Visualization of ion migration pathways

17.09.13 Mette Østergaard Filsø

Danmarks Grundforskningsfond
Danish National Research Foundation
iNANO

Outline

- Introduction
- Procrystal analysis
  - Primary results
- Summary
- Discussion and outlook

Introduction

High demand for portable electronics

↓

High demand for high-quality batteries

- Reliable
- Long lifetime, short recharge time
- Safe
- Light-weight
- Cheap

Requires large amounts of research

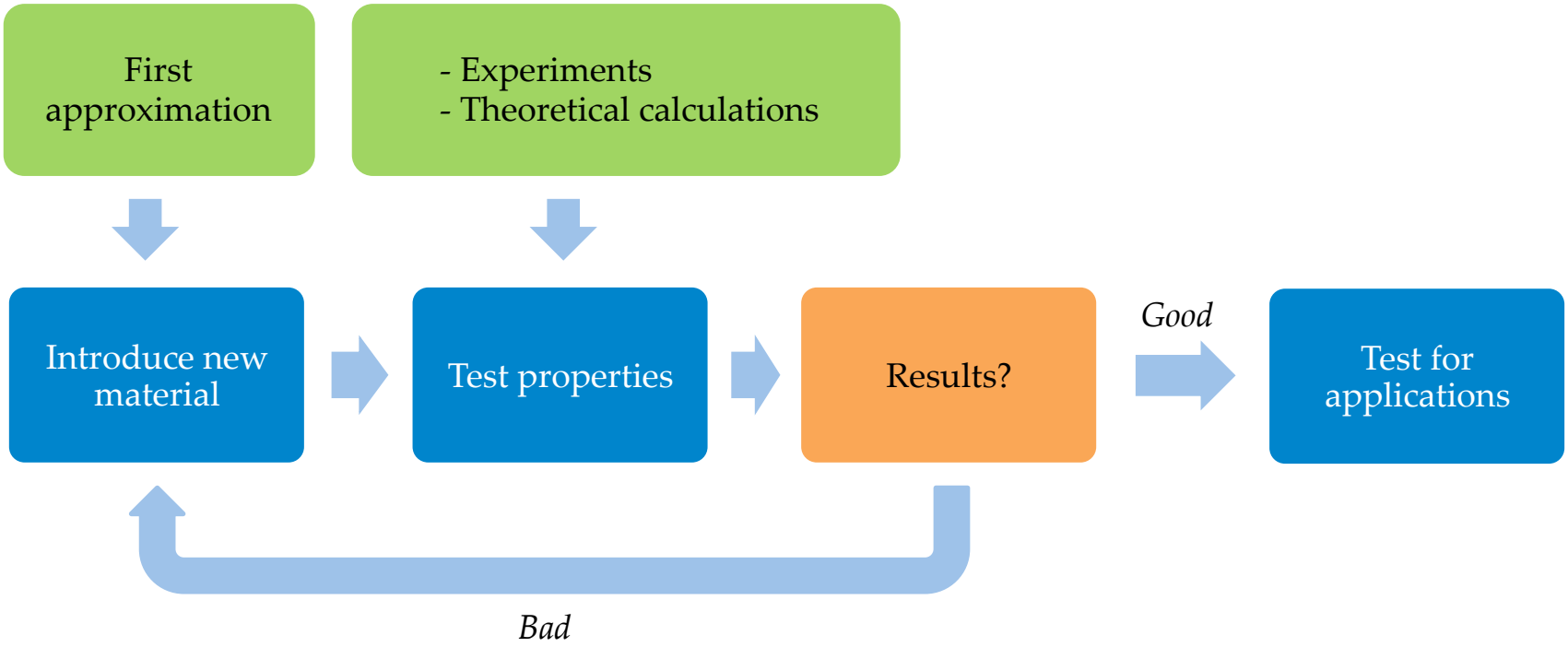






