

## Supplementary Information

### Voltage-Driven Evolution of Lithium Nanoparticle Morphology and SEI Precursors

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# 1 Computational Validation

## 1.1 Bulk Lithium Convergence

Convergence of the bulk lithium total energy was tested with respect to k-point mesh density and plane-wave kinetic energy cutoffs for both wavefunction and charge density.

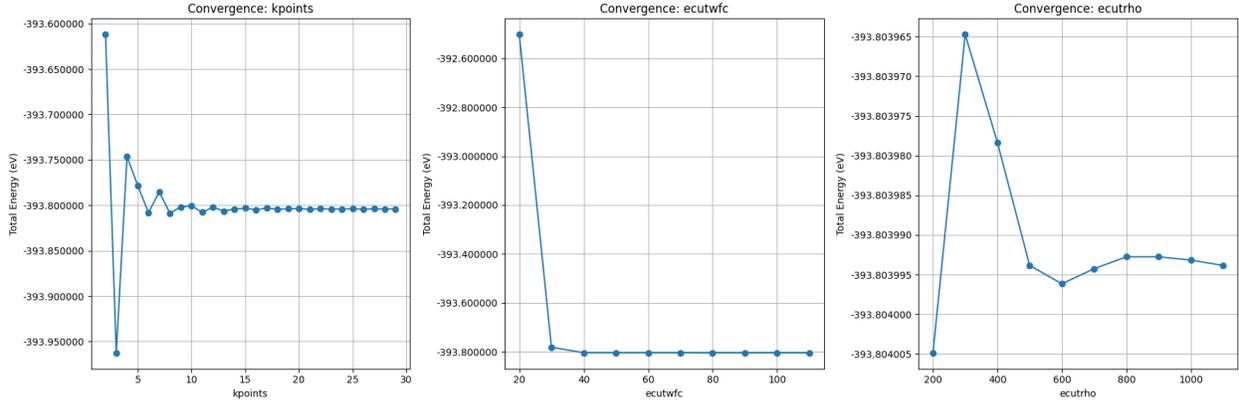


Figure 1: Convergence of bulk lithium total energy with respect to (a) k-point mesh density, (b) wavefunction kinetic energy cutoff (ecutwfc), and (c) charge density cutoff (ecutrho).

## 1.2 Lattice Parameter Optimisation

The equilibrium lattice parameter was determined by fitting a parabola to the total energy as a function of lattice constant.

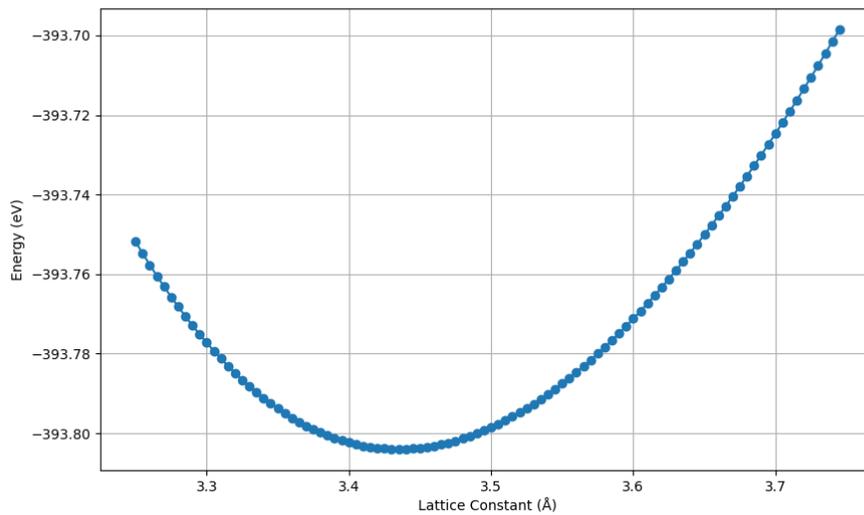
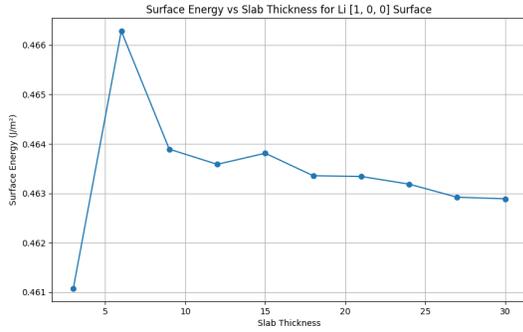


