DFT Predicted XAS Spectra for Al_2O_3-Si Interfaces

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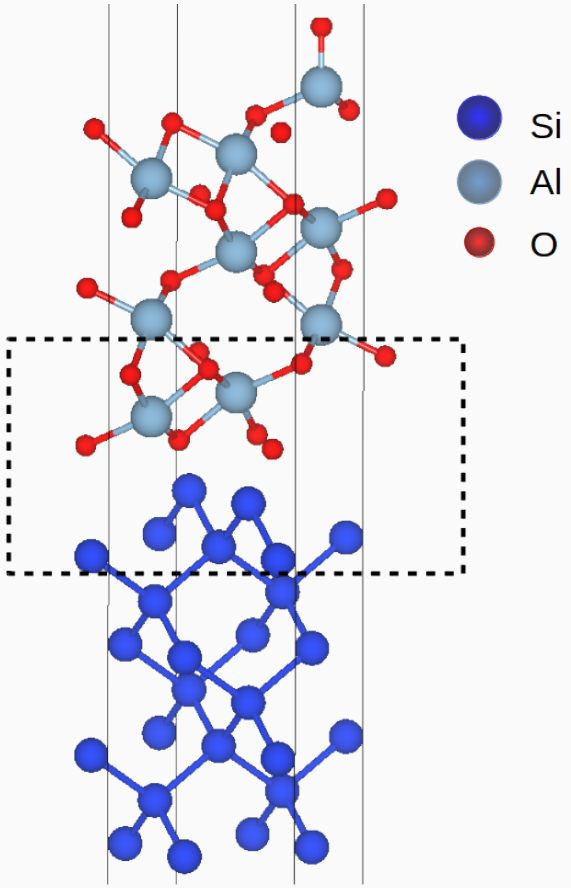
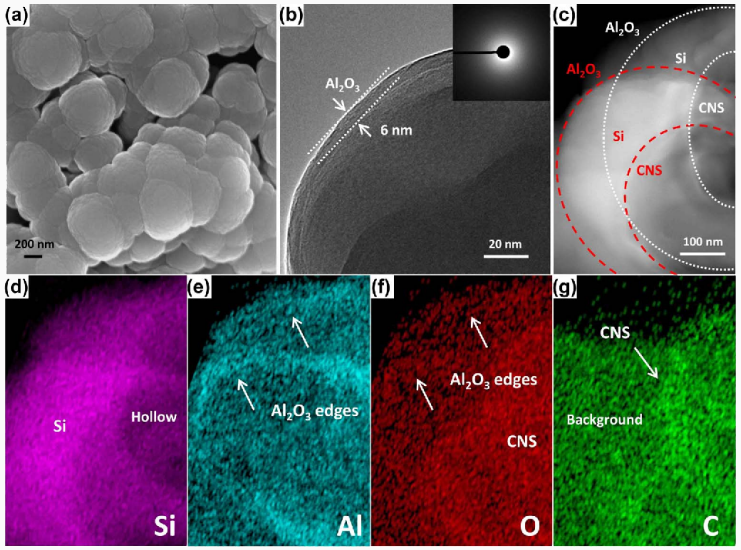


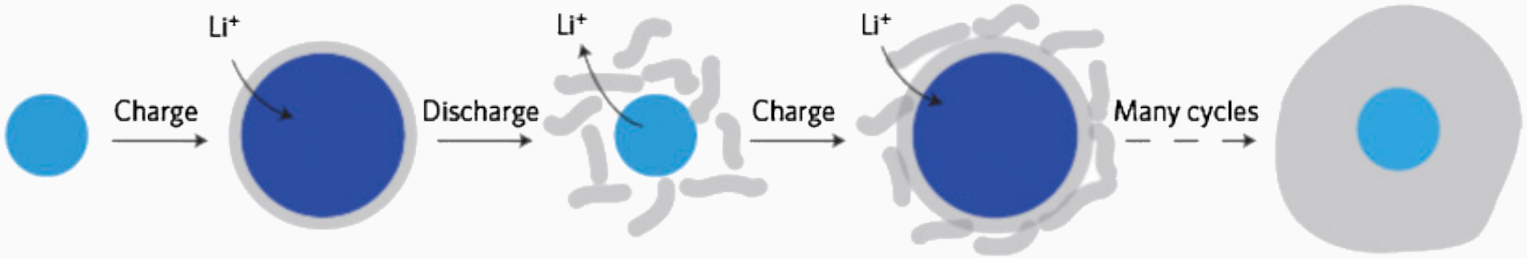
Outline

1. Li-ion battery surface coatings
2. X-ray Absorption Spectroscopy for Surfaces
3. Alumina X-ray Absorption Spectroscopy
4. Conclusions and future work



