

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

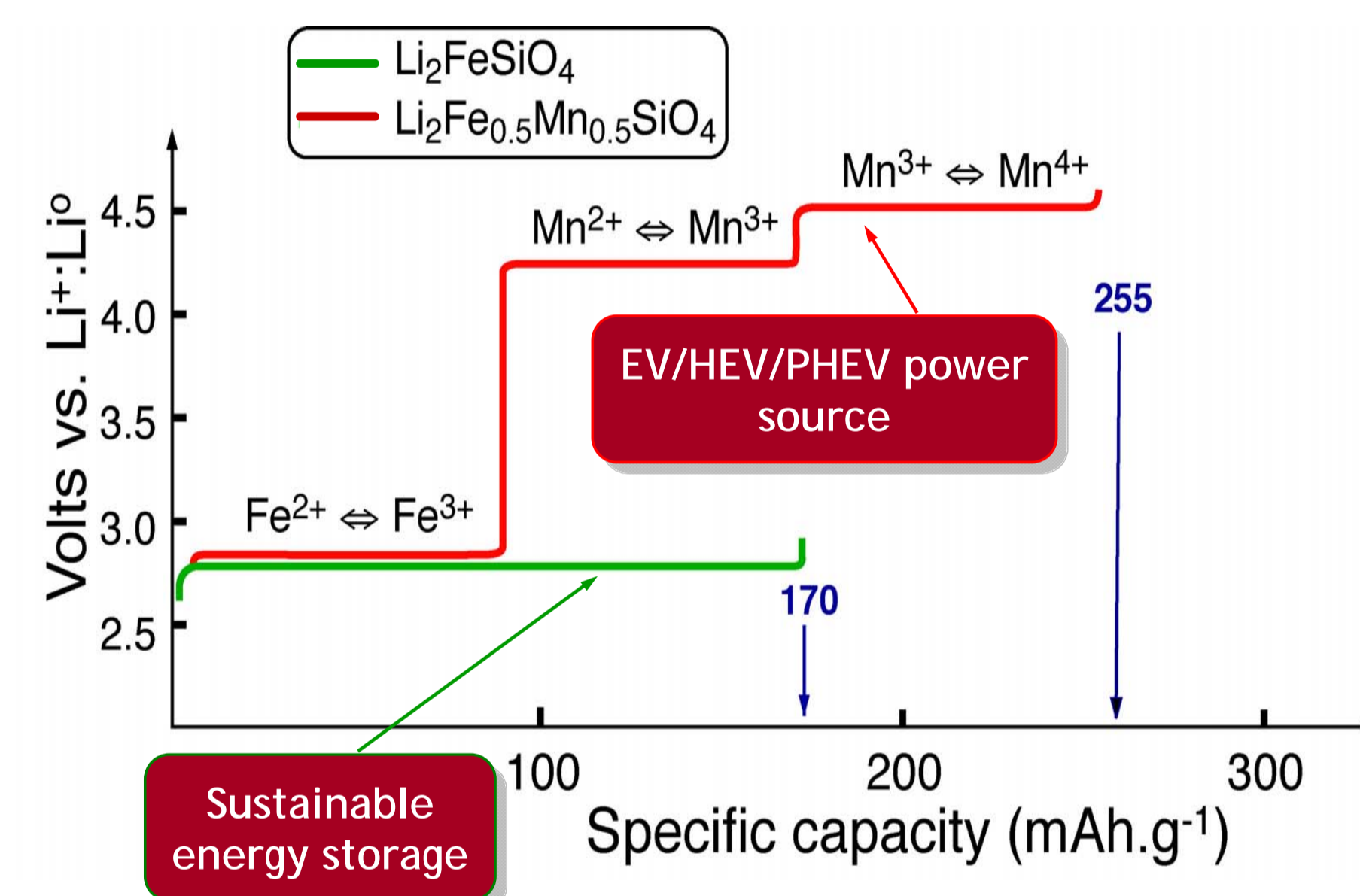
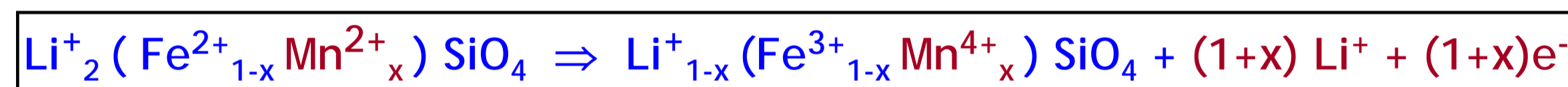
Kinson C. Kam, Anti Liivat, Torbjörn Gustafsson and Josh Thomas

Global Climate & Energy Project

Ångström Advanced Battery Centre/Materials Chemistry, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.

