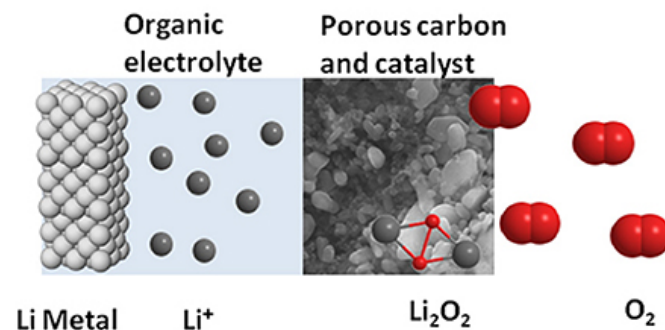


# TUTORIAL SYNOPSIS

## Li-air battery interface

- ❖ Import/create  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$  bulk structures
- ❖ Cleave surfaces
- ❖ Create  $\text{Li}_2\text{O}_2/\text{Li}_2\text{CO}_3$  interface
- ❖ Create device and optimize geometry
- ❖ Calculate electronic transport properties

### Li-air (non-aqueous)





## Add structure from internal database

**Database - Crystal Cupboard**

File Databases Panels Windows Help

Li2O2

Name	Formula	Lattice	Tags
Li2O2	Li2O2	Hexagonal	Oxides

Description

**Li2O2**

Chemical formula: Li<sub>2</sub>O  
Lattice

- Hexagonal
- a = 3.142 Angstrom
- c = 7.65 Angstrom

Symmetry Information

- Space group: 174
- Crystal system: hexagonal
- Pearson: hPn
- Hermann-Mauguin: P-6
- Schoenflies: C<sub>3h</sub><sup>1</sup>

Configuration

## Change lattice parameters or optimize them with DFT

**Lattice Parameters**

Choose the lattice type from the dropdown menu.

Lattice type: Hexagonal

Keep fractional coordinates constant when changing the lattice

Lattice Parameters

Adjust the lattice parameters of the selected lattice type. Only parameters relevant for the lattice type can be changed. Lattice parameters can be exported to the clipboard by right-clicking.

a (Å) 3.187 α 90

b (Å) 3.187 β 90 b/a 1

c (Å) 7.72599 γ 120 c/a 2.42422

Primitive Vectors

Manipulate the Primitive Vectors directly. This is only possible if UnitCell was chosen from the dropdown menu.

	x (Å)	y (Å)	z (Å)
A	1.5935	-2.76002	0
B	1.5935	2.76002	0
C	0	0	7.72599

Volume = 67.9593 Å<sup>3</sup>

**Bulk Tools**

Crystal Symmetry Info

Space group 187

Hermann-Mauguin P-6m2

Hall P -6 2

Schoenflies D<sub>3h</sub><sup>1</sup>

More information... Detect

Fit Cell

Merge Cells

## Check crystal symmetry info

# Cleave Li2O2(1000) surface



- Most stable and predominant facets (80%) in Li2O2
- during charge and discharge in nonaqueous Li-air batteries

## Bulk Tools->Surface (Cleave) plugin

**Surface (Cleave)**

**Define the surface**

Miller indices

$h$   $k$   $i = -(h+k)$   $l$

0 0 0 1

Select an atom for the outer layer

	Element	a	b	c
0	Lithium	0.000	0.000	0.000
1	Lithium	0.333	0.667	0.500
2	Lithium	0.667	0.333	0.250
3	Lithium	0.667	0.333	0.750
4	Oxygen	0.000	0.000	0.401
5	Oxygen	0.000	0.000	0.599
6	Oxygen	0.333	0.667	0.100
7	Oxygen	0.333	0.667	0.900

