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Li-air battery interface

Version: 2015.1

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Li-ion batteries are, at the moment, the most widely used in most most electric vehicles and hybrid electric vehicles. However, there are some disadvantages such as high price, slow charging, and low energy/power density. Li-air batteries are attracting attention due to the higher energy storing capacity and are being seen as possible alternative for Li-ion batteries. Nevertheless, still a lot of research has to be done in order to make Li-air battery competitive. In particular, various complex chemical and electrochemical side-reactions occurs at the interfaces. Li_2O_2/Li_2CO_3 is indeed a very important interface since Li_2CO_3 is formed at the cathode with Li_2O_2 when carbonate-based electrolytes are used. In this tutorial you will use **QuantumATK** to create the Li_2O_2/Li_2CO_3 and use **ATK** study its electronic properties. You will compare the results with Ref. [1].

You will:

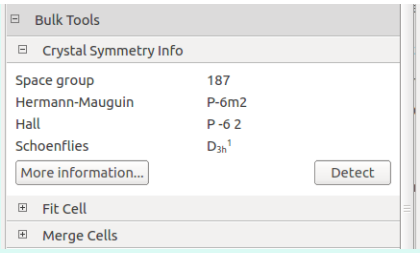
- Import/create Li_2O_2 and Li_2CO_3 bulk structures.
- Cleave surfaces.
- Create Li_2O_2/Li_2CO_3 interface.
- Create device and optimize geometry.
- Calculate electronic properties of the Li_2O_2/Li_2CO_3.

Li_2O_2 bulk and surface structures

Bulk structure

- Open the **Builder** and use Add ▸ From Database to add the Li_2O_2 structure to the **Stash**.

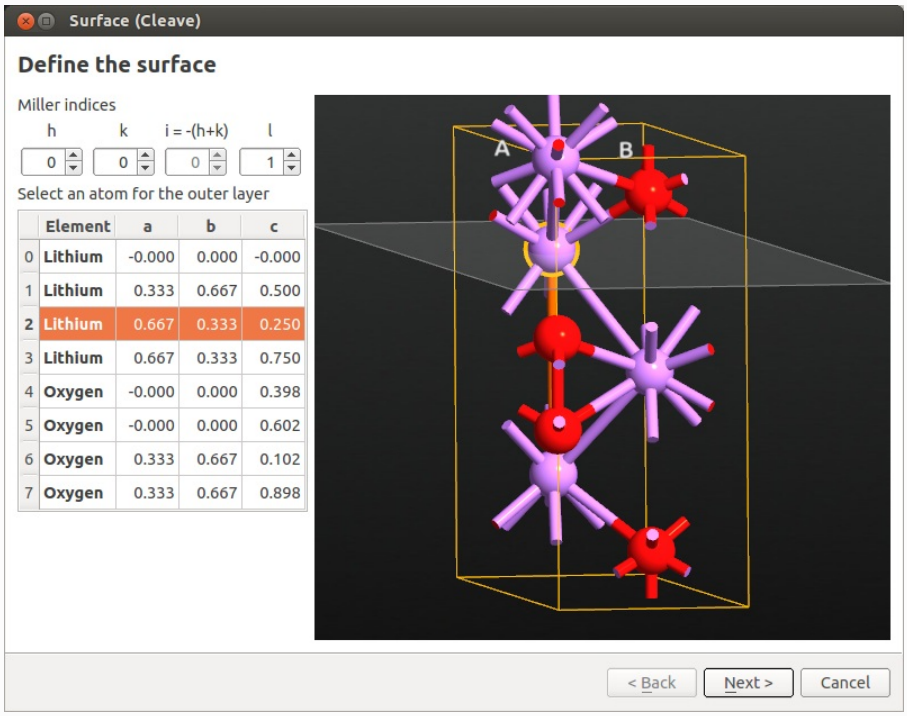
> **Tip**
>
> You can use the Bulk Tools ▸ Crystal Symmetry Info plugin to get the corresponding space group, for example