Li-ion battery surface coatings

Si as a Li-ion battery anode

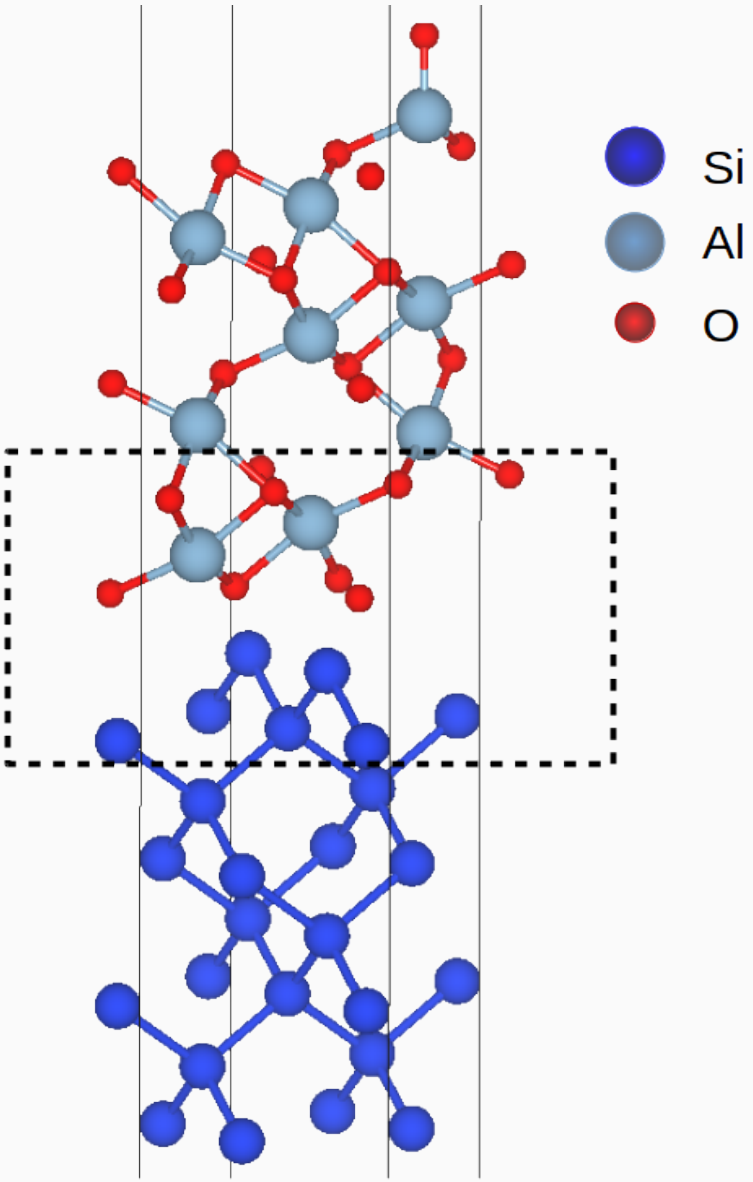


- Si has a theoretical capacity of 4200 mAh g^{-1}
- Volume expansion over 400% results in rapid capacity fading
- Atomic Layer Deposition (ALD) formed coating materials can improve capacity fading by 10-20%

Materials Today, **17**, 6, 285-97 (2014), *Electrochimica Acta* **251**, 710–728 (2017)