Introduction

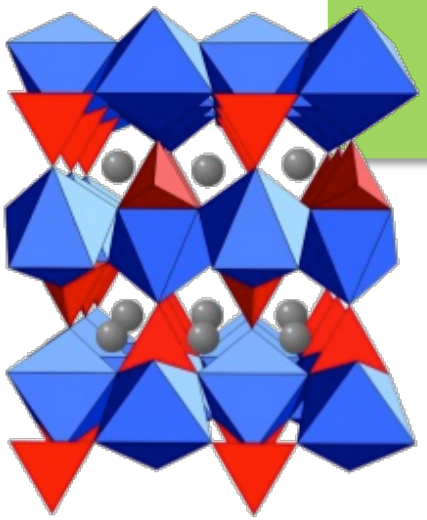
The search for new electrode materials

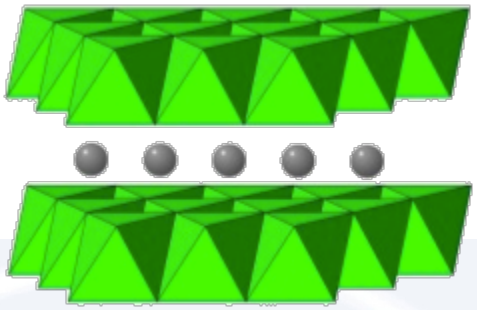


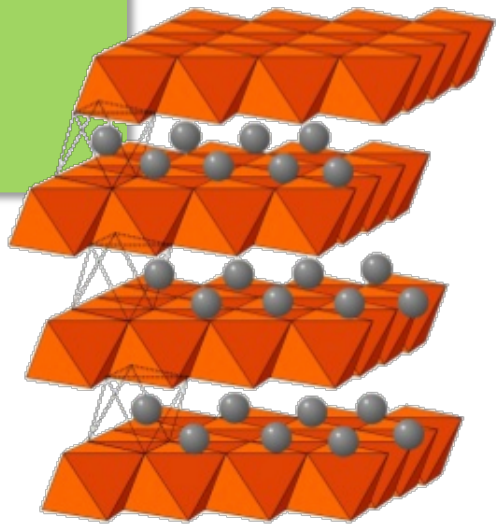
Introduction

- A major contributor to the performance of the electrode is *ionic conductivity*.
- The ionic conductivity is dependant on the ease of migration through the *crystal structure*.

First approximation tool:
Explain ionic migration in the single crystal
- Quick
- Simple
- Cheap