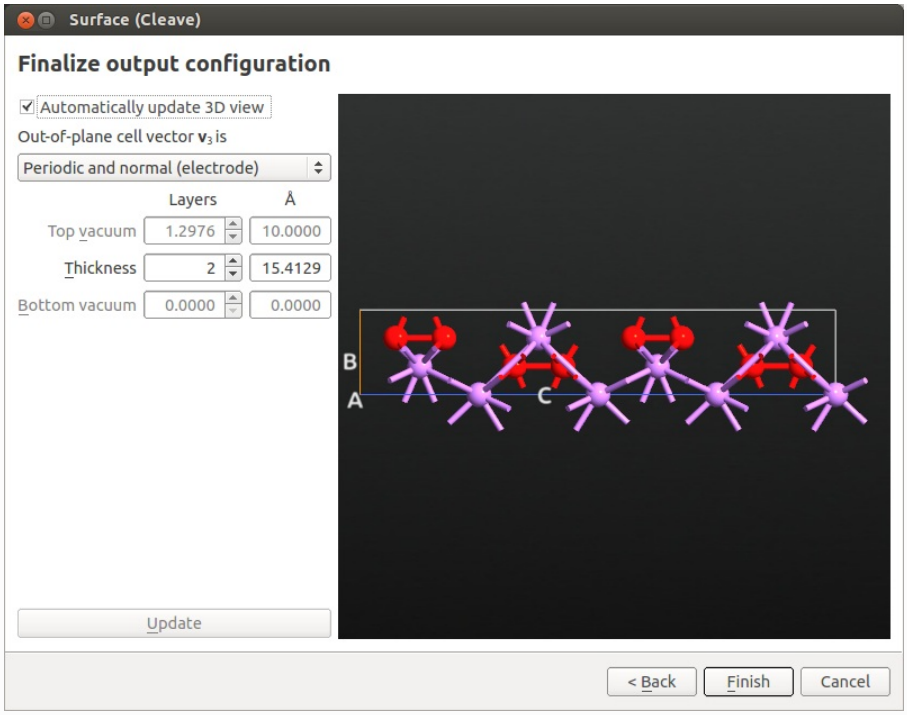


- Optimize the lattice parameters by running the Li2O2_opt.py script or use the experimental ones if you wish. In this tutorial you will use the GGA-RBE exchange-correlation potential by following the computational details as in Ref. [1].

Cleave surface

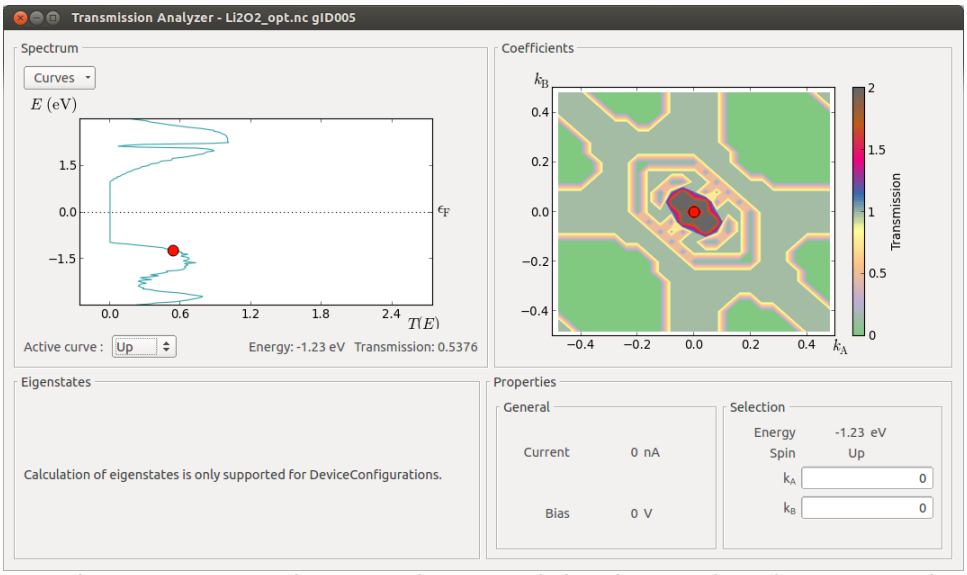
- Use the Builders ▸ Surface(Cleave) tool to cleave the Li_2O_2 (0001) surface from the optimized Li_2O_2 structure as illustrated in the next figures.





Electronic structure at zero bias

In the Li2O2_opt.py script a few analysis have been added such as the $T(\mathbf{k}, \epsilon)$ *TransmissionSpectrum* analysis which you can find loaded in the **LabFloor** once your simulation is done.



From the figure above, you can see that Li_2O_2 shows a wide band gap and no electronic conduction is expected at low bias voltages. Moreover, as demonstrated in [1], when introducing Li vacancies the electronic conduction decreases even more.

