Modelling Defects in Battery Materials

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Batteries

Lithium 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 (e^-) & Li ions
- Electrolyte is insulating towards e^-.
- Li removes itself from the anode, giving up an e^- to do so
- e^- are forced into an external circuit as it cannot travel through the electrolyte.
- Restored to charged state by external potential (provided by e.g. mains charging device)

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.
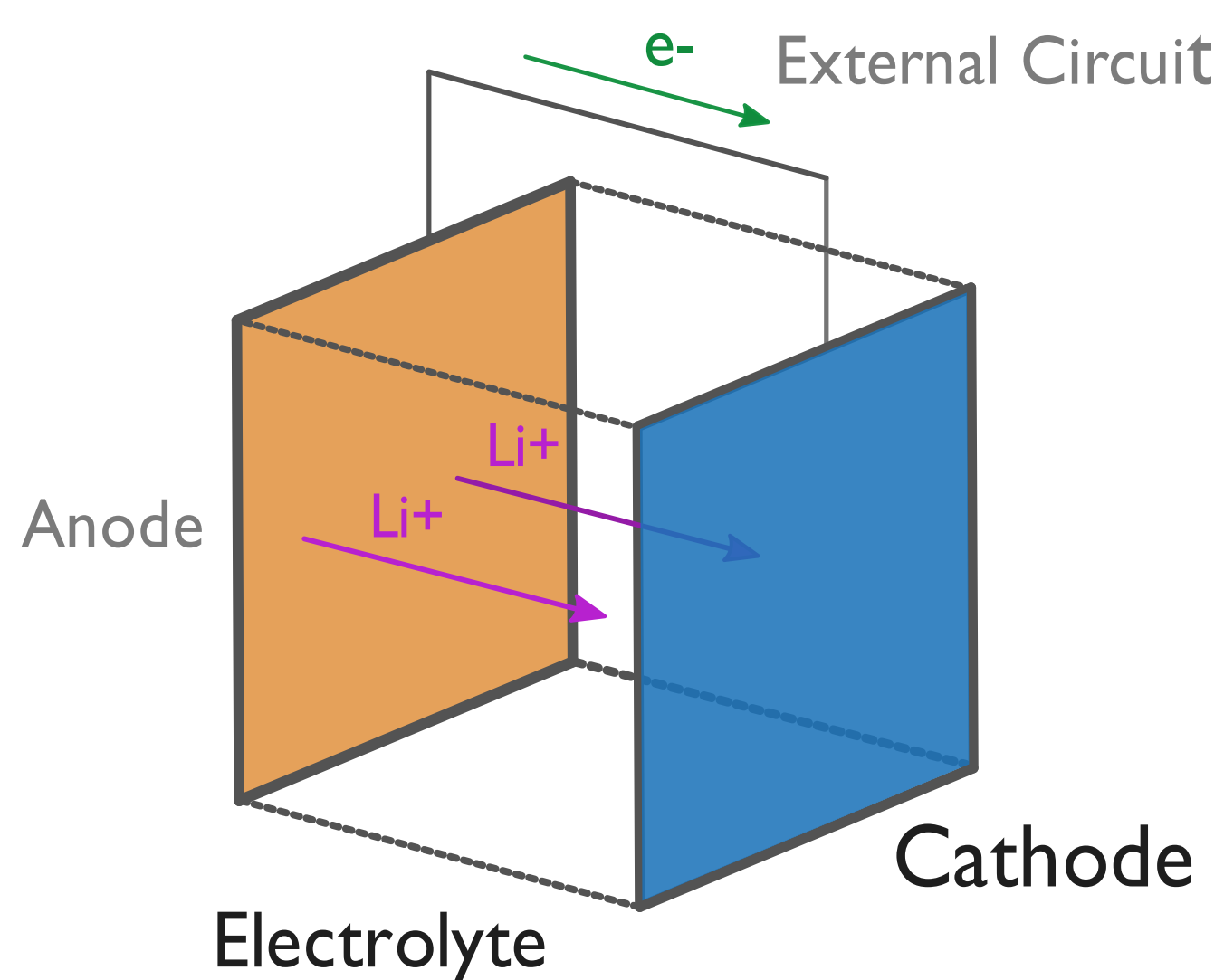

Fig 1. Battery schematic, two electrodes separated by an electrolyte connected to an external circuit.

