Modelling Defects in Battery Materials

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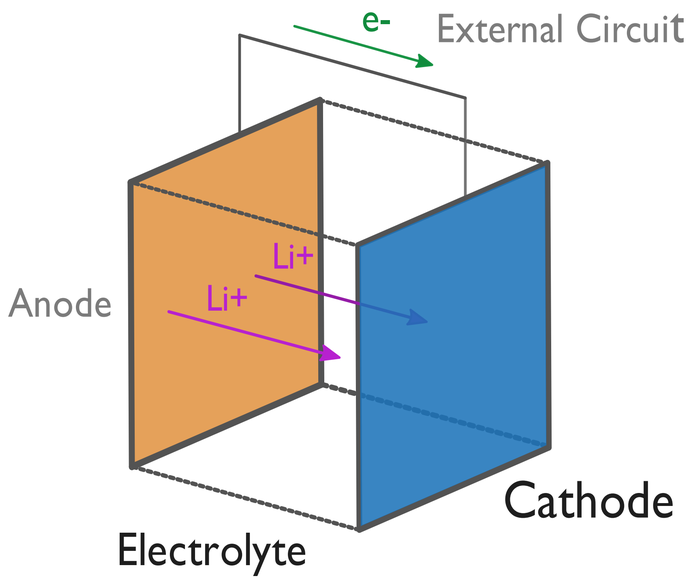
Engineering and Physical Sciences Research Council

Batteries

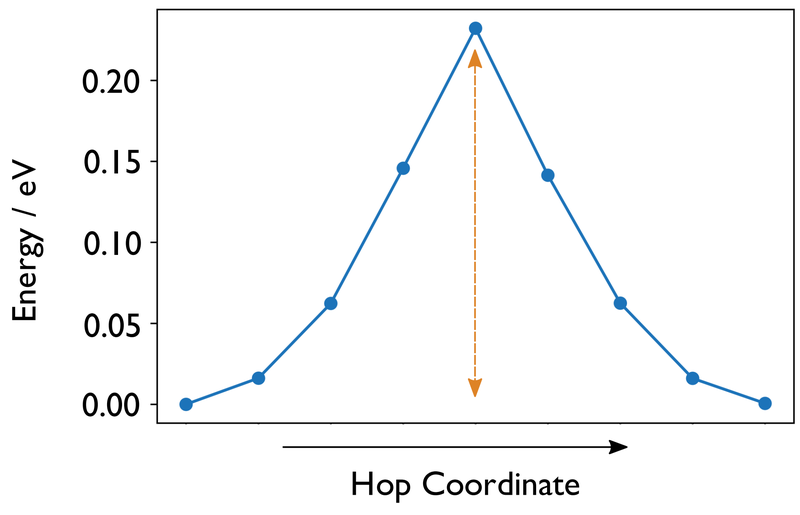


Li-ion batteries are comprised of two electrodes (the anode & cathode) separated by an electrolyte.

- On discharge, Li ions diffuse from the anode to the cathode, via the electrolyte.
- Electrodes conduct both electrons & Li ions
- Electrolyte is insulating towards electrons
- Li removed from the anode, giving up an electron to do so
- electrons are forced into an external circuit (as electrolyte is insulating)
- Restored to charged state by external potential

Cathode & electrolyte materials stand to be improved. Battery capacity could be increased via new cathode materials; increased capacity goes hand-in-hand with increased safety concerns, potentially alleviated by replacing flammable liquid electrolytes with an Li conducting ceramic.