Artificial solid-electrolyte interphase coatings

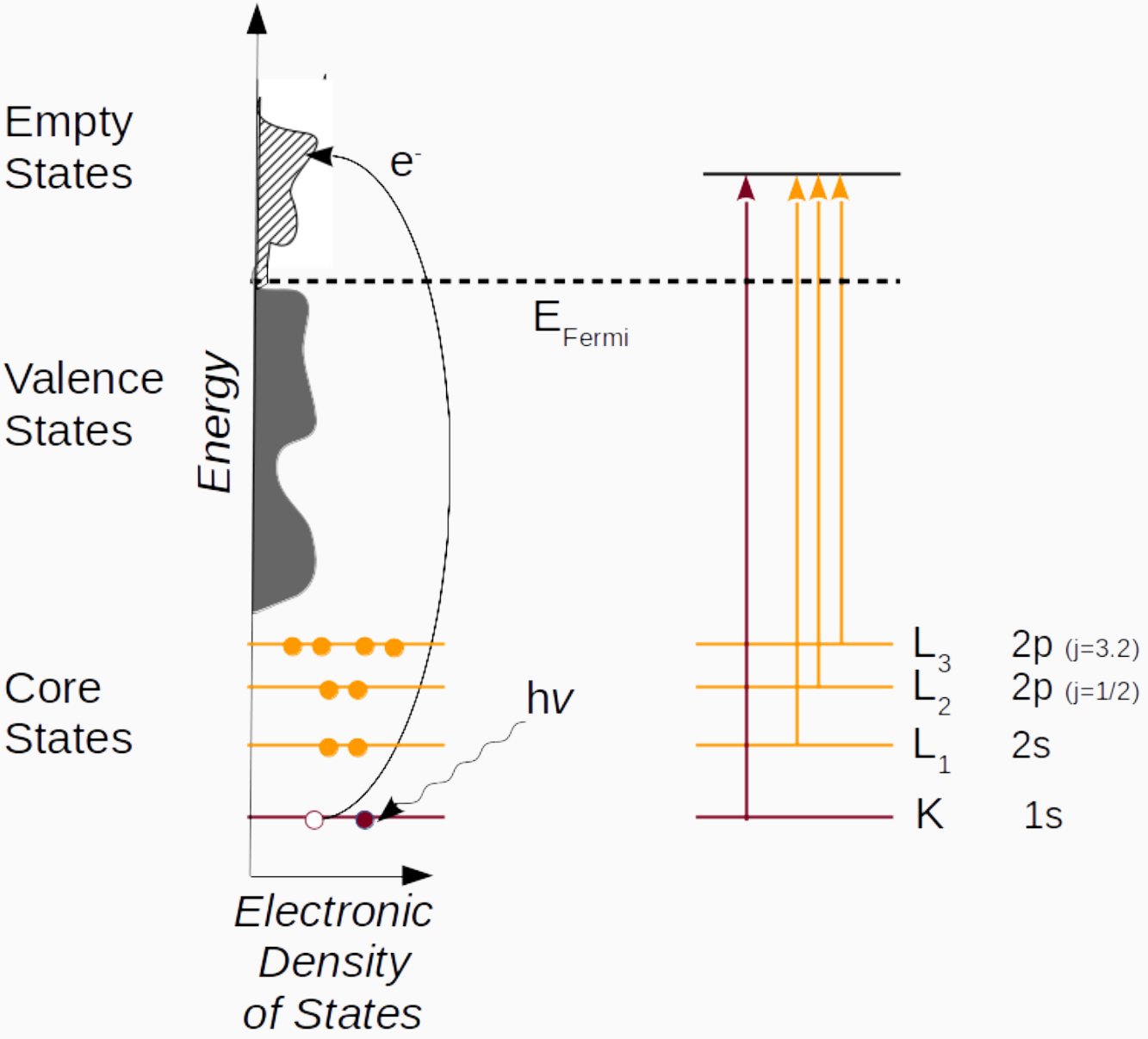
- NMR does not have high enough resolution to scan the interface
- ALD can form stacks, multi-layers, or a thinner substrate to be studied more easily
- X-ray Absorption Spectroscopy (XAS) is able to effectively study coordination at the interface and surface



J. Appl. Phys., **92**, 4, (2002)

X-ray Absorption Spectroscopy for Surfaces

X-ray Absorption Spectroscopy



X-ray Absorption Spectroscopy Using DFT

Electron transitions are described by imaginary part of dielectric function

$$\epsilon_2(\boldsymbol{q},\omega) = \frac{4\pi e^2}{q^2\Omega}\sum_{\sigma}|\langle\sigma|e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}|c\rangle|^2\delta(\hbar\omega - E_\sigma + E_c) \tag{1}$$