< Back Next > Cancel

**Surface (Cleave)**

**Finalize output configuration**

☒ Automatically update 3D view

Out-of-plane cell vector  $v_3$  is

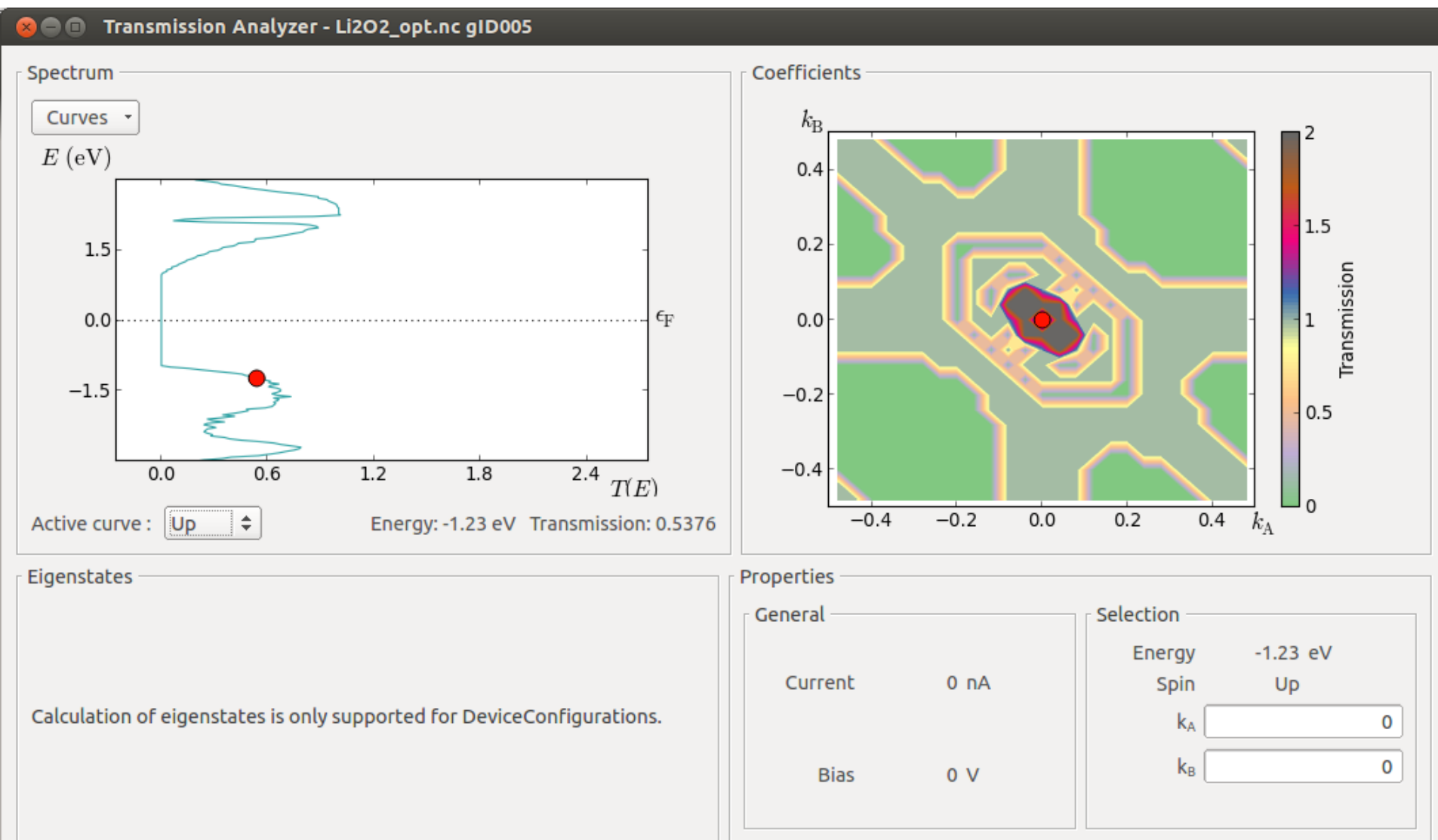
Periodic and normal (electrode)

	Layers	A
Top vacuum	1.2976	10.0000
Thickness	2	15.4129
Bottom vacuum	0.0000	0.0000

Update

< Back Finish Cancel

# Electronic structure of Li2O2





Search structure in online database, e.g. Crystallography Open Database, and download CIF file



