Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for:

Electron leakage through heterogeneous LiF on lithium-metal battery anodes

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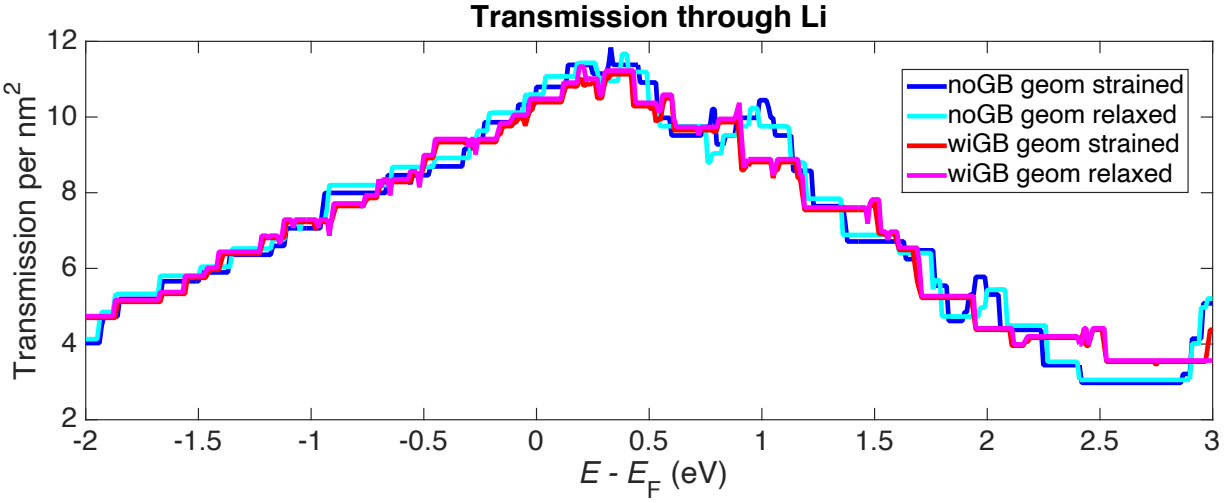

Figure S1: Transmission for different pure Li systems that are strained to adopt the LiF lattice constant or fully relaxed to adopt the Li crystal structure. There is an excess of transmission channels (> 3) at all energies; therefore, the strain and crystal orientations of Li used should not play a factor in the transmission through LiF. Overall, the transmission spectra look very similar with the biggest difference near 2.5 eV, quite far from the E_{F}.

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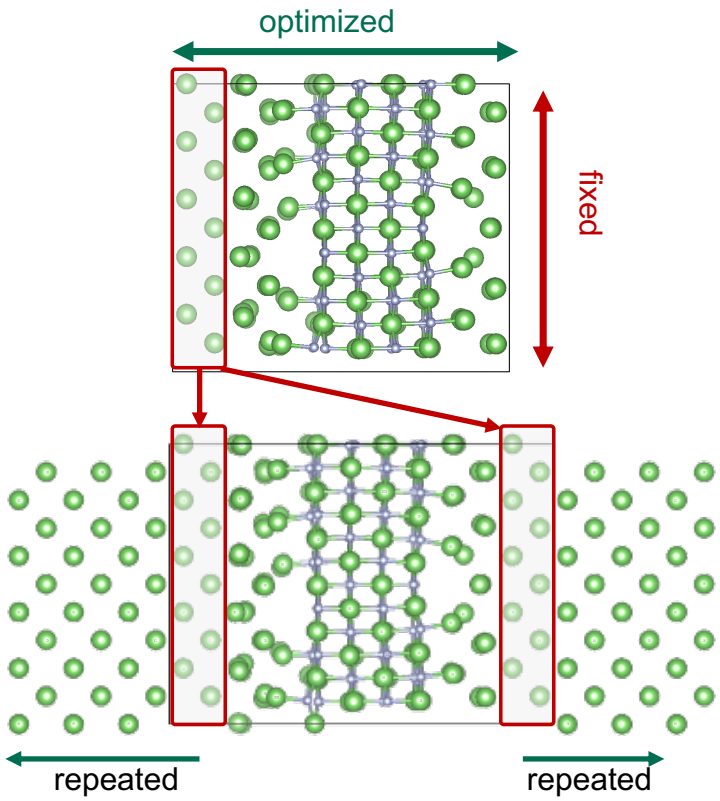

Figure S2: Top: Li/LiF system used for the structure relaxations. The cell was allowed to relax in the direction perpendicular to the interface (green arrow) and fixed to the lattice constant of LiF in the plane of the interface. Two layers of Li atoms (inside red box) were kept frozen in their bulk bcc crystal positions while all other atoms were allowed to relax. Once relaxed, the two-probe structure (bottom) was constructed by extending the bulk bcc Li regions to the left and right.