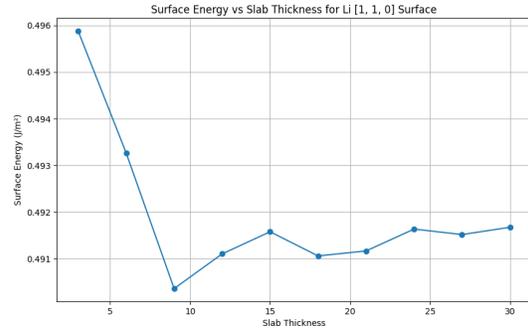
Figure 2: Total energy of bulk lithium as a function of lattice parameter. The equilibrium lattice constant was obtained from a parabolic fit to the energy minimum.

### 1.3 Surface Slab Layer Convergence

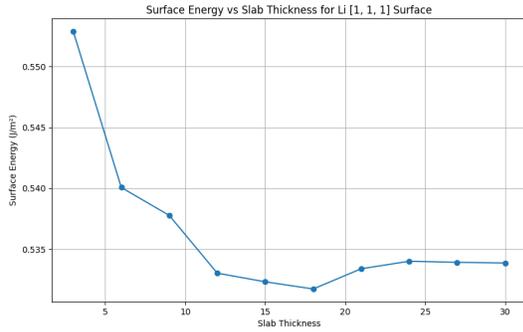
Surface energies were converged with respect to the number of atomic layers for all thirteen crystallographic orientations examined in this study.