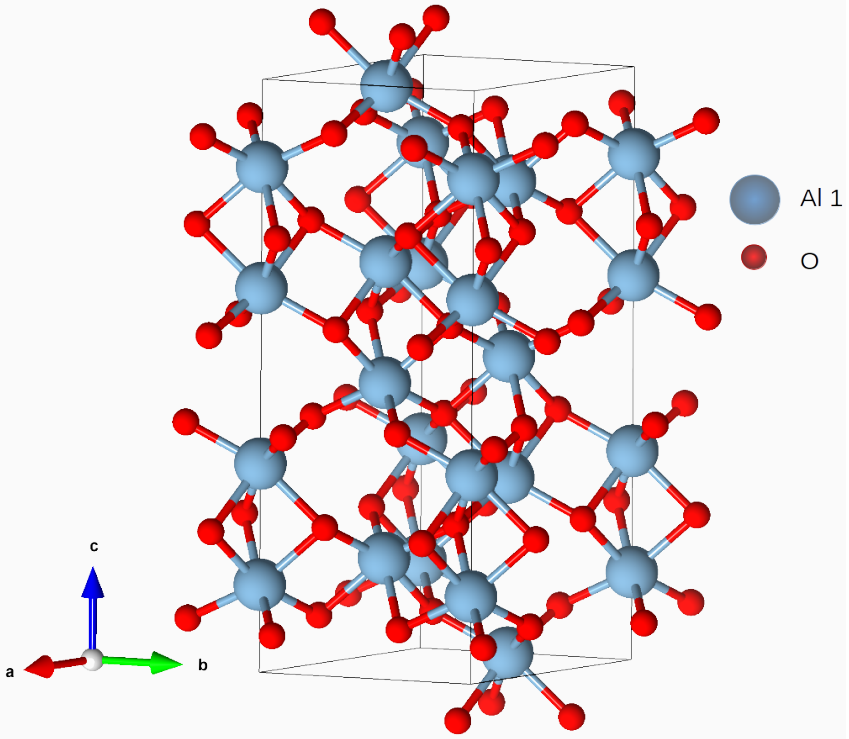
In CASTEP this is combined with the core-hole pseudopotential method combined with supercell construction:

$$1s^2\ 2s^2\ 2p^4 \longrightarrow 1s^1\ 2s^2\ 2p^5 \tag{2}$$

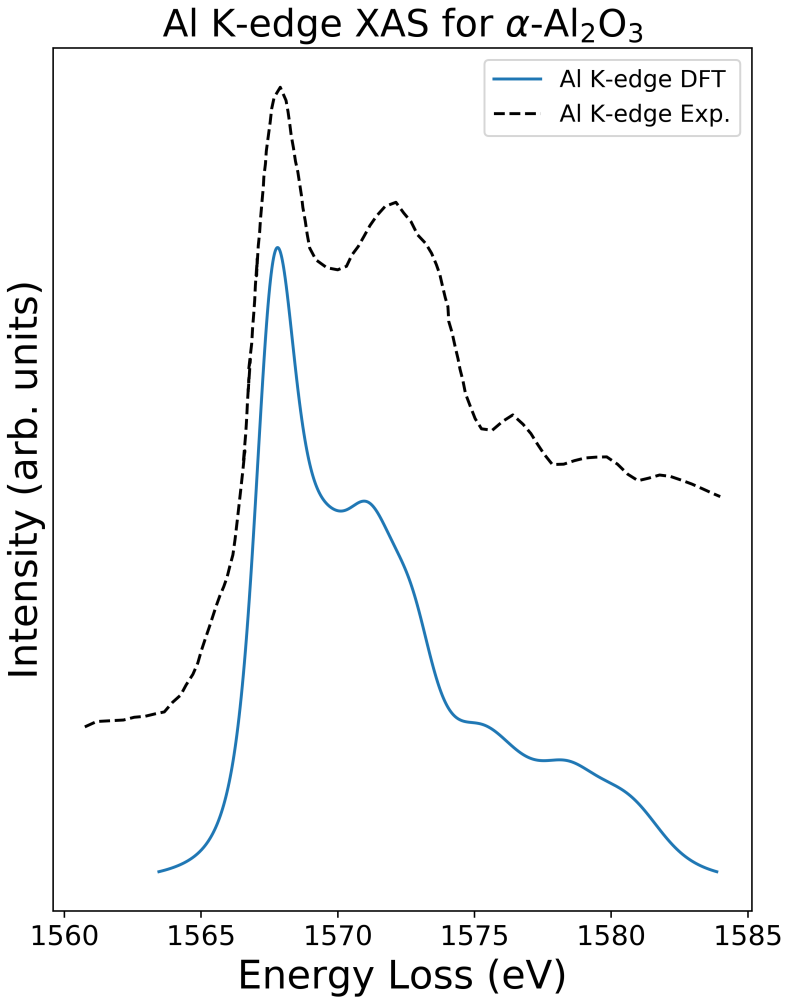
Zeitschrift fuer Kristallographie 220(5-6) pp. 567-570 (2005), *J. Phys. Cond. Mat* **21**, 10 (2009)