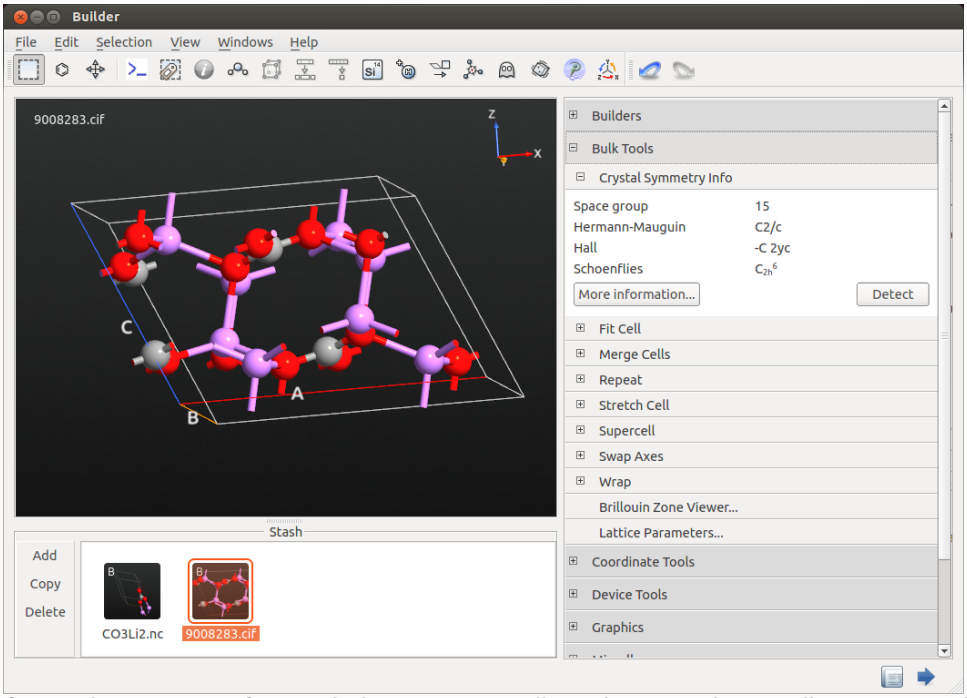
Note

You can follow the Transmission spectrum of perfect sheets of graphene and MoS2 tutorial for more details and how to set up a transmission spectrum analysis for a perfect periodic bulk system.

Li_2CO_3 bulk and surface structures

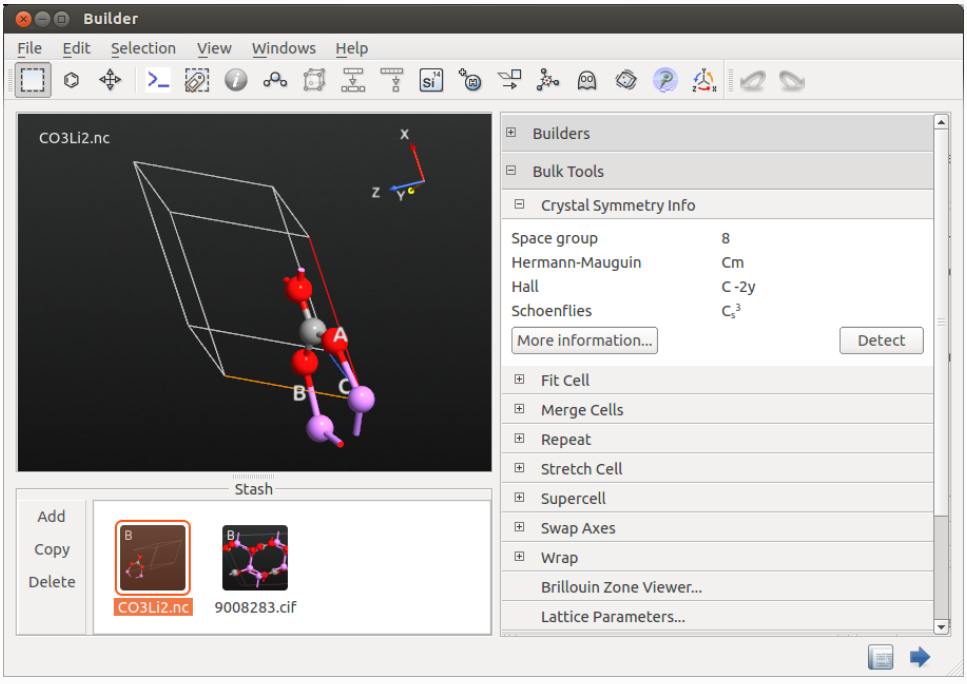
Bulk structure

The Li_2CO_3 bulk structure is not present in the internal database of **QuantumATK**. You need to get the structure file, usually a CIF file, from an external database, e.g. you can use the Crystallography Open Database. Search, download and copy the 9008283.cif file to your project folder. It will be automatically loaded in the **LabFloor**. For more options see Import XYZ, CIF, CAR, VASP Files in QuantumATK tutorial.



