Electronic Supplementary Information

Surface Chemistry Mechanism of Ultra-Low Interfacial Resistance in the Solid-State Electrolyte $Li_7La_3Zr_2O_{12}$

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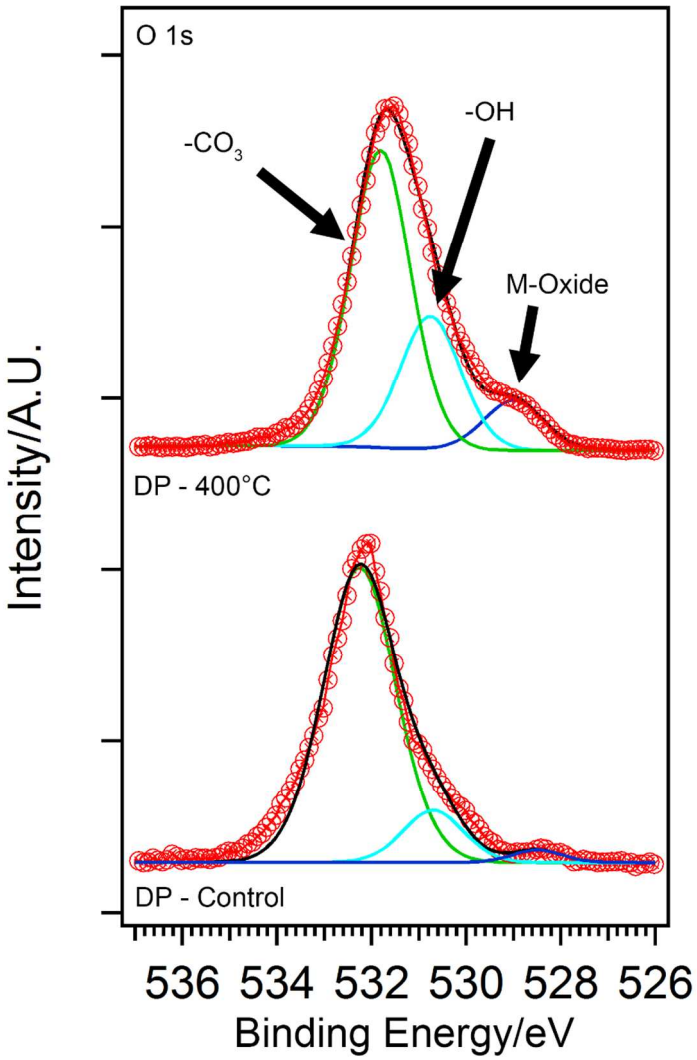

Figure S1. XPS analysis of LLZO showing the O 1s core level of sample after dry polishing (DP-Control) and after dry polishing and heat treatment at 400°C (DP-400°C).

Table S1. Calculated lattice constants for bulk Li, LLZO, Li_2CO_3, and LiOH.

Sample/Lattice constant	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Bulk Li	3.436	-	-	90	-	-
Bulk LLZO	13.026	-	-	90	-	-
Bulk Li_2CO_3	8.432	5.016	6.312	90	114.67	90
Bulk LiOH	3.535	-	4.408	90	-	-

Table S2. Number of atoms in the supercell, lattice parameters in the interfacial plane, the in-plane strain of Li, the calculated W_{ad}, and the contact angle for the Li-LLZO, Li-Li_2CO_3, and Li-LiOH interfaces.

Interface	No. of atoms	a (Å)	b (Å)	$\varepsilon_{x,Li}$ (%)	$\varepsilon_{y,Li}$ (%)	W_{ad} (J.m^{-2})	Contact angle (°)
Li-LLZO	570	18.421	18.421	-0.43	-0.43	0.667	61.6
Li-Li_2CO_3	252	16.864	10.032	-1.83	-2.67	0.096	142.0
Li-LiOH	260	14.140	14.140	-0.18	-0.18	0.191	125.3

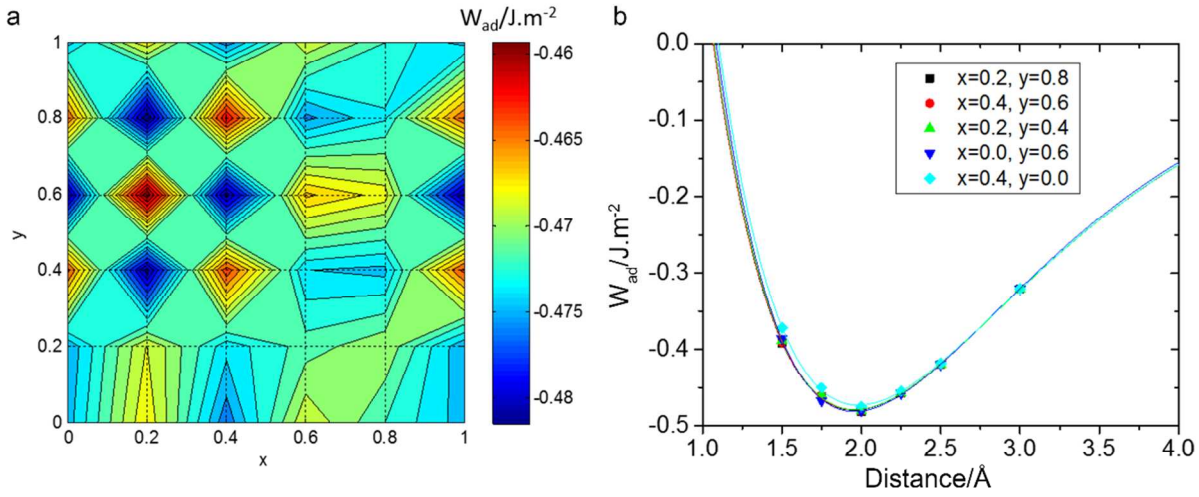

Figure S2. Optimization of the translation state within the interfacial plane and the interfacial distance for the Li-LLZO interface: a) contour plot of W_{ad} as a function of translation state for the Li slab relative to the LLZO slab using a 5×5 grid with a constant interfacial distance of 2 Å. b) W_{ad} as a function of interfacial distance between slabs fitted by the UBER for the five lowest W_{ad} interfaces identified in the contour plot of panel (a).