## Crystallography Open Database

**COD Home**  
Home  
What's new?

**Accessing COD Data**  
Browse  
Search

**Add Your Data**  
Deposit your data  
Manage depositions  
Manage/release  
prepublications

**Documentation**  
COD Wiki  
Obtaining COD  
Querying COD

### Search results

Result: there are 1 entries in the selection

[Switch to the old layout of the page](#)

Download all results as: [list of COD numbers](#) | [list of CIF URLs](#) | [data in CSV format](#) | [archive of CIF files \(ZIP\)](#)

Searching elements including Li, C, O number of elements between 3 and 3 text, file, commonname, chemname, mineral contains li2co3

◀◀ First | ◀ Previous 5 | Page 1 of 1 | Next 5 ▶ | Last ▶▶ | Display 5 20 50 100 200 300 500 1000 entries per page

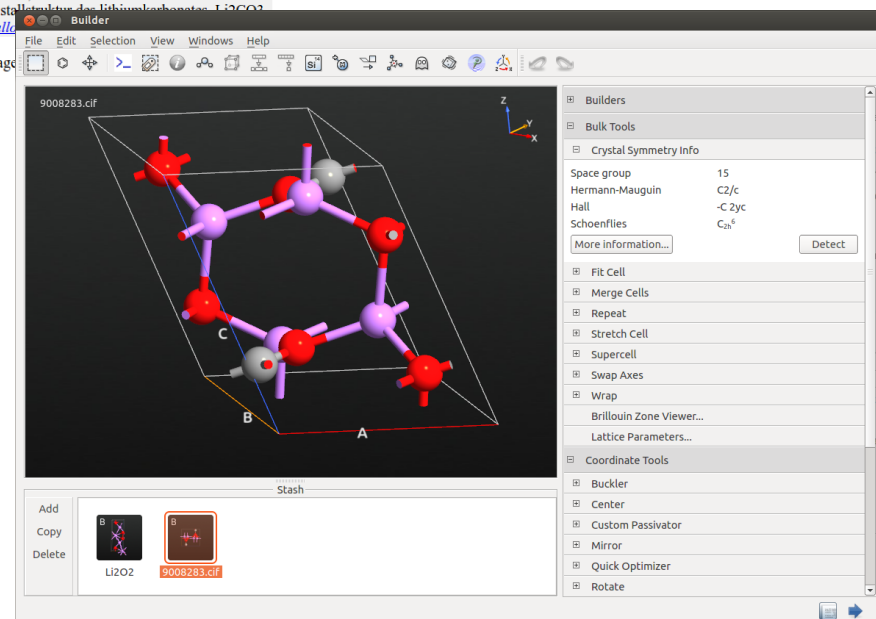
COD ID ▲	Links	Formula ▲	Space group ▲	Cell parameters	Cell volume ▲	Bibliography
9008283	<a href="#">CIF</a>	C Li2 O3	<a href="#">C 1 2/c 1</a>	8.3593; 4.9725; 6.1975 90; 114.83; 90	233.795	Effenberger, H.; Zemann, J. Verfeinerung der kristallstruktur des lithiumpolyoxoborates Li2CO3 <a href="#">Zeitschrift für Kristallographie</a>

◀◀ First | ◀ Previous 5 | Page 1 of 1 | Next 5 ▶ | Last ▶▶ | Display 5 20 50 100 200 300 500 1000 entries per page

[Back to the search form](#)

[Your own data is not in the COD? Deposit it, thanks!](#)