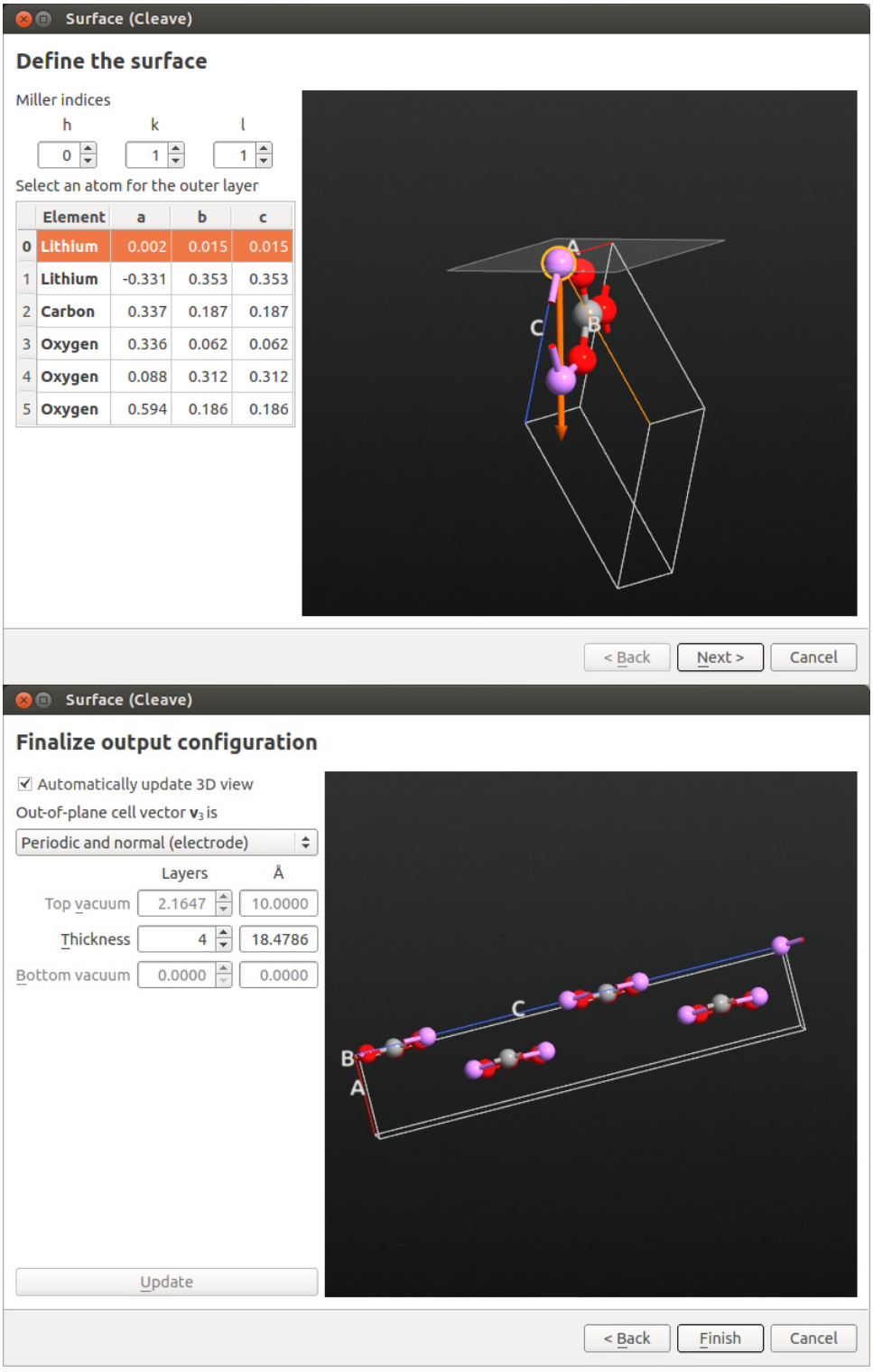
When interfacing the Li_2CO_3 surface with the Li_2O_2 you will need to use a large cell to get a small lattice mismatch. This is because the CO_3 planes in the *C2/c* space group are slightly misaligned from the cell axes. In this tutorial you will use a modified Li_2CO_3 structure with space group *Cm* where the CO_3 planes are perpendicular to the (011) plane. Also, this is the structure used in cite: *Yedilfana2015*.