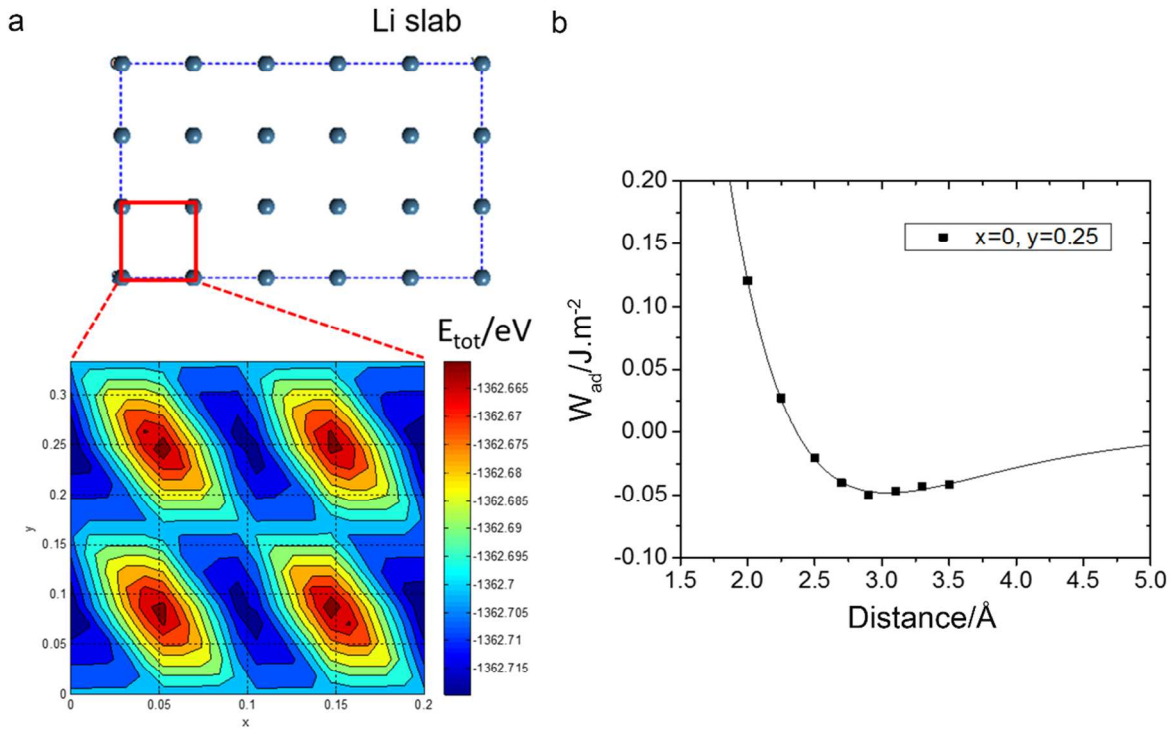

Figure S3. Optimization of the translation state within the interfacial plane and the interfacial distance for the Li-Li_2CO_3 interface. a) contour plot of the total energy as a function of translation state for the Li slab relative to Li_2CO_3 slab with a constant interfacial distance of 3 Å. Due to the symmetry of Li atoms in the Li slab, the translation state was restricted to the red box using a 4x4 grid. b) W_{ad} as a function of interfacial distance fit to the UBER for the lowest total energy interface (translation Li slab to x=0 and y=0.25) identified in panel (a).

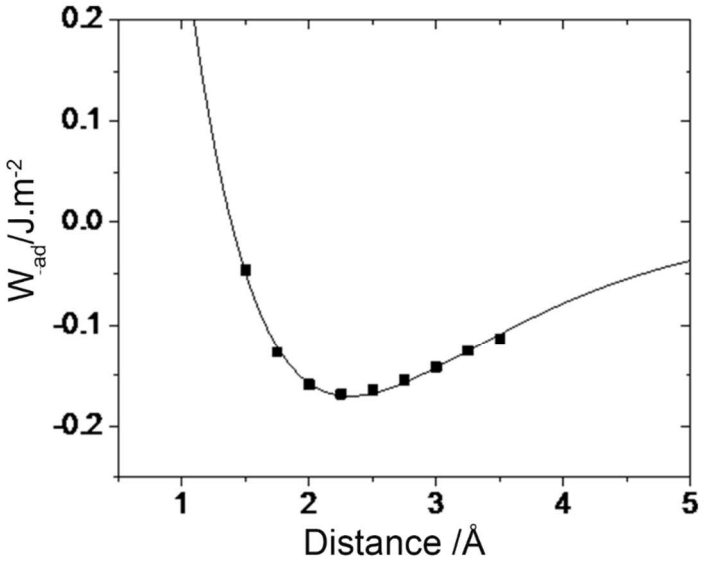

Figure S4. Calculated W_{ad} as a function of interfacial distance for the Li-LiOH interface.