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 - $\text{Li}_2\text{FeSiO}_4$ - 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.):



Example: for $x = 0.5$

$\text{Li}_2\text{FeSiO}_4$ - roadmap strategies

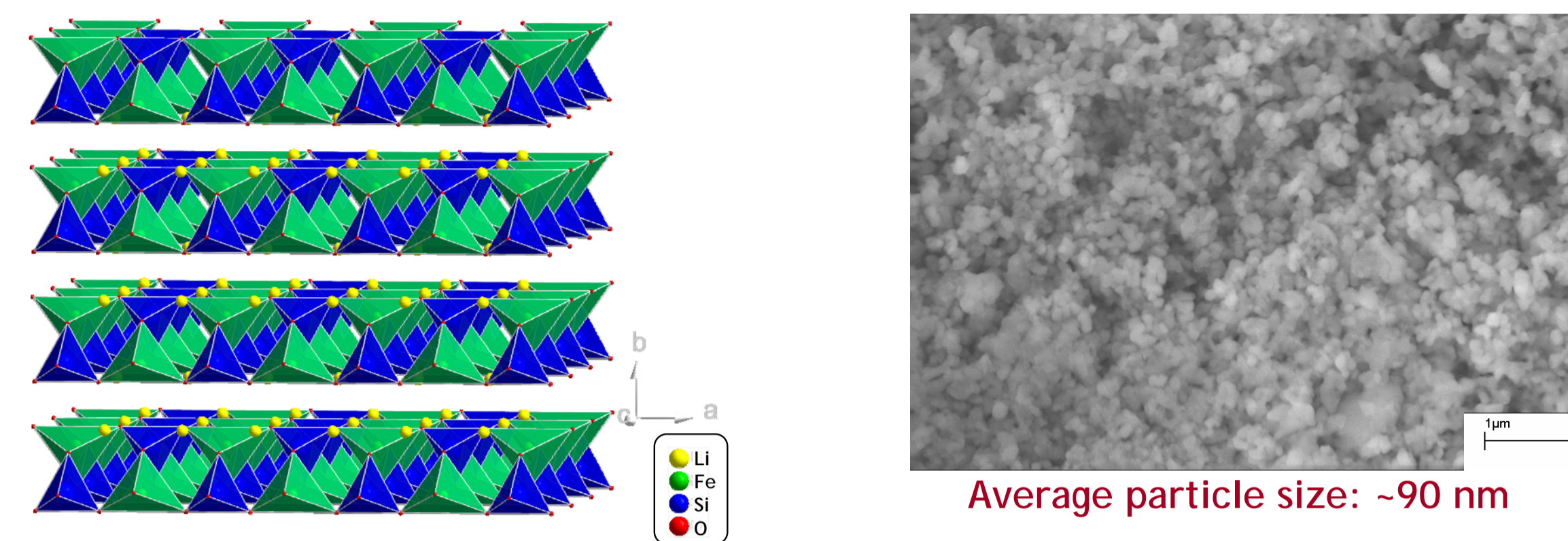
Experiment ↔ Theory

Nanostructure synthesis Composition modification Structures / composition Energetics / stability