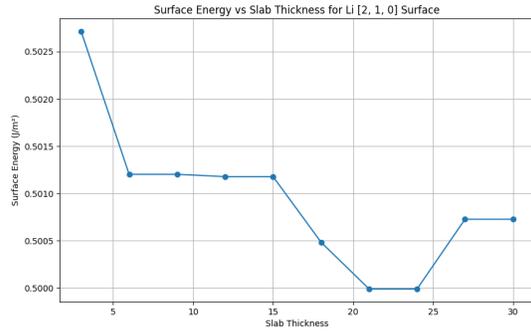
(a) {100}



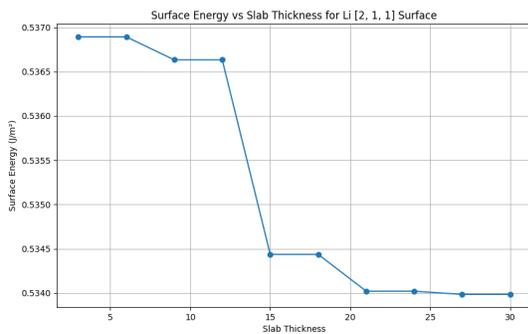
(b) {110}



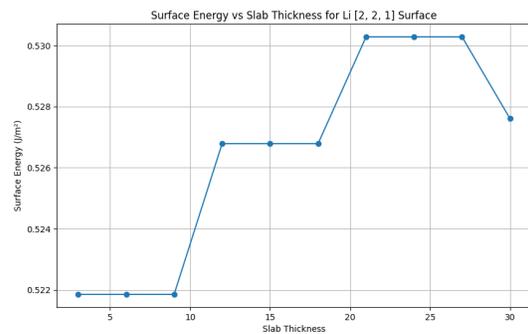
(c) {111}



(d) {210}

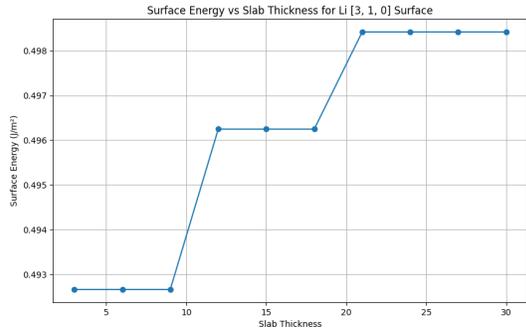


(e) {211}

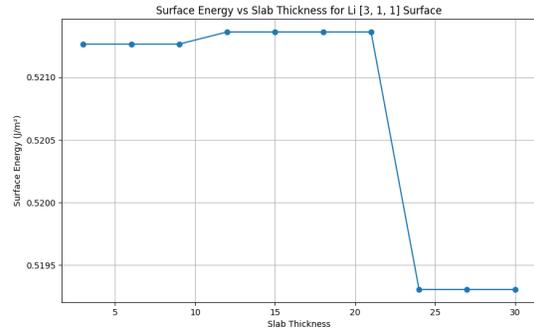


(f) {221}

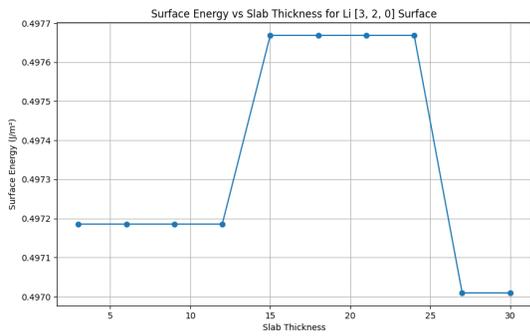
Figure 3: Surface energy convergence with respect to the number of atomic layers for surfaces {100}–{221}.



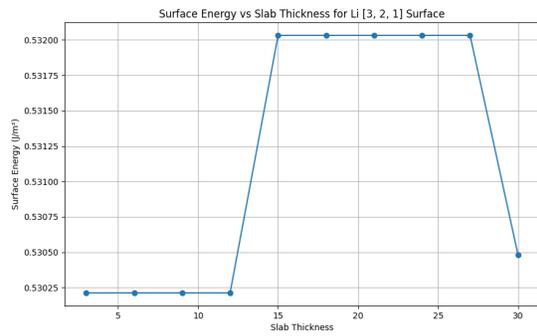
(a) {310}



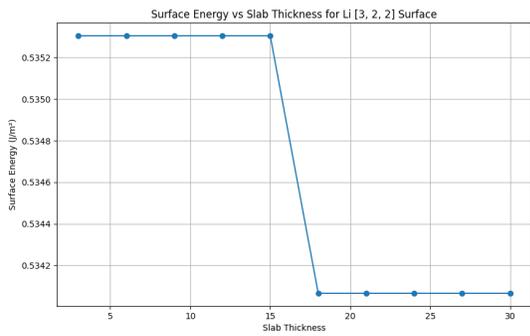
(b) {311}



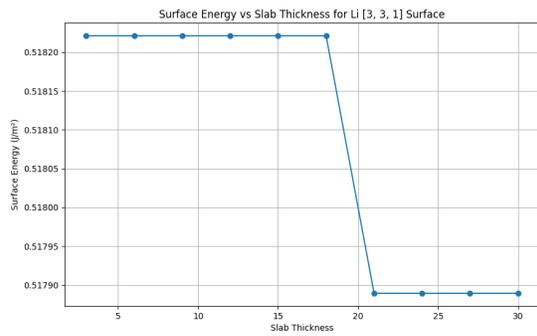
(c) {320}



(d) {321}

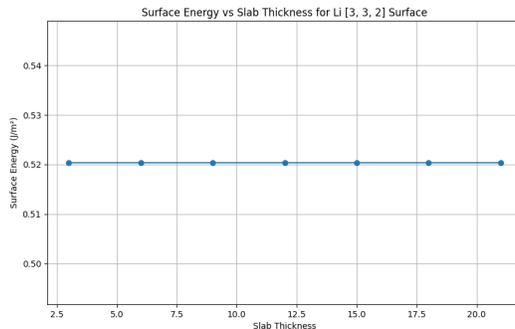


(e) {322}



(f) {331}

Figure 4: Surface energy convergence with respect to the number of atomic layers for surfaces {310}–{331}.



(a)  $\{332\}$

Figure 5: Surface energy convergence with respect to the number of atomic layers for surface  $\{332\}$ .