Download the Li2CO3.py script and import the structure to the **Builder** to analyze it.



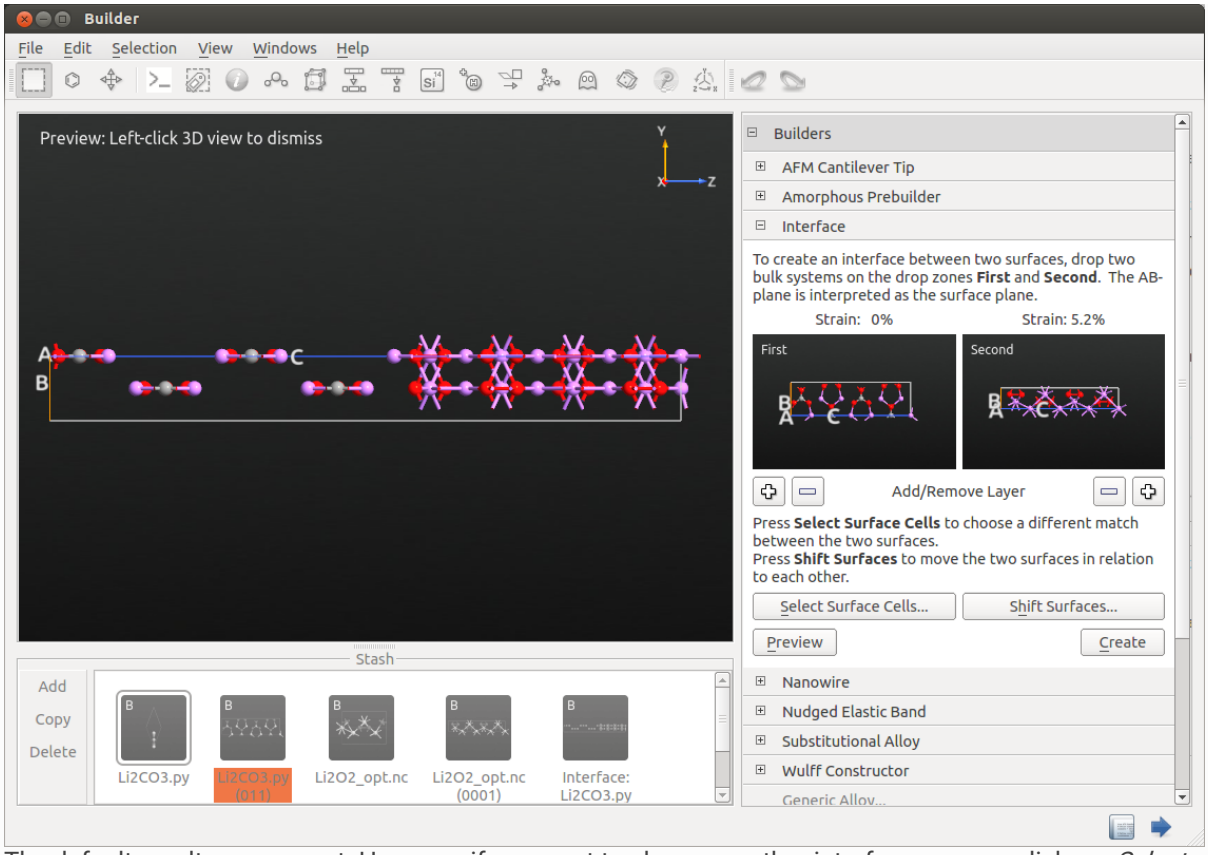
Cleave surface

Use the Builders ▸ Surface(Cleave) tool to cleave the (011) surface as indicated in the figures below.

