB\|}A_{GB\|}}}\right)^{-1} \qquad (4)$$

At this point two assumptions are made:

1) The length l that an ion needs to cross in the bulk material is the same regardless of mechanism used. Therefore, tortuosity effects are not considered and ions travel on a

straight line parallel to the current applied. Under this assumption $l_{Total} = l_{Bulk} = l_{GB\parallel}$.

2) In the first mechanism, the ion has to cross a GB (of thickness l_{GB}) every time it reaches the end of a grain, meaning for every distance d travelled, where d is the grain size, $l_{GB\perp} = l_{gb}\frac{l_{total}}{d}$.

It should be noted that both of these assumptions are beneficial for the total ionic conductivity. In other words, the ionic conductivity calculated this way might be slightly overestimated. Under these assumptions, Eq. (4) becomes independent of the macroscopic sample length:

$$\sigma_{Total}A_{Total} = \frac{1}{\dfrac{l_{gb}}{d}\dfrac{1}{\sigma_{GB\perp}A_{GB\perp}} + \dfrac{1}{\sigma_{Bulk}A_{Bulk}}} + \frac{1}{\dfrac{1}{\sigma_{GB\parallel}A_{GB\parallel}}} \qquad (5)$$

A parameter, y_{Bulk}, is introduced that controls the volume fraction of crystalline domains that exhibit the first mechanism of conduction ("Granular"). Analogously, $y_{GB}(=1-y_{Bulk})$ is the volume fraction of GB domains that exhibit the second mechanism of conduction ("GB"). These parameters reflect the microstructure of a polycrystalline sample in terms of densification. In a real sample, these would be linked to the specific processing, e.g., melt-quenching vs. solid-state reaction, annealing/sintering regime and so on.

Assuming an isotropic microstructure, the areas of conduction for each mechanism depend on the volume fraction of grains compared to GBs, as captured by the parameters y_{Bulk} and y_{GB}. As such, $A_{GB\perp} = A_{Bulk} = y_{Bulk}A_{Total}$ and $A_{GB\parallel} = y_{GB}A_{Total}$. This leads to the final geometry-independent relation for the total ionic conductivity of a polycrystalline sample:

$$\sigma_{Total} = y_{Bulk}\left(\sigma_{Bulk} + \frac{d}{l_{GB}}\sigma_{GB\perp}\right) + y_{GB}\sigma_{GB\parallel} \qquad (6)$$

where σ_{Bulk} is equal to the bulk conductivity of the crystalline material, while $\sigma_{GB\perp}$ and $\sigma_{GB\parallel}$ are the components of the GB conductivity perpendicular and parallel to the grain surface, respectively.

Minimum and maximum bounds

In order to capture the variability stemming from different possible densification behaviors of a polycrystalline sample, two extreme cases are considered utilizing the above-defined y_{Bulk} and y_{GB} parameters. The first extreme case is calculated with minimum y_{Bulk}, representing incomplete sintering. This is set at 0.76, for the packing of spherical grains in a matrix of GBs, as shown in Figure 7. In the second extreme case, GBs only exist in the interface between grains that otherwise occupy the entirety of the volume (similar to the brick layer model used by impedance spectroscopists[2]). As such, y_{Bulk} is set to $\frac{(d-l_{GB})^3}{d^3}$ where d and l_{GB} are the grain size and GB thickness, respectively.

Table S4. Parameters used for the calculation of the total conductivity of a polycrystalline Li$_3$OCl sample at 300 K.

GB	$\Sigma3(111)$	$\Sigma3(112)$	$\Sigma5(210)$	$\Sigma5(310)$
γ [J m^{-2}]	0.34	0.56	1.04	1.01
l_{GB} [Å]	7.05	7.97	9.39	8.87
ρ_N [atoms Å^{-3}]	0.0852	0.120	0.084	0.067
E_f [eV atom^{-1}]	0.035	0.037	0.082	0.107
$\sigma_{GB\perp}$ [S cm^{-1}]	$1.95\cdot10^{-7}$	$1.46\cdot10^{-7}$	$6.33\cdot10^{-6}$	$9.93\cdot10^{-7}$
$\sigma_{GB\parallel}$ [S cm^{-1}]	$2.46\cdot10^{-7}$	$1.34\cdot10^{-7}$	$2.05\cdot10^{-5}$	$1.77\cdot10^{-6}$

We calculate a weighted average of the GB conductivities with respect to their Boltzmann probabilities at 600 K (see Eq. (1)), which is the standard synthesis temperature for Li_3OCl[3]. The resulting parameters used to calculate the grain size dependence of the total ionic conductivity are listed in Table S5.

Table S5. Parameters used in conjunction with Eq. (6) to calculate the conductivity dependence with grain size at 300 K, as presented in Figure 8.

σ_{Bulk}	$6.61 \cdot 10^{-5}$	S cm^{-1}
$\sigma_{GB\perp}$	$1.20 \cdot 10^{-6}$	S cm^{-1}
$\sigma_{GB\parallel}$	$3.47 \cdot 10^{-6}$	S cm^{-1}
l_{gb}	7.97	Å

References

(1)   Reckeweg, O.; Blaschkowski, B.; Schleid, T. *Zeitschrift für Anorg. und Allg. Chemie* **2012**, *638*, 2081.

(2)   Fleig, J.; Maier, J. *J. Eur. Ceram. Soc.* **1999**, *6*, 693–696.

(3)   Li, S.; Zhu, J.; Wang, Y.; Howard, J. W.; Lü, X.; Li, Y.; Kumar, R. S.; Wang, L.; Daemen, L. L.; Zhao, Y. *Solid State Ionics* **2016**, *284*, 14–19.