Defects

Li is transported through solids via *point defects*. These are described in fig 2. For example, Li may travel via vacancies: one Li moves to fill a vacancy, another can move into the vacancy the first Li had created. This allows for collective transport of Li through a crystal lattice.
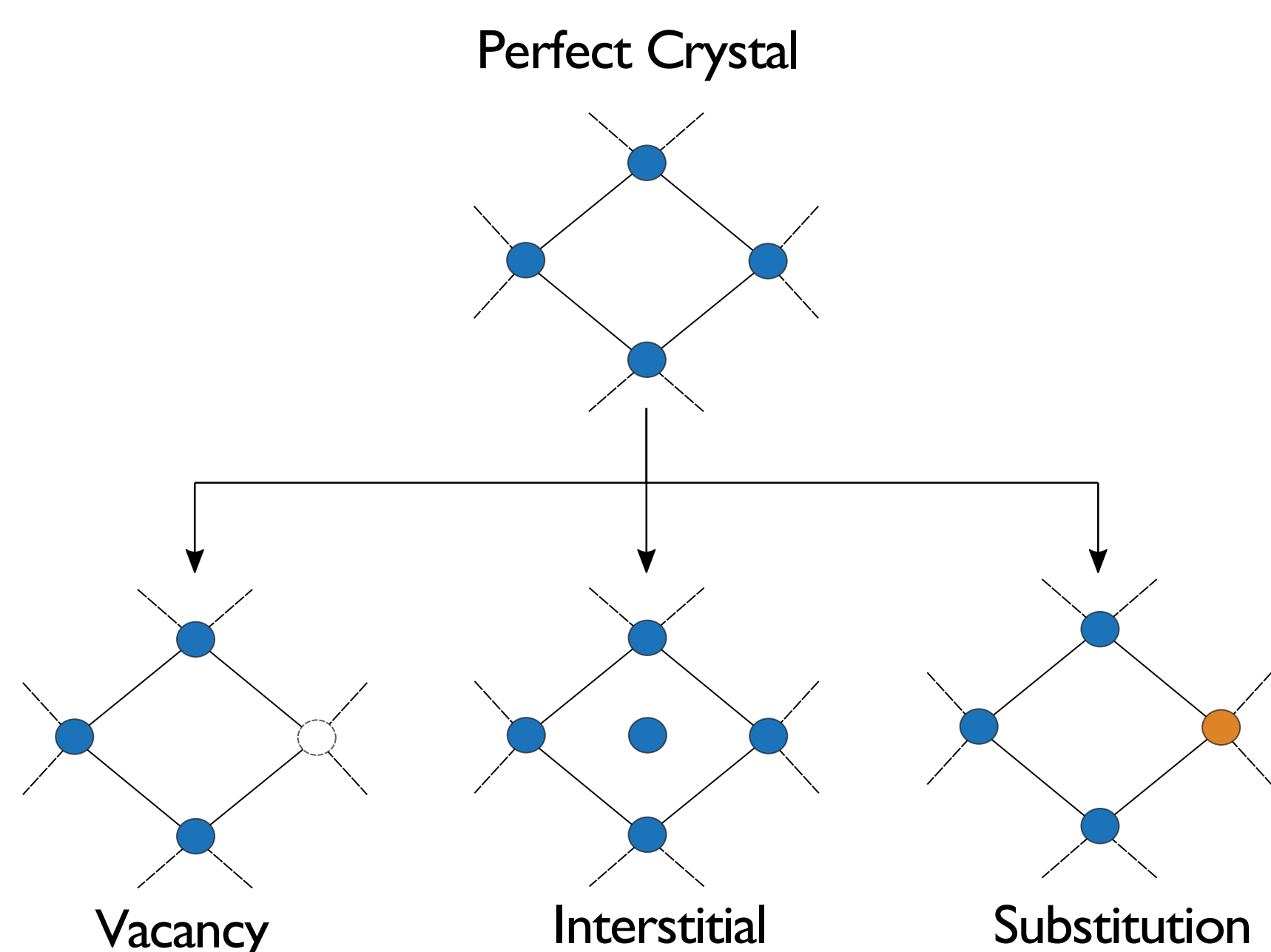