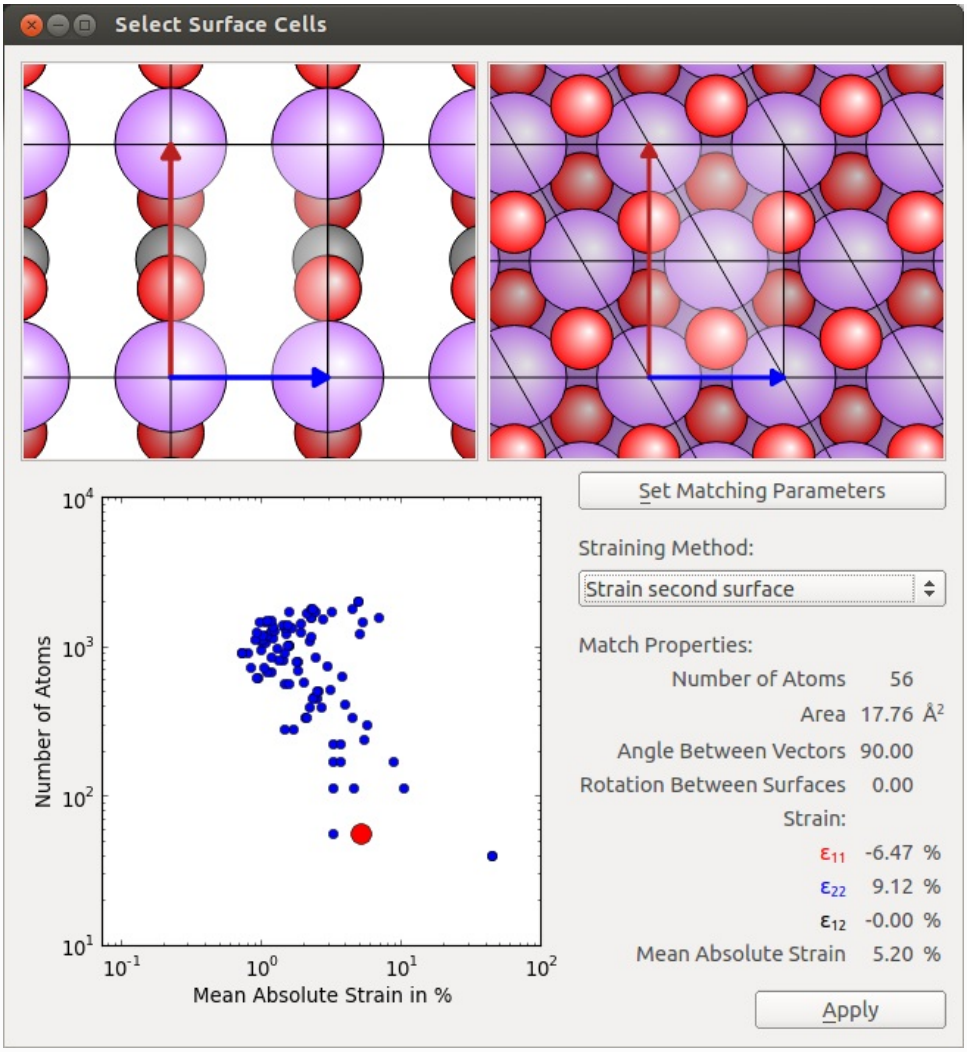


The Li_2O_2/Li_2CO_3 interface

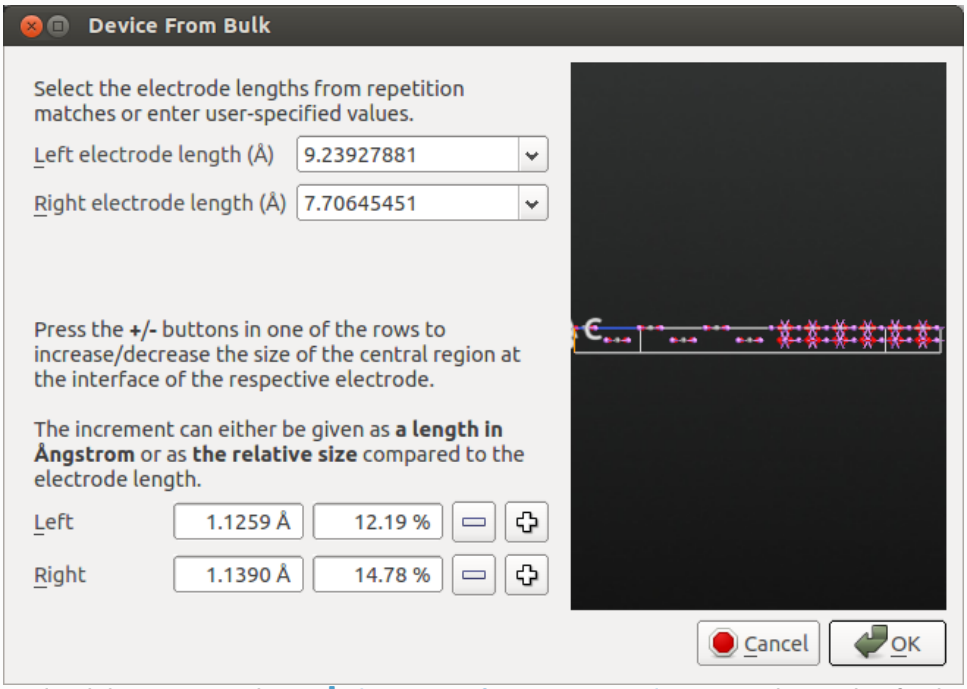
Open the Builders ▸ Interface tool and drag and drop the Li_2CO_3 surface and the optimized Li_2O_2 surface to the first and second drop zones.