Note that the identical values of certain thicknesses is due to some surfaces having equivalent number of atoms despite differing layer counts, due to Pymatgen’s slab generation algorithm.

## 2 Surface Properties

### 2.1 Complete Surface Energy Data (Table S1)

Table 1: Surface energies in vacuum and solvated conditions at zero applied potential, with Fermi level shifts and potentials of zero charge (PZC) for all thirteen crystallographic orientations.

Surface	$\gamma_{\text{vac}}$ (J/m <sup>2</sup> )	$\gamma_{\text{solv}}$ (J/m <sup>2</sup> )	$\Delta\gamma$ (J/m <sup>2</sup> )	$\Delta E_f$ (eV)	PZC (V vs Li/Li <sup>+</sup> )
$\{100\}$	0.462	0.469	0.008	-0.565	-0.659
$\{110\}$	0.495	0.508	0.013	-0.411	-0.805
$\{111\}$	0.540	0.534	-0.007	-1.004	-0.768
$\{210\}$	0.502	0.498	-0.004	-0.813	-0.698
$\{211\}$	0.538	0.531	-0.007	-0.791	-0.712
$\{221\}$	0.521	0.518	-0.003	-1.177	-0.694
$\{310\}$	0.494	0.493	-0.0003	-1.108	-0.679
$\{311\}$	0.522	0.517	-0.005	-1.152	-0.720
$\{320\}$	0.497	0.501	0.004	-1.078	-0.706
$\{321\}$	0.529	0.527	-0.001	-1.117	-0.785
$\{322\}$	0.535	0.529	-0.006	-1.808	-0.682
$\{331\}$	0.518	0.523	0.005	-1.776	-0.725
$\{332\}$	0.520	0.514	-0.006	-1.816	-0.710

## 2.2 Voltage-Dependent Surface Energies

Table 2: Surface energies ( $\text{J}/\text{m}^2$ ) as a function of applied potential for all crystallographic orientations. Empty cells indicate negative surface energies (thermodynamically unstable).

Surface	-1.75 V	-1.5 V	-1.0 V	-0.5 V	0.0 V	+0.5 V	+1.0 V	+1.5 V
{100}	0.053	0.221	0.443	0.456	0.369	0.229	0.051	—
{110}	0.033	0.206	0.451	0.505	0.425	0.295	0.134	—
{111}	0.103	0.264	0.481	0.527	0.424	0.262	0.053	—
{210}	0.062	0.233	0.467	0.489	0.400	0.250	0.058	—
{211}	0.061	0.224	0.469	0.521	0.437	0.289	0.093	—
{221}	0.083	0.255	0.490	0.506	0.410	0.256	0.059	—
{310}	0.065	0.231	0.460	0.482	0.396	0.245	0.046	—
{311}	—	0.258	0.486	0.514	0.407	0.246	0.034	—
{320}	0.057	0.232	0.465	0.490	0.394	0.244	0.059	—
{321}	0.067	0.240	0.482	0.524	0.445	0.301	0.115	—
{322}	0.092	0.258	0.486	0.514	0.413	0.256	0.058	—
{331}	0.074	0.246	0.482	0.513	0.418	0.269	0.082	—
{332}	0.082	0.255	0.483	0.505	0.410	0.254	0.055	—

## 2.3 Wulff Construction Facet Distributions

Table 3: Facet area percentages from Wulff constructions at each voltage. Empty cells indicate facets not present in the equilibrium morphology at that potential.

Surface	-1.75 V	-1.5 V	-1.0 V	-0.5 V	0.0 V	+0.5 V	+1.0 V	Vacuum
{100}	—	15.9	13.7	18.6	—	19.8	—	22.6
{110}	100.0	59.6	29.7	—	—	—	—	14.7
{111}	—	—	2.6	—	—	—	—	—
{210}	—	—	—	7.4	—	—	—	—
{211}	—	23.8	27.4	—	—	—	—	—
{221}	—	—	—	8.8	—	0.8	—	1.8
{310}	—	0.7	20.4	20.4	—	4.6	—	15.1
{311}	—	—	—	1.2	—	24.2	100.0	4.0
{320}	—	—	3.9	25.2	—	34.1	—	22.5
{321}	—	—	—	—	—	—	—	0.9
{322}	—	—	—	3.2	—	1.6	—	—
{331}	—	—	—	—	—	—	—	2.1
{332}	—	—	2.4	15.2	—	14.9	—	16.3

Table 4: Facet area percentages for vacuum and solvated (zero-potential) conditions.