Polaron Transport in $LiFePO_4$



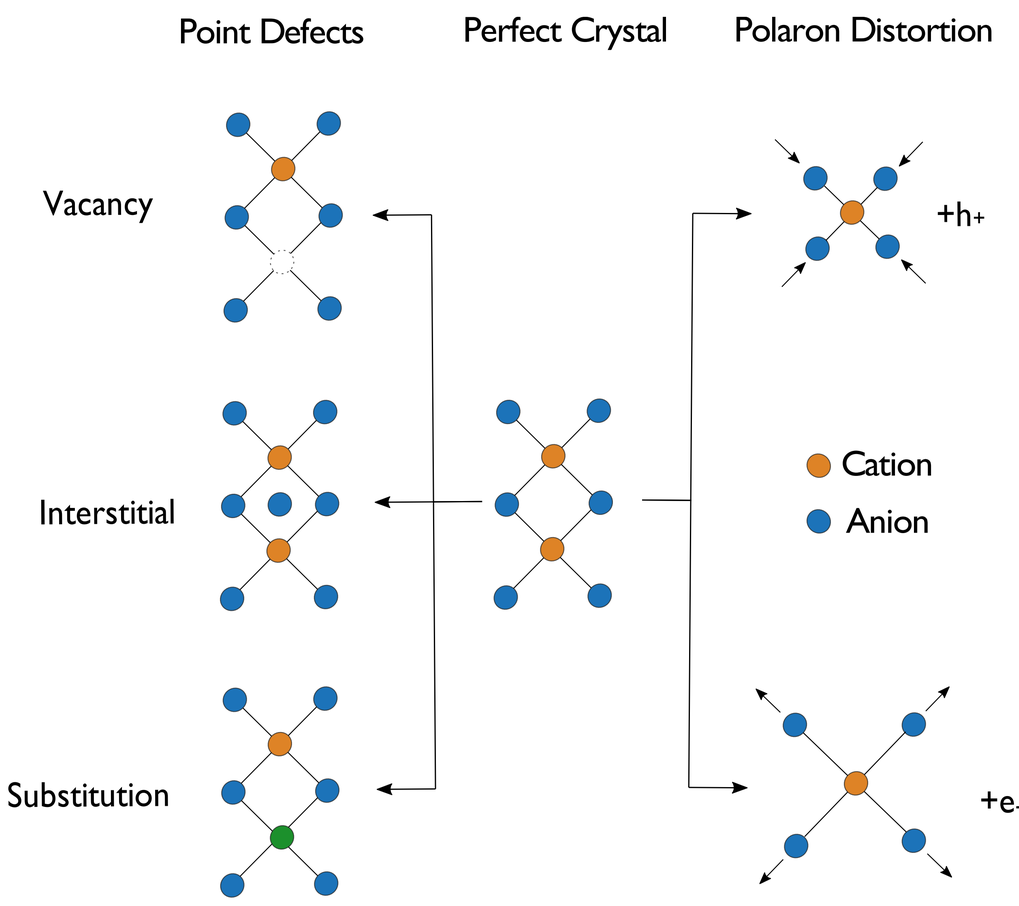
$LiFePO_4$ is a cathode material desirable for its high stability; its low conductivity, however, imposes limitations on rate capability:

- Developing improved models for conductivity for this well studied system means these models can be validated against existing data and then applied to other materials.
- DFT+*U* used to calculate the energy barrier for a polaron hopping from one lattice site to another: 0.23 eV (as shown in the figure above).
- Use this information to parameterise kinetic Monte Carlo calculations to get a full picture of electron transport through the cathode.

Methods:

- DFT+*U* (*U*{Fe_d} = 4.2 eV – *ab Initio* fitting) [1]
- Linear interpolation between hole localised on two adjacent Fe ions
- ENCUT = 600 eV
- Gamma point only ***k***-point grid on a 1 x 2 x 2 supercell

Defects



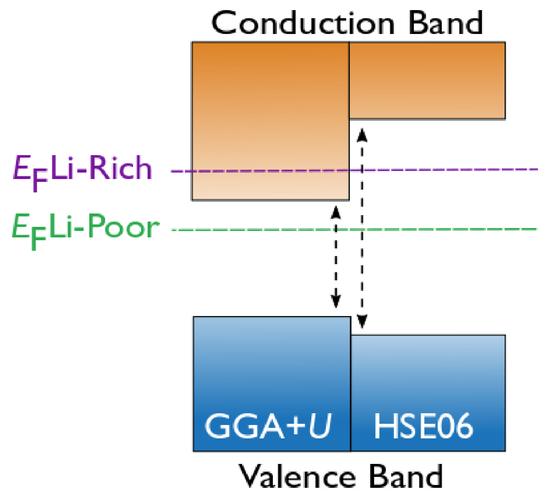
Point defects:

- Vacancy, an ion missing from the lattice,
- Interstitial, an ion on a site that is not part of the lattice
- Substitution, an atom not native to the lattice in the place of a native ion.

Polaron distortion:

- a hole localised on a cation will cause a contraction of anions
- an electron localised on a cation will repel anions.

Point Defects in $Li_7La_3Zr_2O_{12}$



$Li_7La_3Zr_2O_{12}$ (LLZO) is a ceramic electrolyte candidate:

- Experiment suggests that LLZO could support a large number of O vacancies.[2]
- DFT+*U* study suggests O vacancies are compensated by Li vacancies – exact stoichiometry has significant implications on conductivity.
- However, under this treatment Fermi level lies in the conduction band when synthesis takes place under Li rich conditions - not expected behaviour for wide-gap insulators
- Having established a qualitative basis for O vacancy formation, we are now using hybrid-DFT to get a better physical description of the system and widen the band gap.

Methods:

- DFT+*U* (*U*{O_p} = 6.7 eV – *ab Initio* fitting)[1]
- HSE06 Hybrid functional
- ENCUT = 520 eV
- 2 x 2 x 2 ***k***-point grid

1. Lany, S. Phys. Status Solidi B, 2011, 48(5), 1052–1060.
2. Kubicek, M.; Wachter-Welzl, A.; Rettenwander, D.; Wagner, R.; Berendts, S.; Uecker, R.; Amthauer, G.; Hutter, H.; Fleig, J. Chem. Mater., 2017, 29 (17), 7189–7196.