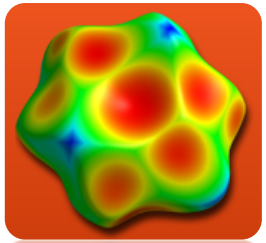




Procrystal analysis

A clever description of the crystal structure

Unit cell dimensions
Space group
Atomic positions

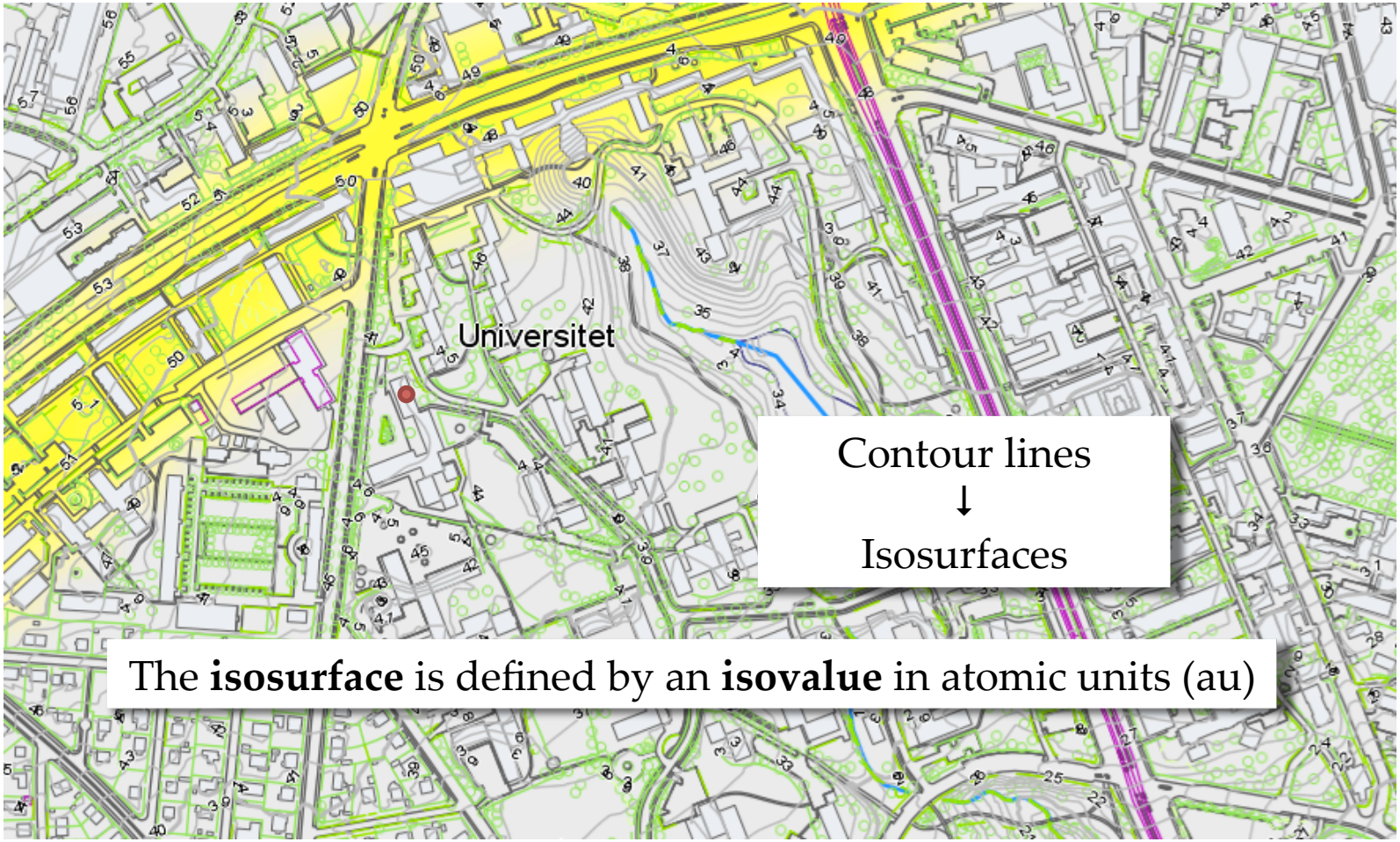


Procrystal

$$\rho_{pro}(r) = \sum_{A \in crystal} \rho_A(r)$$

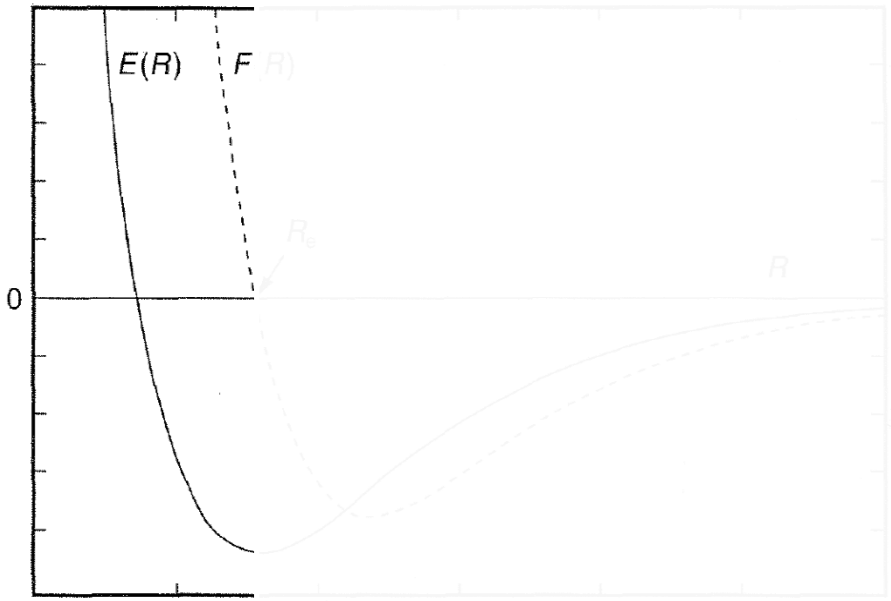
Ball-and-stick model → **Continuous landscape of electron density**