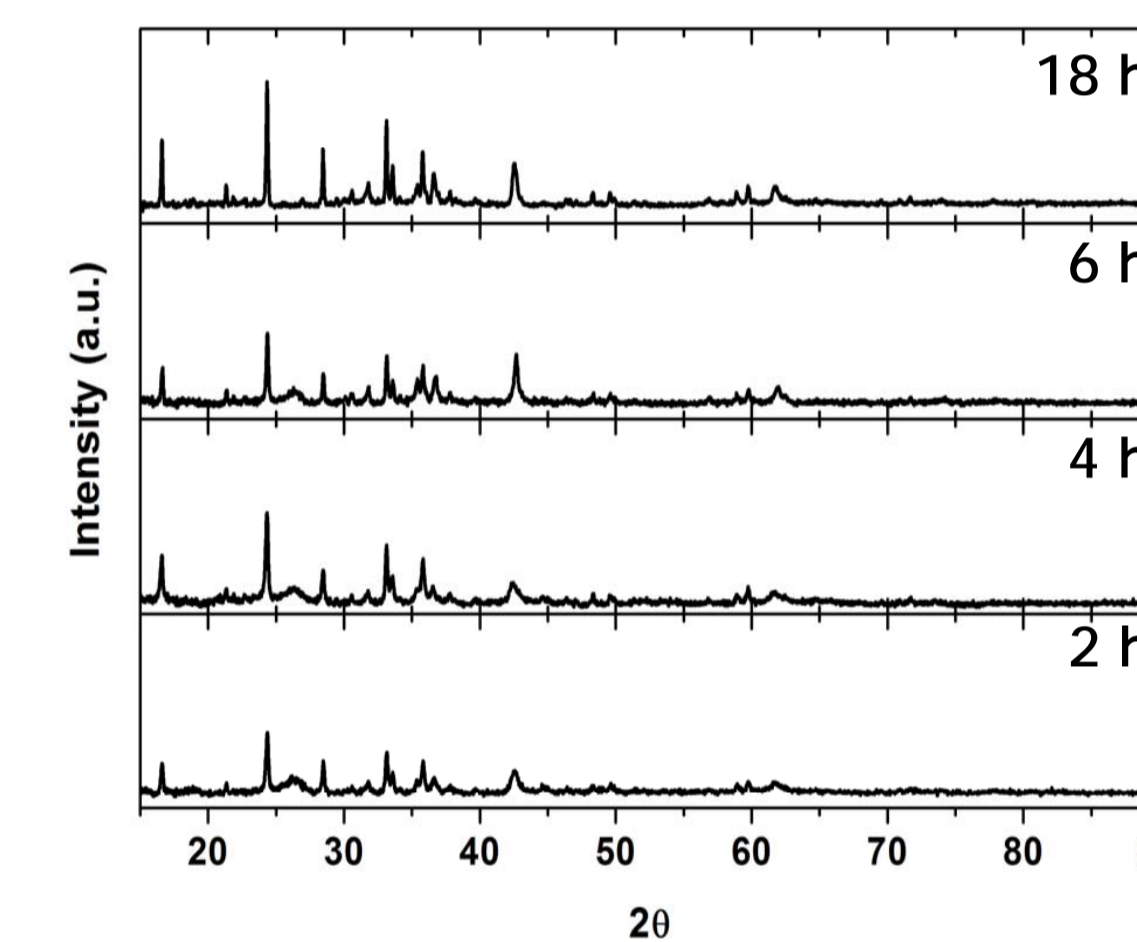
Materials characterization, cell fabrication and electrochemical performance

See our other poster on surface stability studies of cathode materials using XPS/PES techniques!