The system shown at the top of Fig. S2 was used for the structure relaxations. The LiF region in the middle is sandwiched between Li regions, and periodic boundary conditions are used. Since the LiF region was previously relaxed in bulk form, the lattice dimensions were fixed along the **a** and **b** directions but optimized along the **c** direction. Meanwhile, the Li atoms in the red box were held frozen in their bulk bcc positions, while all other atoms were free to relax. Once the structure was optimized, the system was extended to build the two-probe geometry shown at the bottom of Fig. S2, where the frozen Li atoms (enclosed in the red boxes) are repeated as semi-infinite left/right electrodes. Note that the systems shown in Fig. S2 are periodic (repeating) in the plane of the Li-LiF interfaces, *i.e.*, vertically and into/out of the page. The same approach was used for the system with GBs.

While the system shown in Fig. S2 (and its GB counterpart) are strained to accommodate the transition region between Li and LiF, the stresses after the relaxation are not too severe. The largest residual force on the system shown in Fig. S2 is 0.22 eV/Å and it is 0.23 eV/Å for the corresponding system with the GBs; these forces are found on the frozen Li atoms. All forces on the atoms that were not frozen were below 0.02 eV/Å.

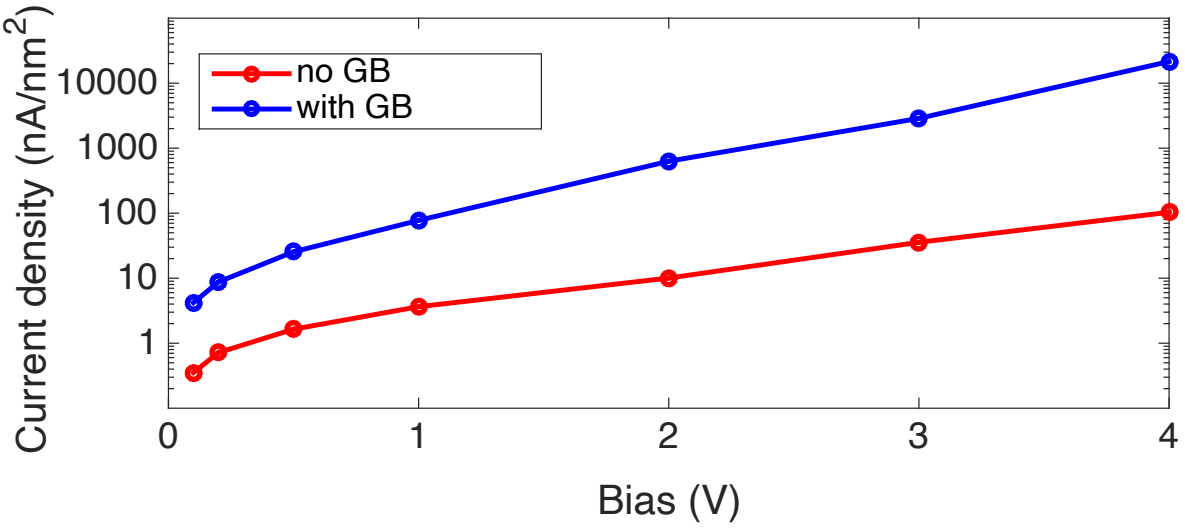

Figure S3: Current density as a function of bias voltage for LiF without and with grain boundaries. These results were calculated with a lower precision in terms of real space density, k-point grid density and convergence criteria. The results are qualitatively similar to the higher precision results presented in the main text, but allowed for a larger range of biases to be calculated.