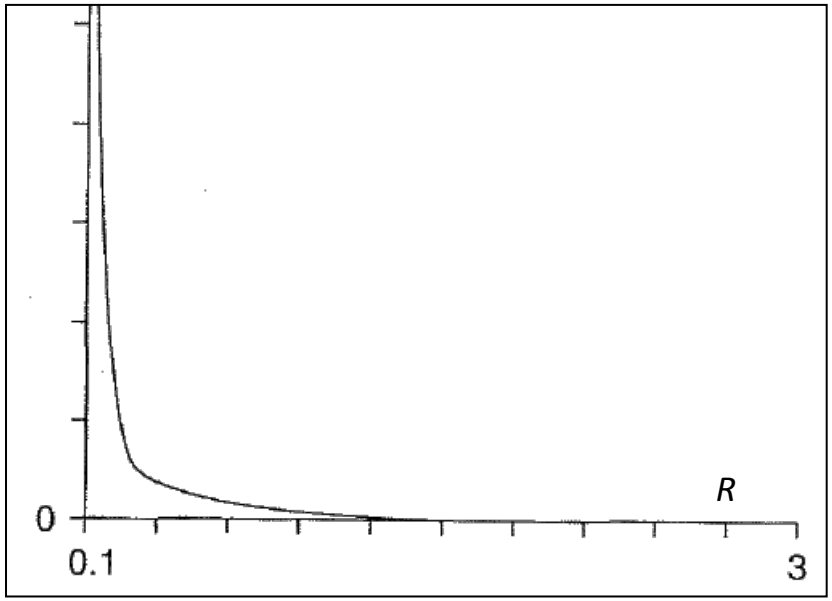
Procrystal analysis



Procrystal analysis

Relation between potential energy and electron density





Popelier 'Atoms in molecules: an introduction', *Prentice Hall*, PTR (2000),

Procrystal analysis

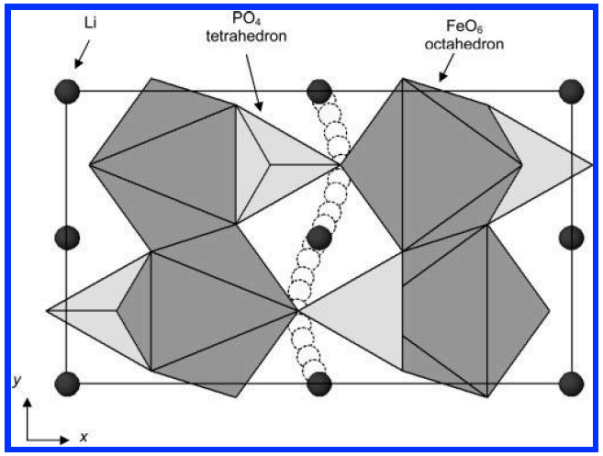
Migrating ions follow paths of **low electron density**

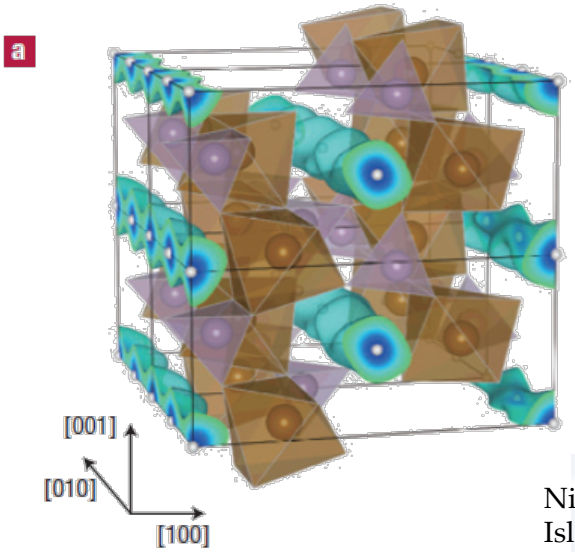
$\rho_{pro}(r)$ can show regions of low electron density

