Introduction

- The focus of our work - Li$_2$FeSiO$_4$ - holds great promise as a new cathode material for Li-ion batteries through its low potential cost, high abundance and non-toxicity.
- This material offers the possibility of extracting ~1 Li$^+$ per formula unit through novel materials design.
- The poor electronic conductivity of the corner-shared SiO$_4^{4-}$ network must be improved.

Goals

- Use DFT modelling to understand and improve the performance of Li$_2$FeSiO$_4$.
- Explore the VO$_4^{3-}$/VO$_4^{4-}$ redox-activity.

Models

- Five models for LiFeXO$_4$: three polyhedral sites: X = Si, P, V:
  - Fe in octahedral site
    - "LiFeSiO$_4"$ (Pmn2$_1$)
    - "LiFePO$_4"$ (Pmn2$_1$)
    - "LiFeVO$_4"$ (Pmn2$_1$)
  - LiFeSiO$_4$ models with 12.5% VO$_4^{3-}$ for SiO$_4^{4-}$:
    - Model A
      - "LiFePO$_4"$ (Pmn2$_1$)
    - Model B
      - "LiFeSiO$_4"$ (Pmn2$_1$)

Cation mixing

Models for Li$_2$FeSiO$_4$: relative energies from DFT

- LiFe-site-mixing is thermodynamically favoured in the delithiated state.
- Appropriate ion-substitution into the Li-layer could suppress cation mixing and the resulting voltage drop 3.1 V $\rightarrow$ 2.8 V.

Li$^+$ migration barriers

Pathways in unmixed ("Fe", Pmn2$_1$) and mixed ("Co", Pbn2$_1$) Li$_2$FeSiO$_4$ models:

Conclusions

- Li/Fe site-mixing is thermodynamically favoured.
- 2D Li$^+$-ion conductivity in Li$_2$FeSiO$_4$: higher tolerance to pathway-blocking (by impurities)?
- $<$ 30% substitution of the SiO$_4^{4-}$ polyhedral by VO$_4^{3-}$ is possible in Li$_2$FeSiO$_4$.
- VO$_4^{3-}$/VO$_4^{4-}$ substitution changes the electronic structure to give improved $e^-$ transfer.
- VO$_4^{3-}$/VO$_4^{4-}$ redox-activity is predicted in the LiFeSiO$_4$ host, allowing exchange of $>$1 Li$^+$/f.u.

Structural stability

Is it possible to substitute SiO$_4^{4-}$ for VO$_4^{3-}$ in the Li$_2$FeSiO$_4$ structure?

Formation energy of Li$_2$Fe$_{x-y}$Si$_y$V$_x$O$_4$

- $E_{formation}$ (product) + $E_{formation}$ (reactant) - $E_{formation}$ (Li$_2$FeSiO$_4$)

- Lowest-energy structures:
  - VO$_4^{3-}$ substitution destabilizes the tetrahedral structures.
  - LiFe-site-mixing is thermodynamically favoured in the delithiated state.

Electrochemical properties

What changes occur on VO$_4^{3-}$ substitution?

Low (12.5%) VO$_4^{3-}$ substitution: LiFe$_{0.875}$Fe$_{0.125}$O$_4$

- $E_{formation}$ (product) + $E_{formation}$ (reactant) - $E_{formation}$ (Li$_2$FeSiO$_4$)

- Calculation of Li$^+$ deintercalation.

Acknowledgements:
- The Swedish National Infrastructure for Computing (UPPEN, HICPC20).
- Computational facilities: PDC (PDC Parallel Data Center), UPPEN supercomputer.
- Frontal database access: PDC, HPC20.
- Research funds from Uppsala University.

References:
- Larsson, P., Liivat, A., Rajeev, A., Nytén, A. and Thomas, J.O., Structural and electrochemical aspects of Mn-substitution into LiFePO$_4$: Li/Fe site-mixing is therodynamically favourable. (Submitted to Solid State Ionics.
- Liivat, A. and Thomas, J.O.: 2D Li$^+$-ion migration in LiFe$_{1-x}$Si$_x$O$_4$-related cathode materials: a DFT study; submitted to Solid State Ionics.
- Kresse, G., Joubert, D.: from ultrasoft pseudopotentials...