Fig 2. Different types of point defect in a lattice a vacancy is an missing ion from the lattice, an interstitial is an ion sitting on a site that is not in the lattice, a substitution is an atom not native to the lattice in the place of a native ion.

Computational Modelling

Properties of materials can be derived from system energy. To calculate system energy from first principles, we must have knowledge of all e^- & their interactions.

- Impossible for the number of e^- found in materials.
- Use *density functional theory*.[1] System energy determined by subsuming e^- & their interactions into e^- density (ρ).
- Only need to calculate the interactions between ρ & nuclei.
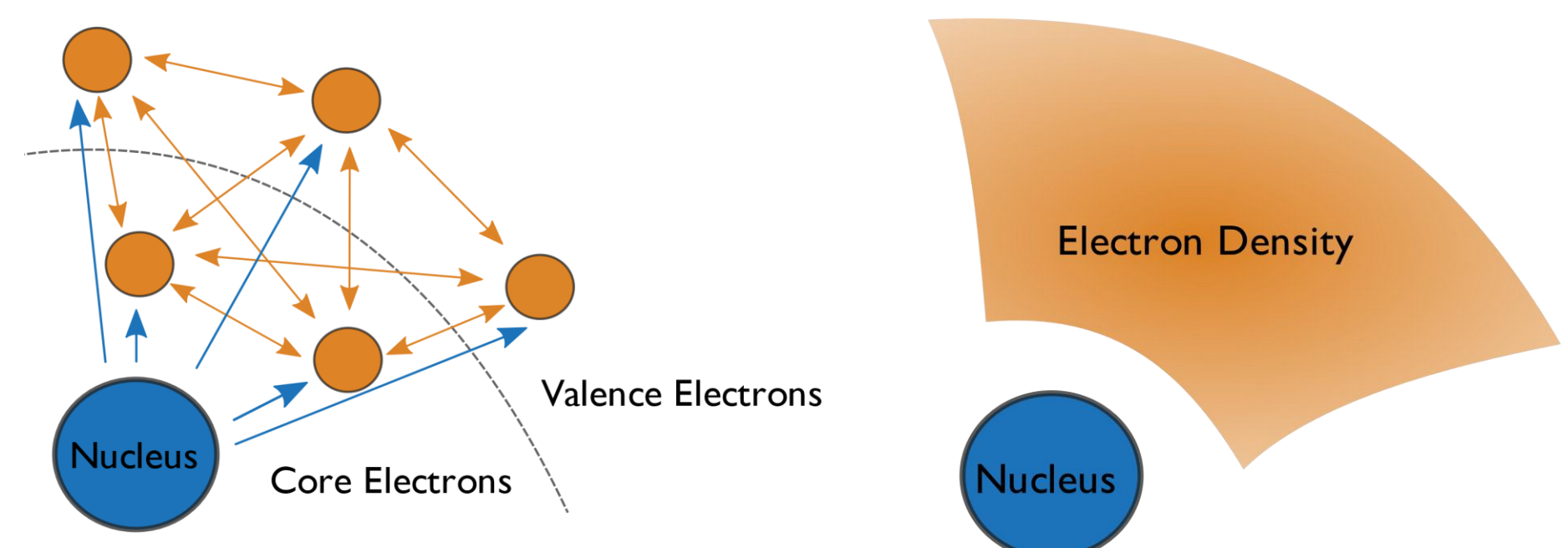

Fig 3. A. Shows a depiction of the all e^- approach to modelling atomic scale phenomena & the interactions involved, vs. the density functional theory approach.