For dense structures, $\rho_{pro}(r)$ can show **migration pathways**

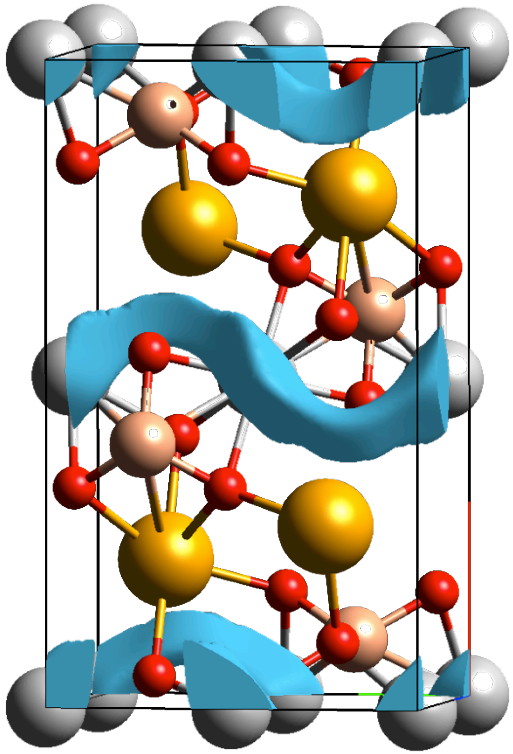
Primary results

$LiFePO_4$





Procrystal analysis



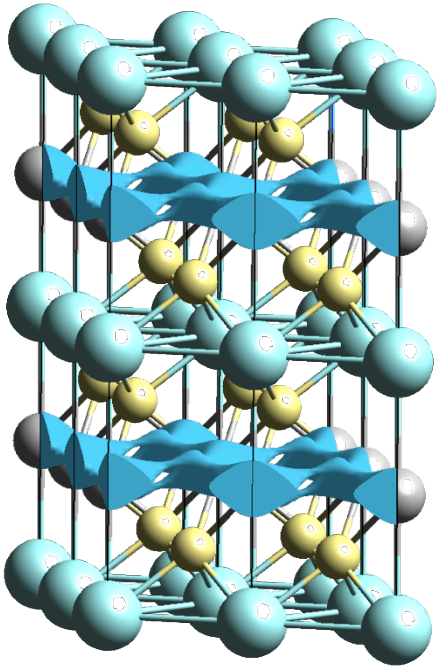
Isovalue: 0.003 au
1D conductor (*b*)

Nishimura *et al.*, *Nature mat*, **7** (2008), 707-711
Islam *et al.*, *Chem. Mater.* **17** (2005), 5085-5092

Danmarks Grundforskningsfond
Danish National Research Foundation
iNANO

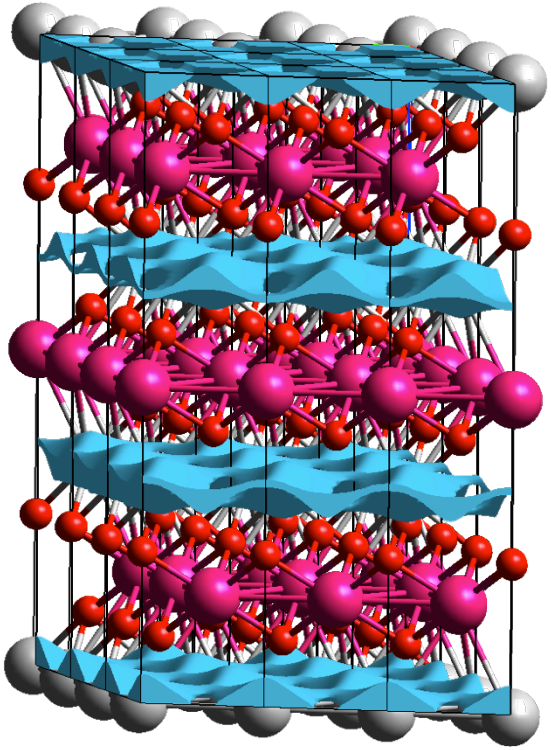
Primary results

$LiTiS_2$



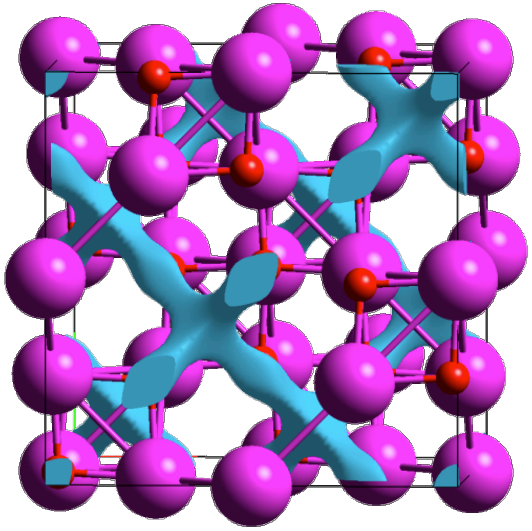
Isovalue: 0.0042 au
2D conductor (*ab*)

