Strategies for optimizing the performance of iron silicate cathode materials for up-scaled Li-ion batteries

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Motivation
- There has been tremendous interest in recent years in developing new cathode materials for high-performance Hybrid Electric Vehicles (HEVs).
- The focus of our work - Li$_2$FeSiO$_4$ - holds great promise in this context through its low potential cost, high abundance and non-toxicity.
- This material offers the possibility of extracting >1 electron per 3d-metal through novel materials design (substitutions, nanostructures, etc.)

Polyanion substitution
- DFT modelling of substitution of redox-active VO$_4^{3-/4-}$ at the SiO$_4^{4-}$-site
- Complete delithiation possible!
- Less strain ($\delta_{FeO4^2-}$)
- Higher $\Delta_u$ (smaller band-gap)
- Volume expansion: 10%
- Low V$^{4+/5+}$ voltage: 2.2V

Transition-metal substitution
- Li$_2$M$_x$Fe$_{1-x}$SiO$_4$
- Mn substitution at Fe-site:
  - Complete delithiation possible!
  - Higher $\Delta_u$ (smaller band-gap)
  - Volume expansion: 10%
  - Low V$^{4+/5+}$ voltage: 2.2V
- V$^{3+/4+}$ states reduce the band-gap.

Conclusions
- Mn-doped systems: structural instability!
- V-doped systems: higher $\Delta_u$, increased capacity - and higher V$^{3+/4+}$ voltage (~4.1V)
- Fe-systems: capacities of ~ 300mAh/g attainable with redox-active VO$_4^{3-/4-}$ instead of SiO$_4^{4-}$
- Energy-density needs optimal (VO$_4^{3-/4-}$):SiO$_4^{4-}$ ratio (to raise the V$^{3+/4+}$ voltage)

References
- Ensling, D., Stjerndahl, M., Nybtn, A., Hensino, H., Gustafsson, T. and Thomas, J.O., A comparative XPS surface study of Li$_2$FeSiO$_4$ cycled with LiTFSI- and LiPF$_6$-based electrolytes. Accepted in J. Mater. Chem.