Lithium Garnet Electrolytes

$Li_7La_3Zr_2O_{12}$ (LLZO) is a ceramic electrolyte candidate. While showing promise it is not efficient enough for application.

- Closing the gap between promising theoretical properties & real-world performance requires study of defects.
- Recent work suggests that LLZO could support a large number of O vacancies. [2]
- Vacancy formation requires charge balance, (as with any chemical reaction).
- O vacancies will remove two e^- from the lattice with it, leaving behind a +2 charge. What compensates this charge?

This work has established theoretical basis to expect that compensation to be provided by 2 -1 charged Li vacancies. Could this increase Li conductivity as we provide more Li vacancies for the remaining Li to move into? With this qualitative understanding, we now want to take this forward to quantitatively understand this phenomena.
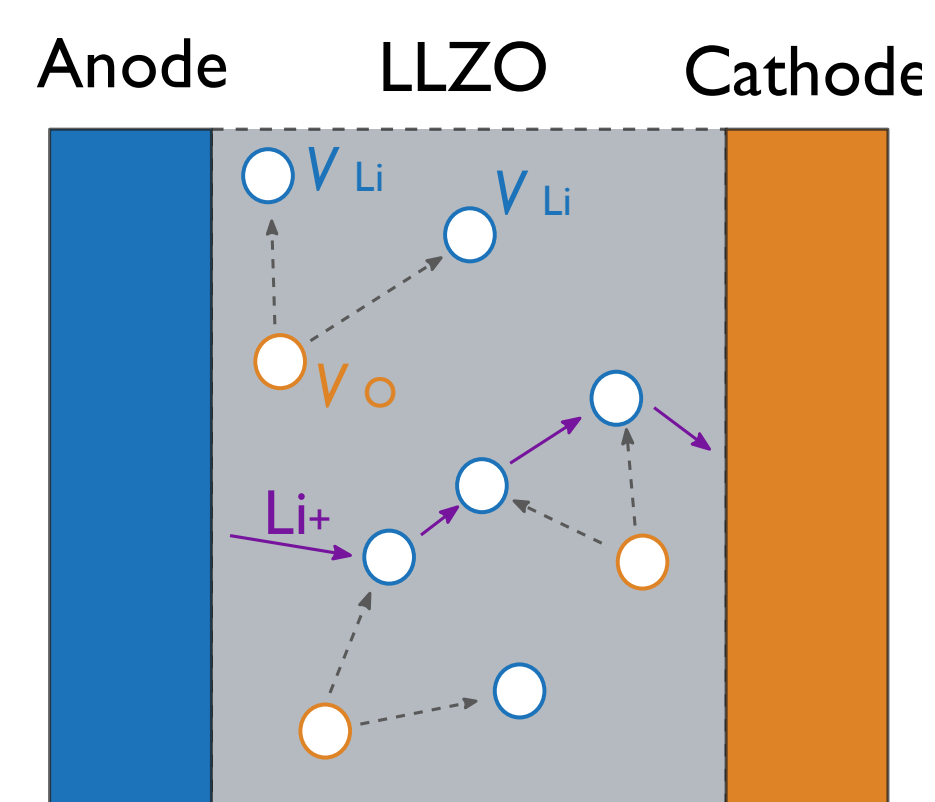

Fig 4. A schematic illustrating O^{2+}/Li^- vacancy formation in LLZO and how this may effect Li transport.

1. Hohenberg, P.; Kohn, W. Hohenberg, P.; Kohn, W. Phys. Rev. 1964, 136 (3B), B864–B871.
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.