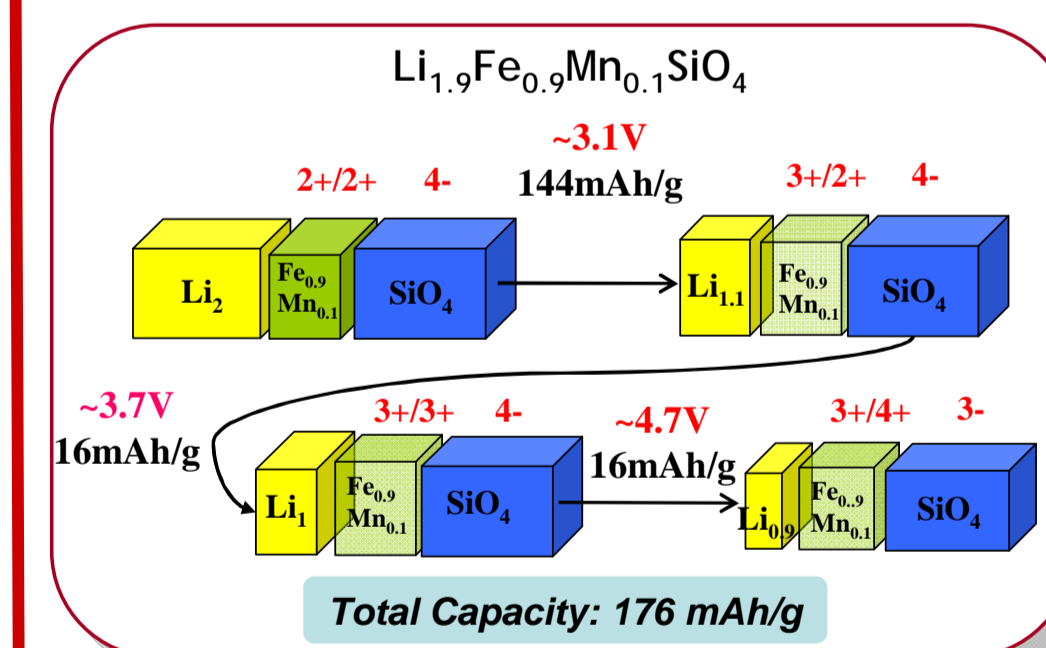
Nanostructures



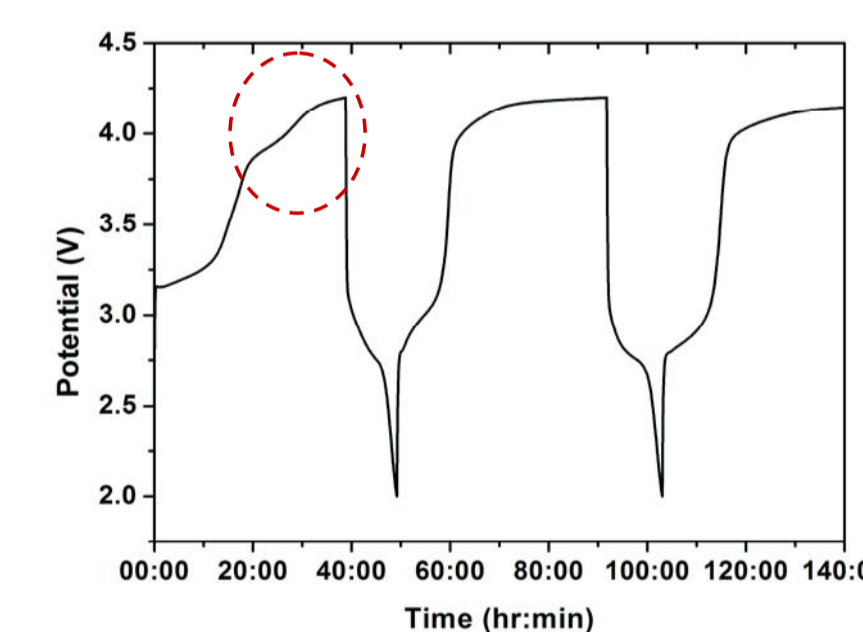
- $\text{Li}_2\text{FeSiO}_4$ can be prepared via a solution-based method
- Particle-size can be tuned by post heat-treatment processing
- Similar redox behaviour is observed as in the bulk (CV, galvanostatic)