Alumina X-ray Absorption Spectroscopy

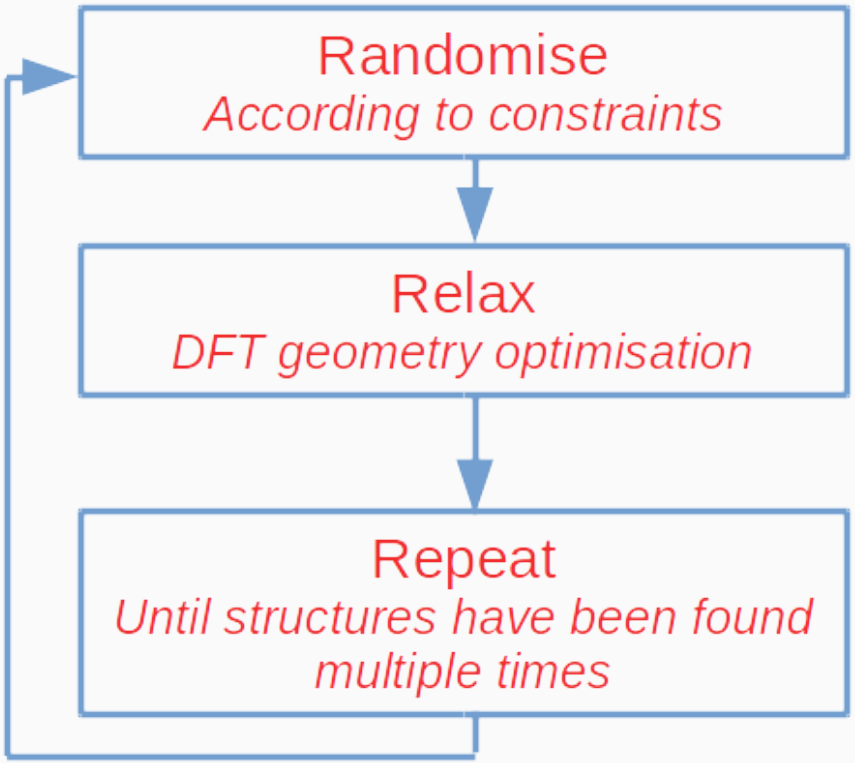
α-alumina

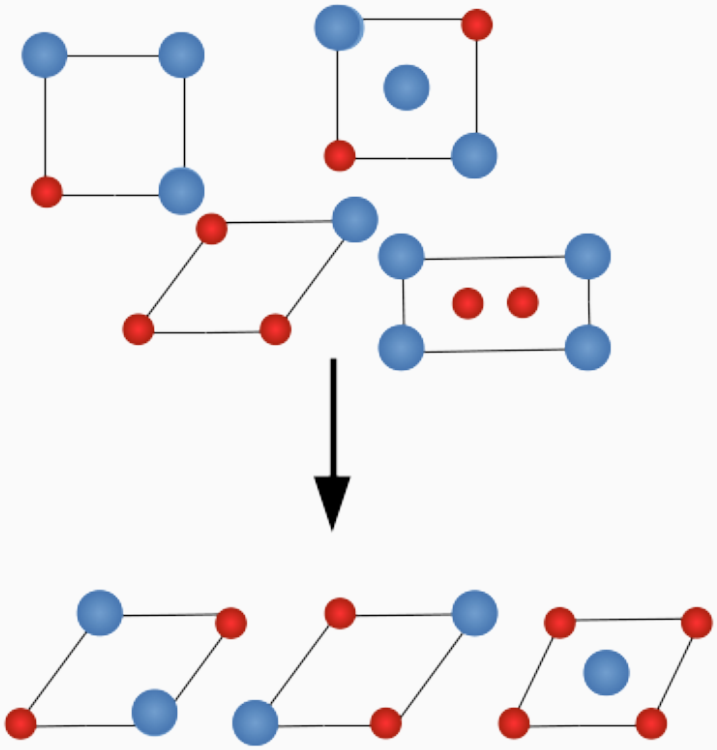


α-alumina
1 Al site