Load CIF file structure in the Builder



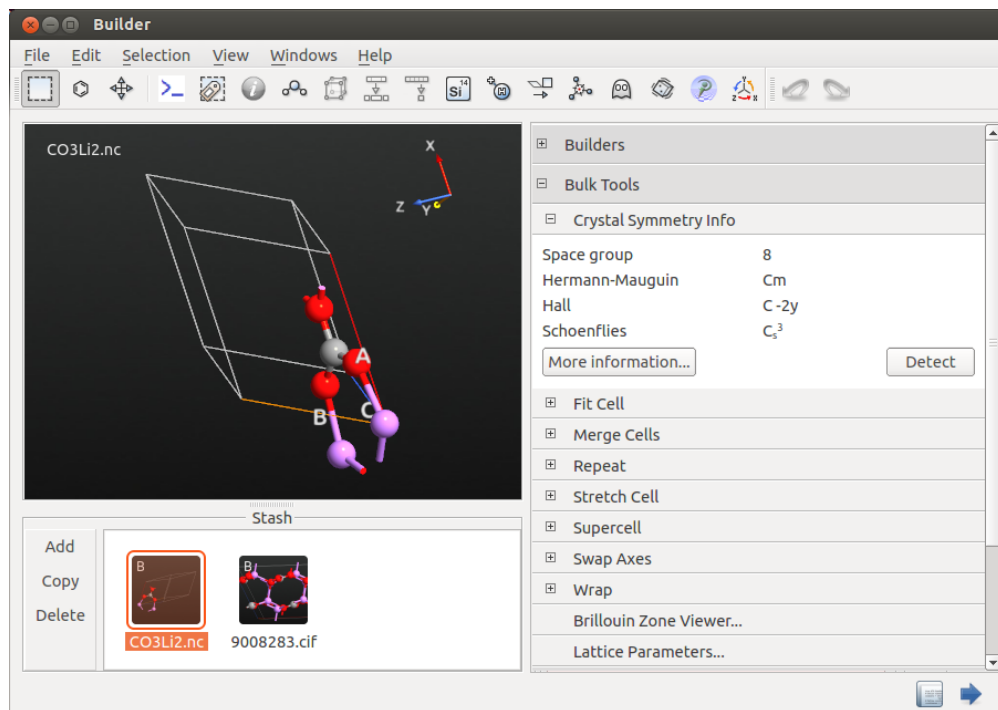


When interfacing the Li<sub>2</sub>CO<sub>3</sub> surface with the Li<sub>2</sub>O<sub>2</sub> you will need to use a large cell due to the lattice mismatch.

This is because the CO<sub>3</sub> planes in the C2/c space group are slightly misaligned from the cell axes.

In this tutorial you will use a modified Li<sub>2</sub>CO<sub>3</sub> structure with space group Cm where the CO<sub>3</sub> planes are perpendicular to the (011) plane.

Also, this is the structure used in Yedilfana *et al.* JPCC (2015)



# Li<sub>2</sub>CO<sub>2</sub>(011) surface



- Oxygen-terminated surface
- CO<sub>3</sub> planes perpendicular to the CB plane

**Surface (Cleave)**

**Define the surface**

Miller indices

h: 0 k: 1 l: 1

Select an atom for the outer layer

	Element	a	b	c
0	Lithium	0.002	0.015	0.015
1	Lithium	-0.331	0.353	0.353
2	Carbon	0.337	0.187	0.187
3	Oxygen	0.336	0.062	0.062
4	Oxygen	0.088	0.312	0.312
5	Oxygen	0.594	0.186	0.186

< Back Next > Cancel

**Surface (Cleave)**

**Finalize output configuration**

☒ Automatically update 3D view

Out-of-plane cell vector  $v_3$  is

Periodic and normal (electrode)