The default results are correct. However, if you want to choose another interface you can click on *Select Surface Cells* button and choose the desired matching parameters.



You can now create the device configuration with the Device Tools ▸ Device From Bulk plugin. The default electrode lengths are fine.



You can download this structure here: device_configuration_initial.py. Note that in this final structure the Li_2CO_3 side has been slightly shifted towards the Li_2O_2 side to allow for a proper relaxation

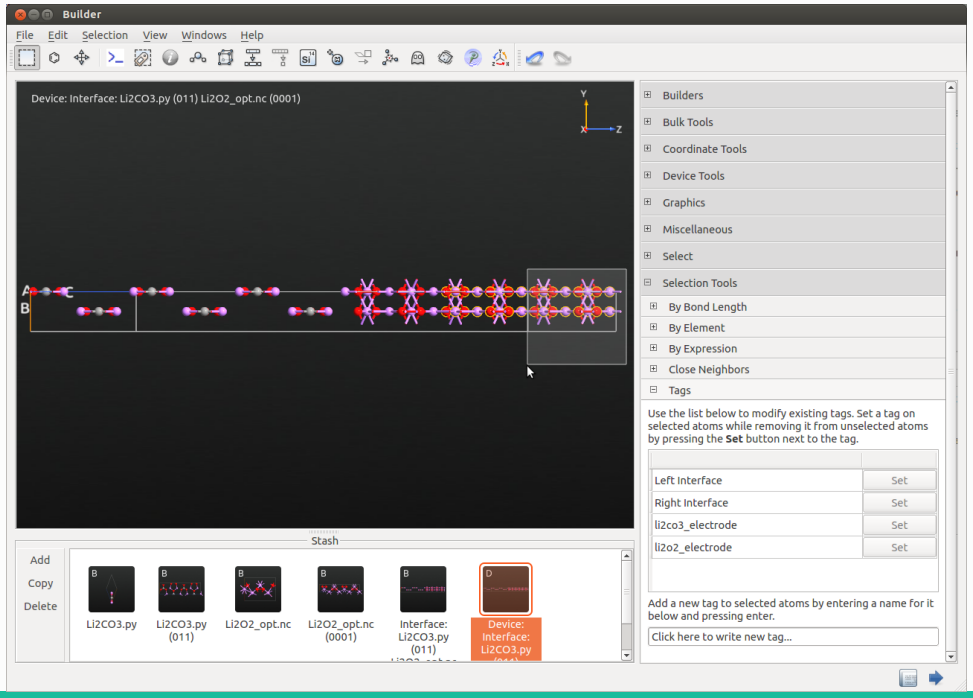
Tip

You can learn more about the Interface Builder in the Technical Notes on Interface Builder.

Optimizing the interface

A step-by-step procedure on how to optimize the geometry of a device configuration is described in the Advanced device relaxation - manual workflow. The main steps are the following:

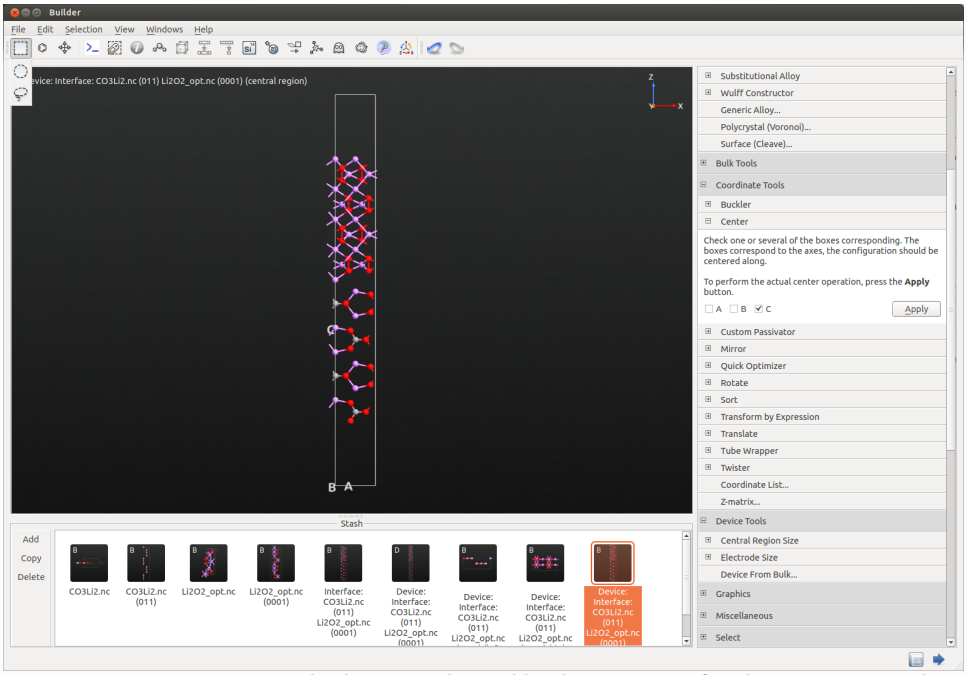
- Tag the electrode extension regions by using the Selection Tools ▸ Tags plugin. You can do that by selecting the atoms in the electrodes, the electrode extension region will be automatically selected.