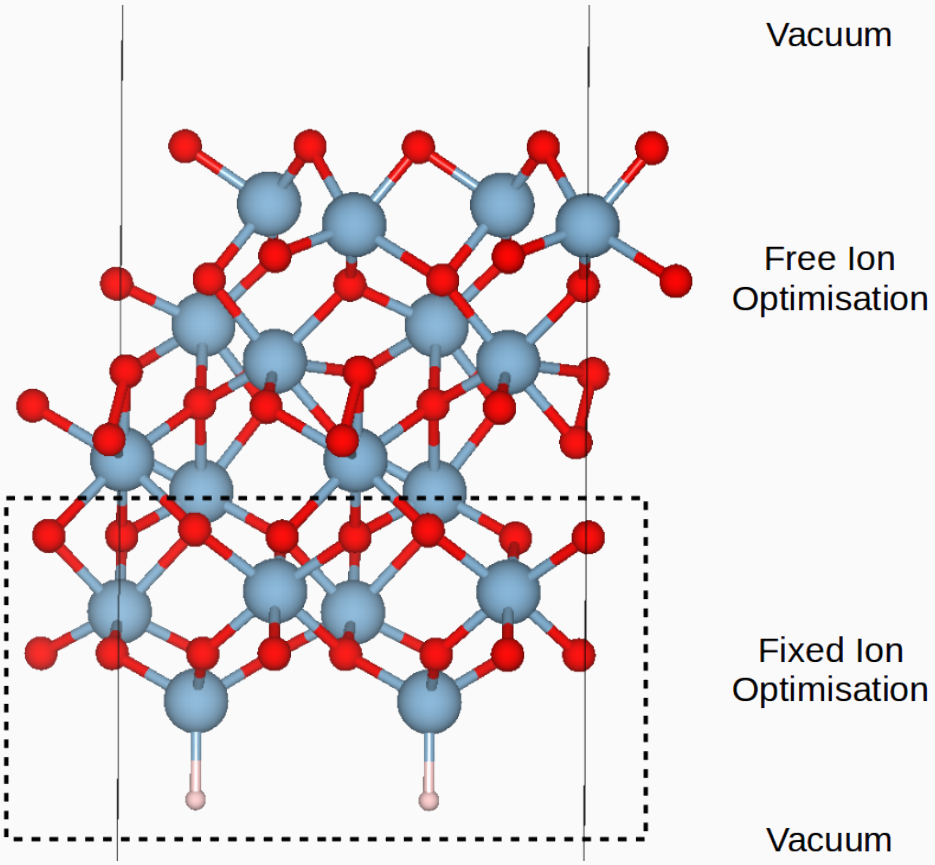
Surface AIRSS





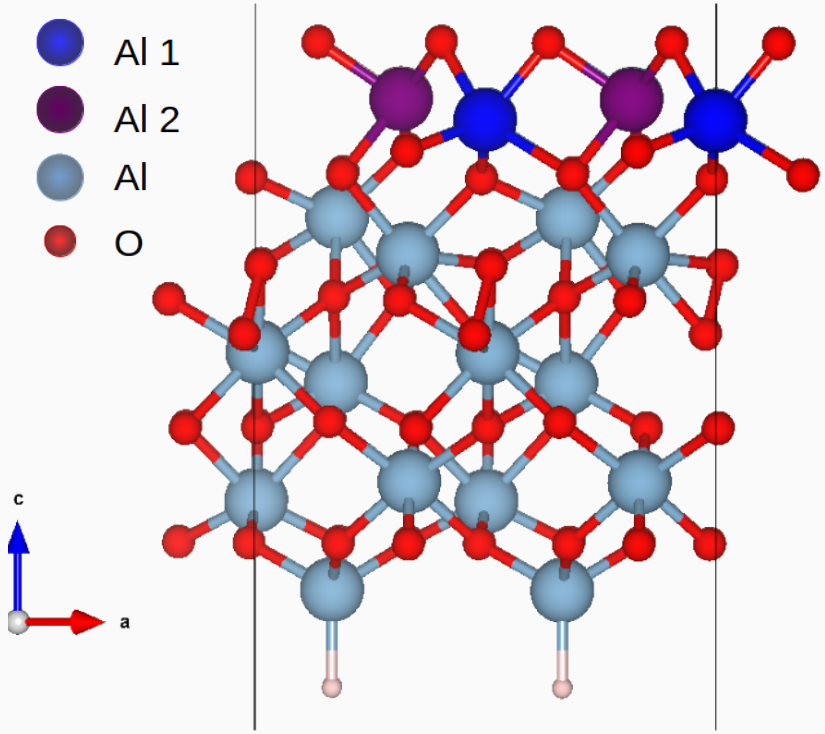
Using *ab initio* Random Structure Searching (AIRSS) to find the lowest energy surfaces