Layers      Å

Top vacuum: 2.1647      10.0000

Thickness: 4      18.4786

Bottom vacuum: 0.0000      0.0000

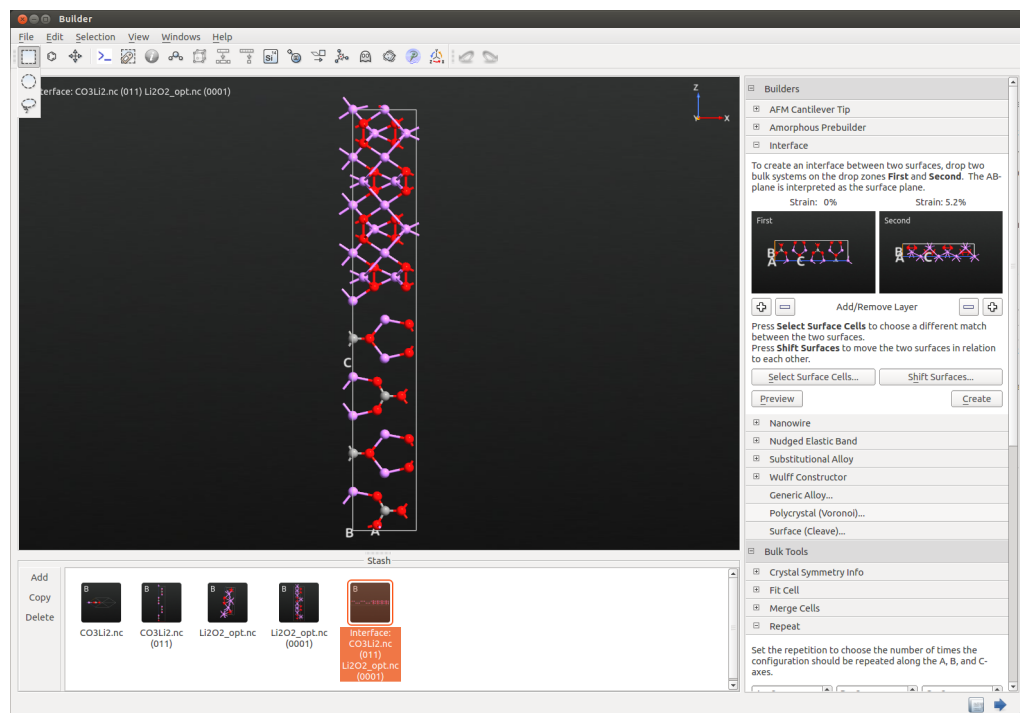
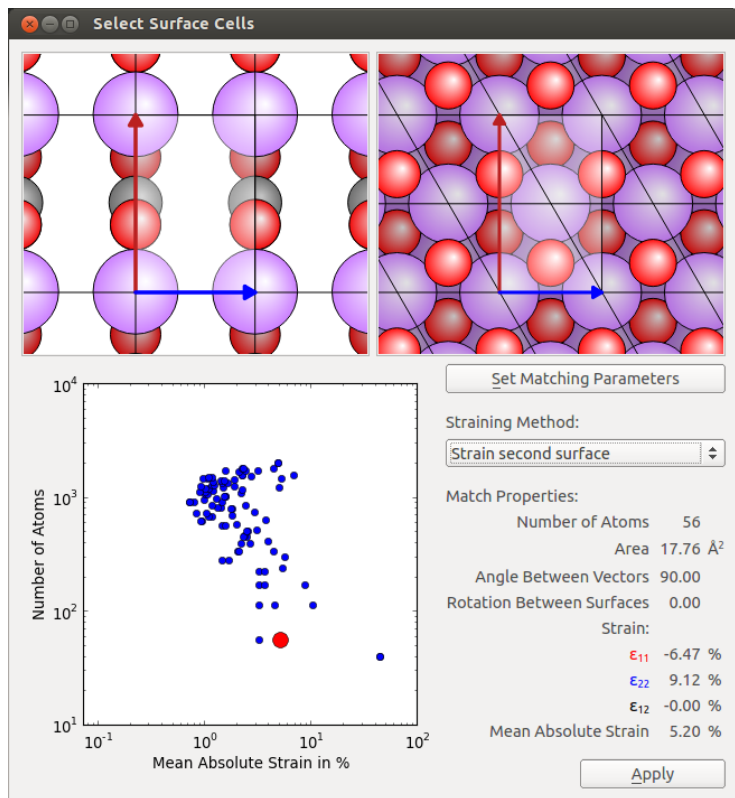
Update

< Back Finish Cancel





- Builders → Interface plugin
- Strain Li<sub>2</sub>O<sub>2</sub> surface
- Mean absolute strain of 5.2%
- Depending on how you choose to cut the surface you may need to adjust the interface, *e.g.* remove Li atoms and shift surface







## Device Tools → Device From Bulk plugin

**Device From Bulk**

Select the electrode lengths from repetition matches or enter user-specified values.