Surface	Vacuum (%)	Solvated (%)
{100}	22.6	16.8
{110}	14.7	2.7
{111}	—	—
{210}	—	15.5
{211}	—	—
{221}	1.8	4.6
{310}	15.1	16.1
{311}	4.0	6.2
{320}	22.5	17.8
{321}	0.9	0.06
{322}	—	—
{331}	2.1	—
{332}	16.3	20.3

### 3 Complete Adsorption Data

#### 3.1 Carbonate Adsorption Energies

Table 5: Adsorption energies (eV) for  $\text{CO}_3^{2-}$  on the dominant surface at each voltage. The most stable site at each voltage is indicated in bold. The surface identity changes with voltage: {110} at reducing potentials ( $-1.75$  to  $-1.0$  V), {320} at intermediate potentials ( $-0.5$  to  $+0.5$  V), and {311} at  $+1.0$  V.

Voltage (V)	Surface	On-top	Bridge	3-fold	4-fold
+1.0	<b>{311}</b>	-8.241	-7.713	-6.285	—
+0.5	<b>{320}</b>	-7.600	-8.756	—	-9.622
0.0	<b>{320}</b>	-6.819	-7.878	—	-8.567
-0.5	<b>{320}</b>	-6.512	-7.458	—	-7.985
-1.0	<b>{110}</b>	-7.289	-7.793	-5.925	—
-1.5	<b>{110}</b>	-8.194	-8.574	-6.621	—
-1.75	<b>{110}</b>	-8.769	-9.085	-7.090	—

### 3.2 Fluoride Adsorption Energies

Table 6: Adsorption energies (eV) for  $F^-$  on the dominant surface at each voltage. The most stable site at each voltage is indicated in bold.

Voltage (V)	Surface	On-top	Bridge	3-fold	4-fold
+1.0	{311}	-7.696	-8.477	-9.028	—
+0.5	{320}	-6.740	-7.869	—	-7.754
0.0	{320}	-5.511	-6.413	—	-6.351
-0.5	{320}	-4.798	-5.454	—	-5.461
-1.0	{110}	-4.764	-5.088	-5.375	—
-1.5	{110}	-5.600	-6.071	-6.324	—
-1.75	{110}	-6.263	-6.786	-7.037	—

### 3.3 Oxide Adsorption Energies

Table 7: Adsorption energies (eV) for  $O^{2-}$  on the dominant surface at each voltage. The most stable site at each voltage is indicated in bold.

Voltage (V)	Surface	On-top	Bridge	3-fold	4-fold
+1.0	{311}	-4.597	-6.242	-7.699	—
+0.5	{320}	-4.404	-6.855	—	-7.235
0.0	{320}	-3.413	-5.522	—	-5.773
-0.5	{320}	-2.943	-4.675	—	-4.835
-1.0	{110}	-3.065	-4.418	-5.005	—
-1.5	{110}	-4.064	-5.308	-5.912	—
-1.75	{110}	-4.729	-6.008	-6.612	—

### 3.4 Competitive Adsorption Summary

Table 8: Lowest adsorption energies for each species at each voltage, with the energy difference between fluoride and carbonate ( $\Delta E = E_{\text{ads}}^{F^-} - E_{\text{ads}}^{CO_3^{2-}}$ ). Positive  $\Delta E$  indicates carbonate preference; negative  $\Delta E$  indicates fluoride preference.