Surface optimisation

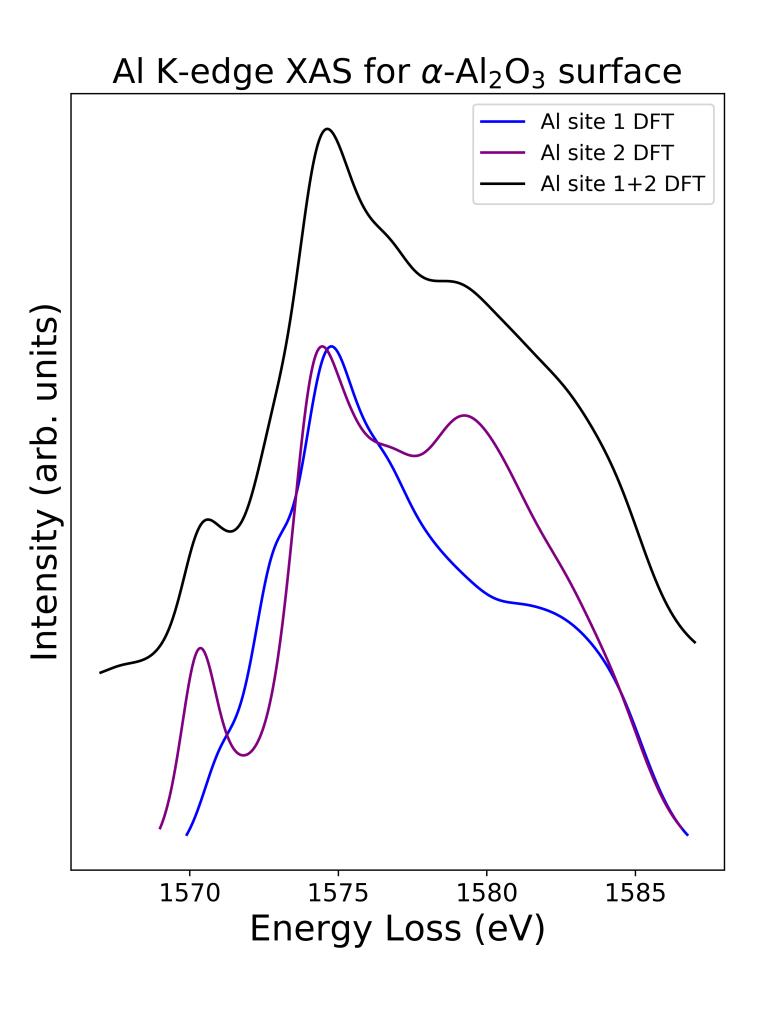


Geometry optimisation on surfaces using periodic boundary conditions requires a fixed cell optimisation and vacuum layers around the cell in the z direction