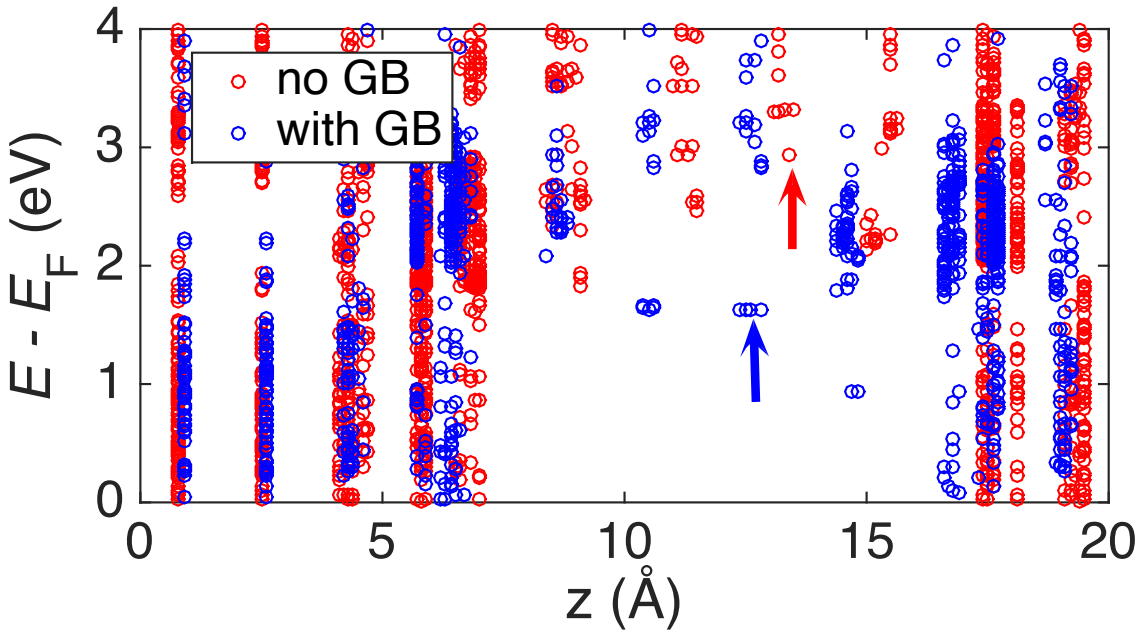

Figure S4: Local densities-of-state for the Li-LiF-Li system, decomposed in the direction perpendicular to the interface. Circles depict atoms with $> 0.2\%$ of wavefunction amplitude at an energy of ΔE. E_{F} is set at $\Delta E = 0$ eV. These data were calculated with $3 \times 3 \times 1$ k-point sampling. E_{offset} values that are used in Eq. 5 of the manuscript are taken from the points labeled with the red (2.93 eV) and blue (1.63 eV) arrows. They are selected as the maximum ΔE values that are not immediately adjacent to the Li surface but represent a flat plateau near the middle of the GB region. This is also consistent with the specific form of the WKB formula used, which is appropriate for a flat barrier, not a point-like barrier.

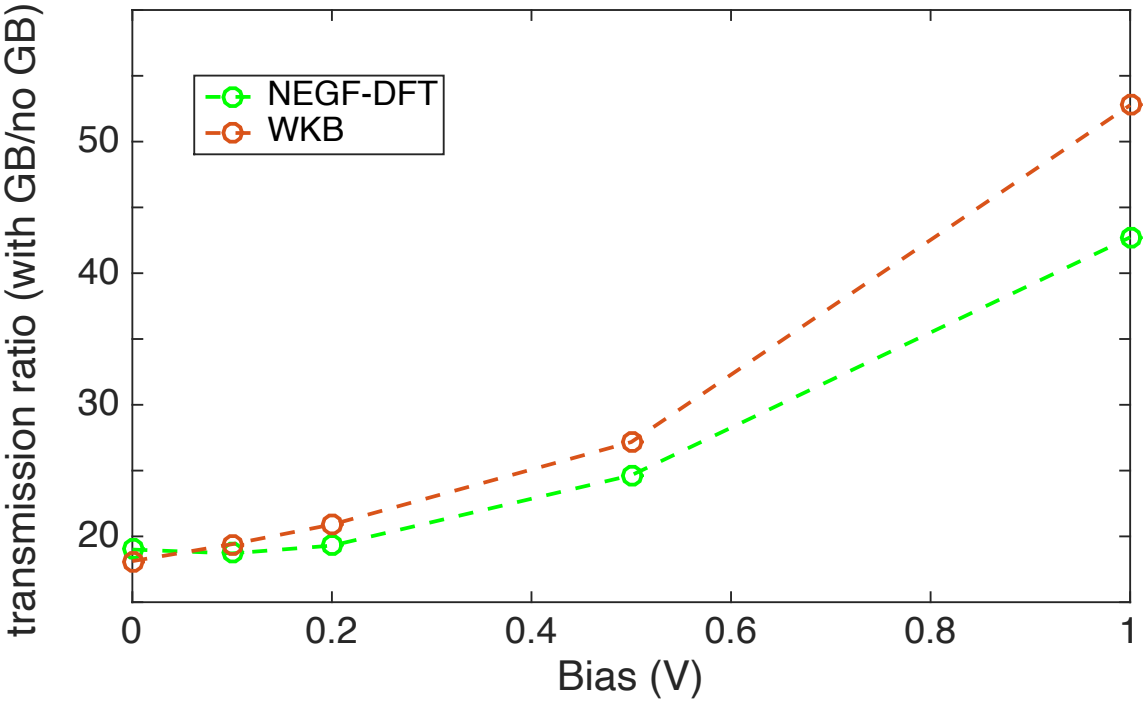

Figure S5: Transmission ratios between system with GB vs no GB, calculated with NEGF-DFT and WKB ($R = 6.5$ Å) as a function of bias.