Hint

Tag also the first layer outside the electrode extension regions which is already part of the central region.By doing so, the *Device From Bulk* plugin will be able to recognize the proper periodicity and recreate the device structure (see below).

- Extract the central region as *BulkConfiguration* by using the split device plugin, increase the C vector and center the configuration.



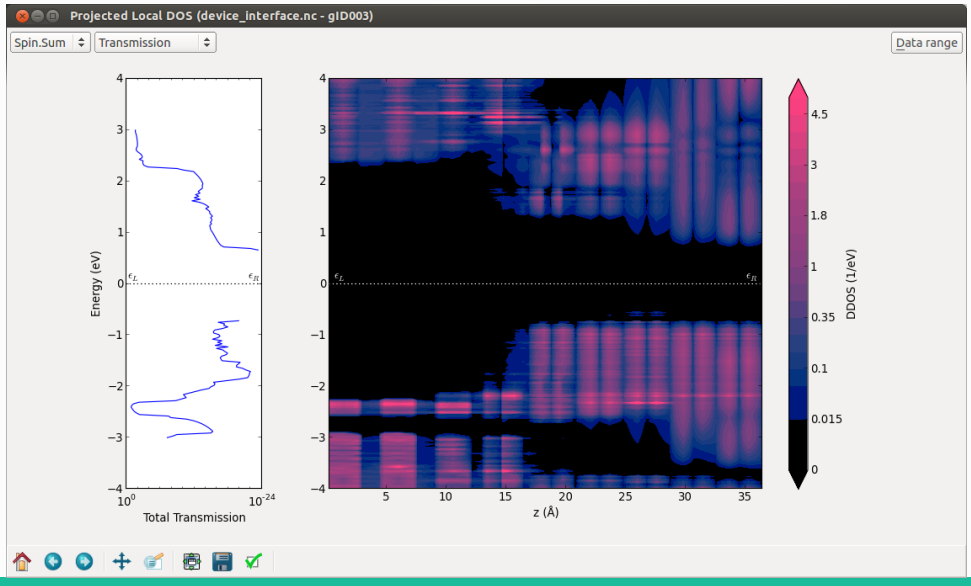
- Set up a geometry optimization calculation with rigid body constrain for the Li_2O_2 tagged region and fixed constrain for the Li_2CO_3 one. You can also download the corresponding interface_bulk_opt.py.

- Finally, when the optimization of the interface in a bulk configuration is done, import in the **Builder** the optimized structure and recreate the device as described in the previous section.

Electronic structure

Send the device configuration from the **Stash** to the **Scripter** and set up a new device calculator with the GGA-RPBE exchange-correlation potential and a 7x15x200 k-point sampling. You can leave all other parameters as defaults. Here, you can download the whole script: device_interface.py.

You can add various analysis to investigate in more detail the electronic structure and the transport properties. Below, for example, the projected device density of state analysis is shown in the picture. Here you can see that Li_2CO_3, on the left side, has a much higher band gap than Li_2O_2. Electronic conduction is thus expected to be very low, as it is indeed shown in [1].



Hint

You can further investigate the Li diffusion processes in Li_2O_2 and Li_2CO_3 crystals by following the Li-ion diffusion in LiFePO4 for battery applications.

References

[1] (1,2,3,4)
Yedilfana S. Mekonnen, Juan M. Garcia-Lastra, Jens S. Hummelshøj, Chengjun Jin, and Tejs Vegge. Role of li2o2-li2co3 interfaces on charge transport in nonaqueous li–air batteries. *The Journal of Physical Chemistry C*, 119(32):18066–18073, 2015. doi:10.1021/acs.jpcc.5b04432.

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