Voltage (V)	Surface	$CO_3^{2-}$ (eV)	$F^-$ (eV)	$O^{2-}$ (eV)	$\Delta E$ (eV)	Preferred
+1.0	{311}	-8.241	-9.028	-7.699	-0.79	$F^-$
+0.5	{320}	-9.622	-7.869	-7.235	+1.75	$CO_3^{2-}$
0.0	{320}	-8.567	-6.413	-5.773	+2.15	$CO_3^{2-}$
-0.5	{320}	-7.985	-5.461	-4.835	+2.52	$CO_3^{2-}$
-1.0	{110}	-7.793	-5.375	-5.005	+2.42	$CO_3^{2-}$
-1.5	{110}	-8.574	-6.324	-5.912	+2.25	$CO_3^{2-}$
-1.75	{110}	-9.085	-7.037	-6.612	+2.05	$CO_3^{2-}$

## 4 Additional Wulff Construction Data

### 4.1 Surface Energy Ranges at Each Voltage

Table 9: Range of surface energies and the resulting morphological complexity at each voltage.

Voltage (V)	$\gamma_{\min}$ (J/m <sup>2</sup> )	$\gamma_{\max}$ (J/m <sup>2</sup> )	$\gamma_{\max}/\gamma_{\min}$	Number of facets	Dominant facet
+1.0	0.034	0.134	3.94	1	{311}
+0.5	0.229	0.301	1.31	7	{320}
0.0	0.369	0.445	1.21	—	{320}
-0.5	0.456	0.527	1.16	8	{320}
-1.0	0.443	0.490	1.11	7	{110}/{211}
-1.5	0.206	0.264	1.28	4	{110}
-1.75	0.033	0.103	3.12	1	{110}

## 5 Computational Parameters

Example input files for the Quantum ESPRESSO and Environ calculations are provided below.

### 5.1 Quantum ESPRESSO Input

```
&CONTROL
  calculation      = 'scf'
  restart_mode    = 'from_scratch'
  nstep           = 200
  tprnfor        = .true.
  outdir          = './Li/'
  prefix          = 'Lithium'
  etot_conv_thr   = 1e-05
  forc_conv_thr   = 0.000388
  disk_io         = 'low'
  pseudo_dir      = '/path/to/SSSP_1.3.0_PBE_efficiency'
/
&SYSTEM
 ibrav            = 0
  nbnd            = 140
  ecutwfc         = 40.0
  ecutrho         = 600
  occupations     = 'smearing'
  degauss         = 0.01
  smearing        = 'mv'
  input_dft       = 'pbe'
  lgscf           = .true.
  gcscf_mu        = -3.404
  gcscf_conv_thr  = 0.0001
  gcscf_beta      = 0.05
  ntyp            = 1
/
&ELECTRONS
  electron_maxstep = 250
  conv_thr          = 1e-06
  mixing_mode       = 'local-TF'
  mixing_beta       = 0.1
  mixing_ndim       = 14
  diagonalization  = 'paro'
  startingpot       = 'atomic'
  startingwfc       = 'atomic+random'
/
&IONS
  ion_dynamics     = 'bfgs'
  upscale          = 1E+5
  bfgs_ndim        = 1
/
```

## 5.2 Environ Input

```
&ENVIRON
  verbose          = 0
  cion(1)          = 1.0
  cion(2)          = 1.0
  zion(1)          = 1.0
  zion(2)          = -1.0
  cionmax          = 10.0
  system_dim       = 2
  system_axis      = 3
  environ_thr      = 1.0
  env_pressure     = 0.0
  temperature      = 300.0
  environ_type     = 'input'
  env_electrostatic = .true.
  env_electrolyte_ntyp = 2
  env_surface_tension = 37.3
  electrolyte_entropy = 'full'
  env_static_permittivity = 89.9
/
&BOUNDARY
  alpha           = 1.32
  radius_mode     = 'bondi'
  solvent_mode    = 'ionic'
  electrolyte_mode = 'ionic'
/
&ELECTROSTATIC
  pbc_dim         = 2
  pbc_axis        = 3
  tol             = 1e-15
  inner_tol       = 1e-20
  pbc_correction  = 'parabolic'
/
```

## Data and Code Availability

All input files, output data, computational workflows, and analysis scripts used in this study are available at:



[https://github.com/BCAyers2000/li\\_morphology.git](https://github.com/BCAyers2000/li_morphology.git)

The repository includes:

- Quantum ESPRESSO input files for all surface and adsorption calculations
- Raw output data and extracted energies
- All python scripts used to run calculations via ASE
- Jupyter notebooks for figure generation