Left electrode length (Å)  ▼

Right electrode length (Å)  ▼

Press the +/- buttons in one of the rows to increase/decrease the size of the central region at the interface of the respective electrode.

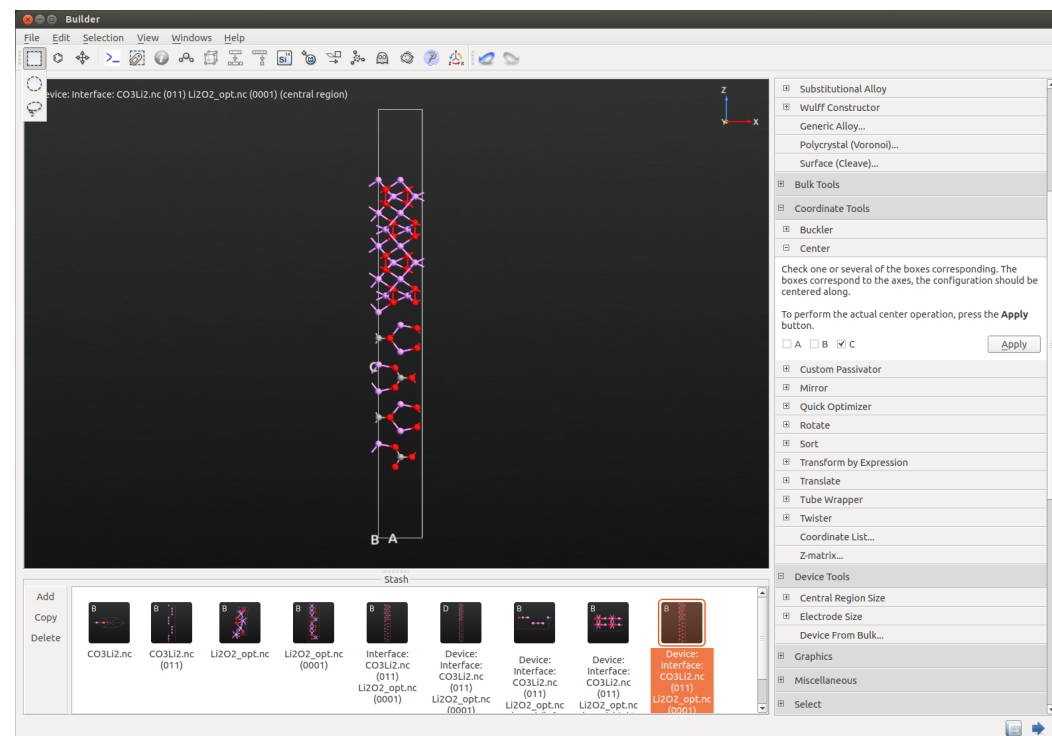
The increment can either be given as a **length in Ångstrom** or as the **relative size** compared to the electrode length.

Left	<input type="text" value="1.1400 Å"/>	<input type="text" value="12.34 %"/>	<input type="button" value="−"/>	<input type="button" value="⊕"/>
Right	<input type="text" value="1.1390 Å"/>	<input type="text" value="14.78 %"/>	<input type="button" value="−"/>	<input type="button" value="⊕"/>

# Li2CO2/Li2O2 geometry optimization



Optimize the interface: [http://docs.quantumwise.com/tutorials/device\\_relaxation.html](http://docs.quantumwise.com/tutorials/device_relaxation.html)



For the atom indices associated with a given tag, change the combo box in the **Constraint** column to the desired constraint. To apply constraints to the current selection, press the **Add Selection** button. Notice, that *rigid body* constraints may not share atom indices. In this case, their table are entries are displayed in **red**.

Tag	Constraint
Left Interface	None
Right Interface	None
li2co3_electrode	Fixed
li2o2_electrode	Rigid

Buttons: Add tag from Selection, Cancel, OK

- Take central region and add vacuum
- Tag electrode extensions + one more layer
- Optimize geometry for fixed and rigid body constrain
- Create a new device



## Projected Device Density of States