α-alumina surface

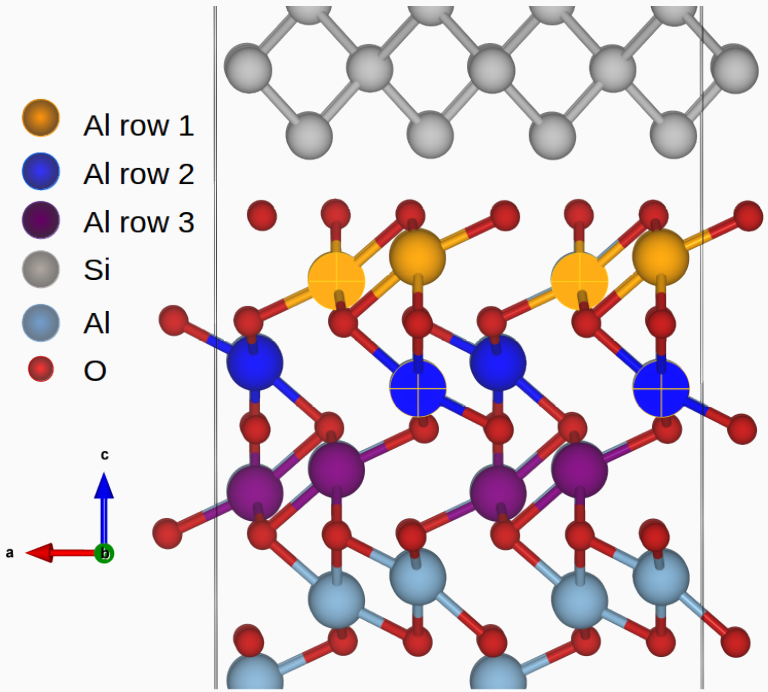


Optimised α-alumina surface, hydrogen terminated

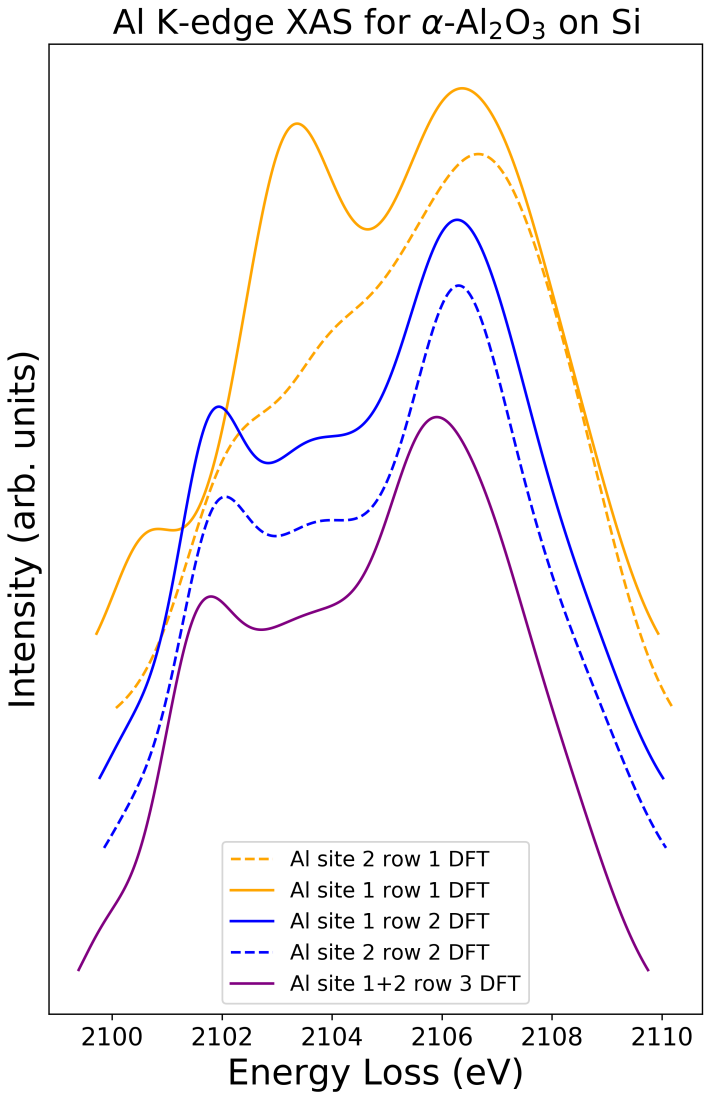


α-Al_2O_3 surface K-edge spectra for two asymmetric sites at the surface edge

XAS on Al_2O_3-Si interface



Al K-edge XAS by row for the Si-α-Al_2O_3 interface



Conclusions and future work

Conclusions

- XAS spectra for the α-Al_2O_3-Si interface shows a convergence to bulk after 3 layers of alumina
- Use AIRSS to predict hydrogen and oxygen sites at the interface, and assess the stability of various interfaces
- Conduct the K-edge XAS at Diamond Light Source
- Consider the formation of Al_2O_3 at other interfaces

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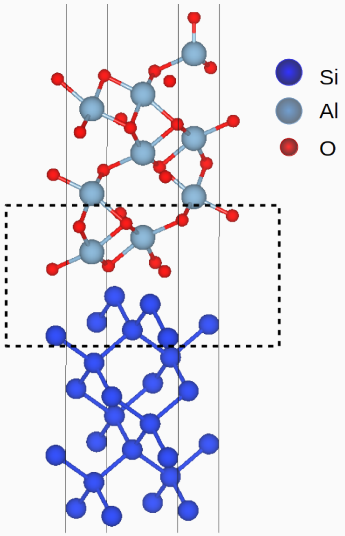

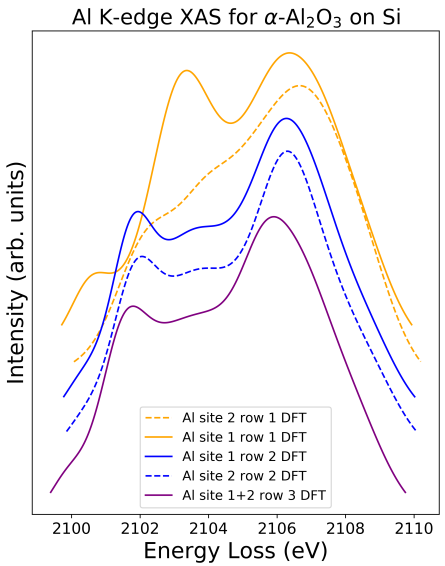

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