$LiCoO_2$



Isovalue: 0.0060 au
2D conductor (*ab*)

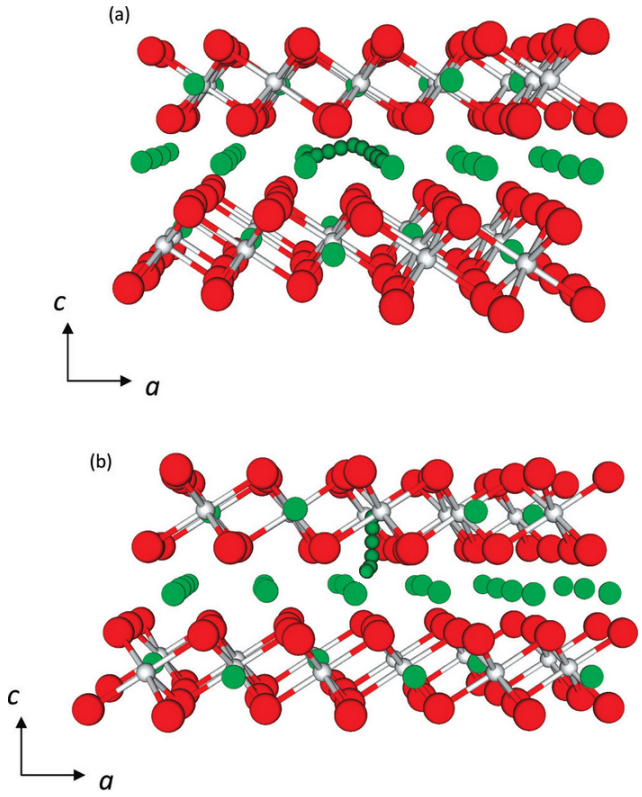
$LiMn_2O_4$



Isovalue: 0.0040 au
3D conductor

Primary results

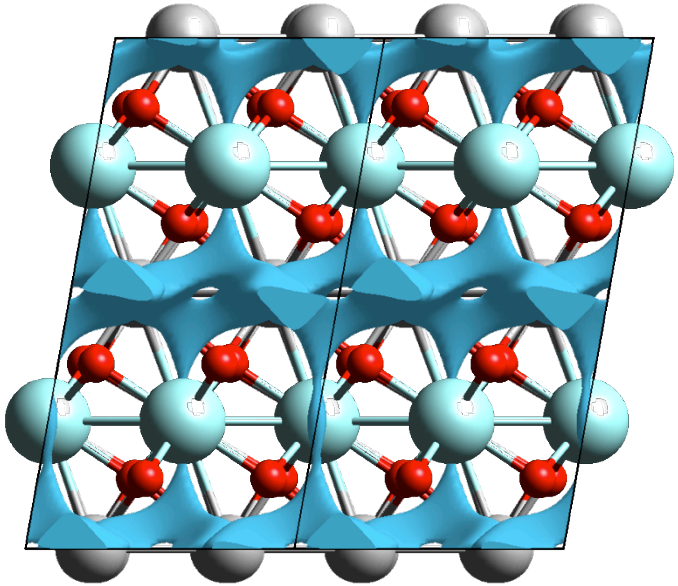
Li_2TiO_3



E_A = 0.20 eV

E_A = 0.30 eV

Procrystal analysis



Vijayakumar *et al.*, *J. Phys. Chem, C* **113** (2009), 20108-20116

Summary

- Procrystal: $\rho_{pro}(r)$
  - Visual appeal
  - Strong qualitative predictions
  - Results ($LiTiS_2$, $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, Li_2TiO_3)

With thanks:
Prof. Bo Brummerstedt Iversen *CMC/iNANO*
Prof. Mark Arthur Spackman *Danish National Research Foundation*
The Aarhus battery group