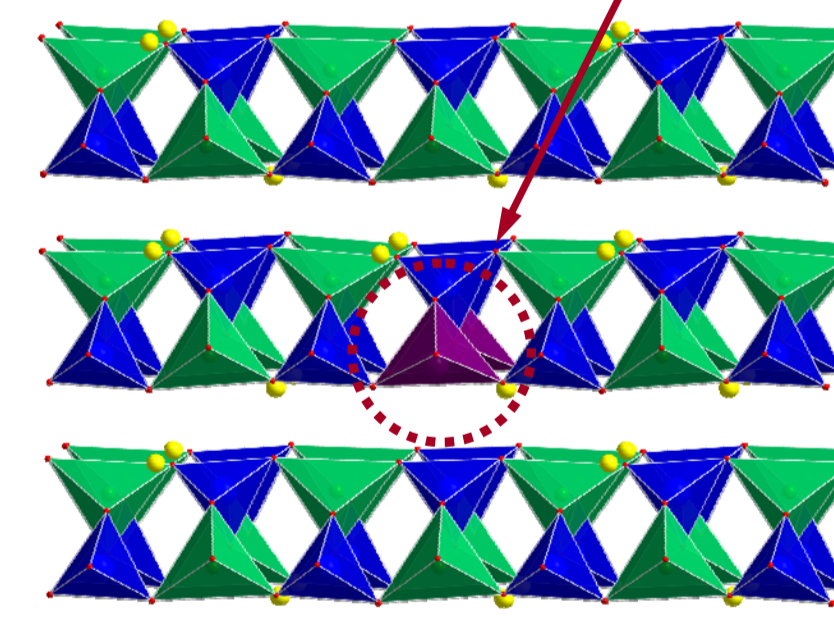
Transition-metal substitution



Mn substitution at Fe-site:

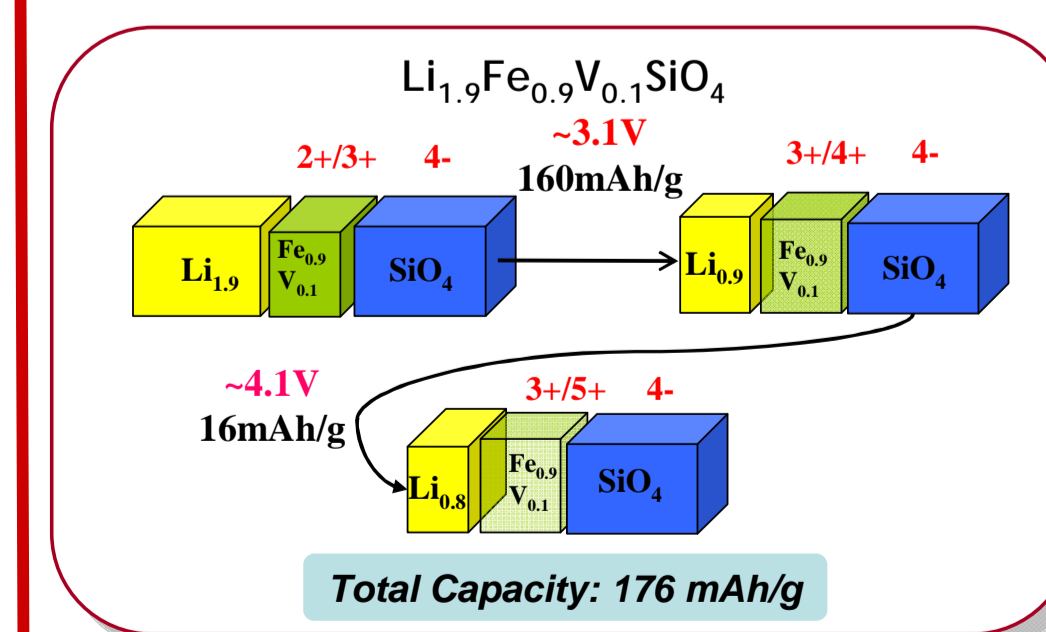


Electrochemical cell-cycling test

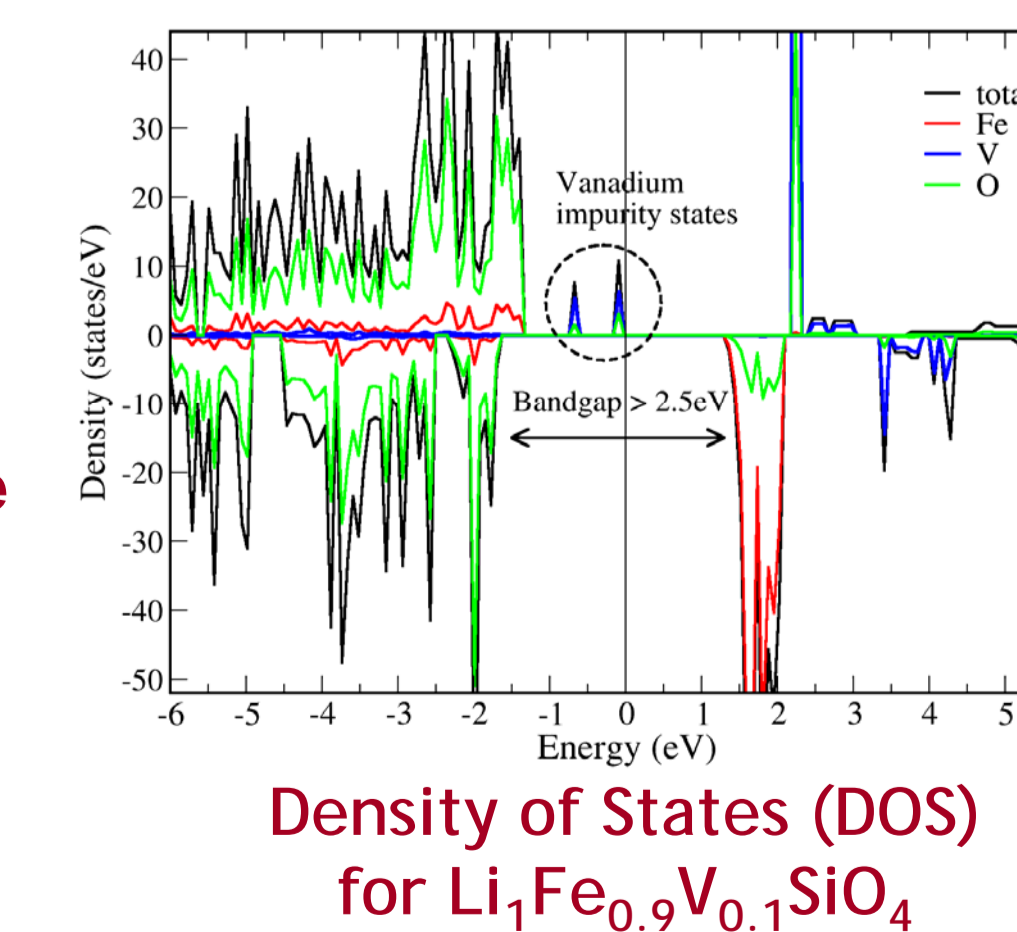


delithiated structure: distorted MnO_4

V substitution at Fe-site:



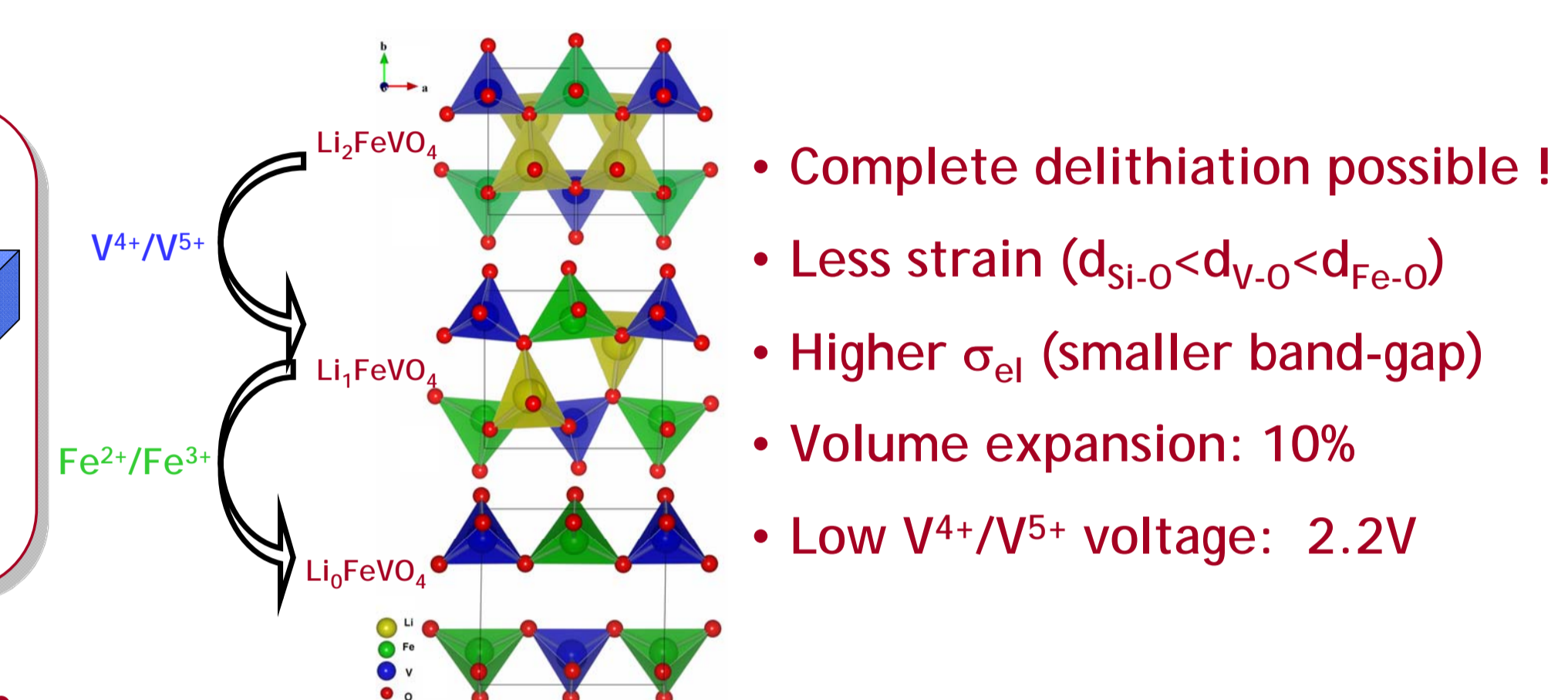
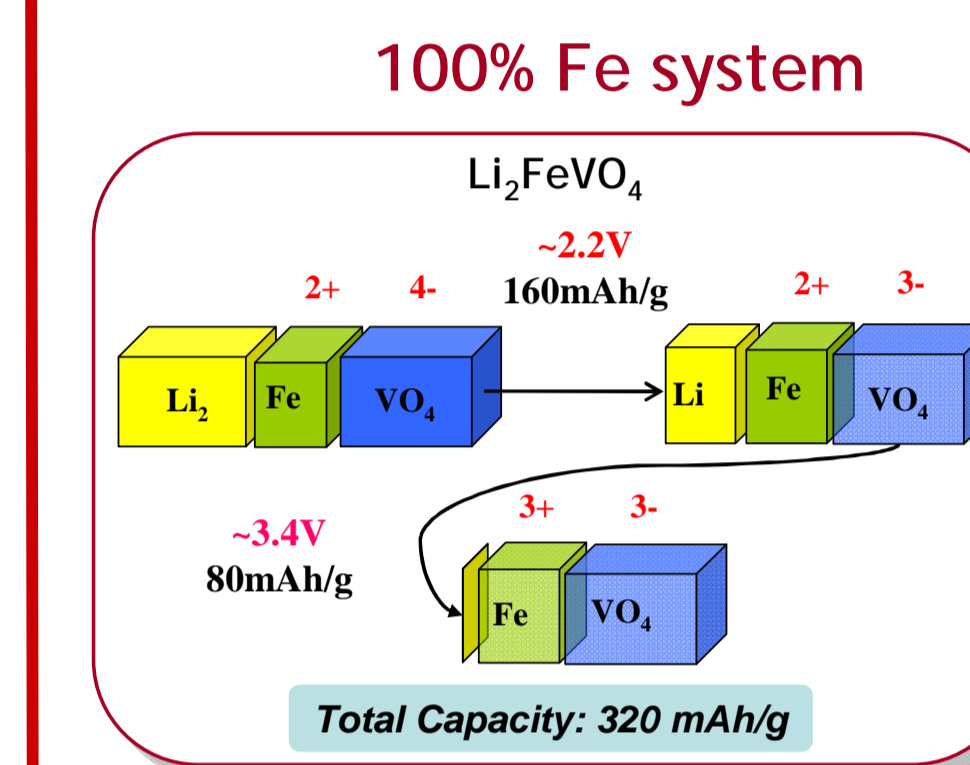
- No significant distortion in VO_4 tetrahedra.
- $\text{V}^{4+}/\text{V}^{5+}$ states reduce the band-gap.



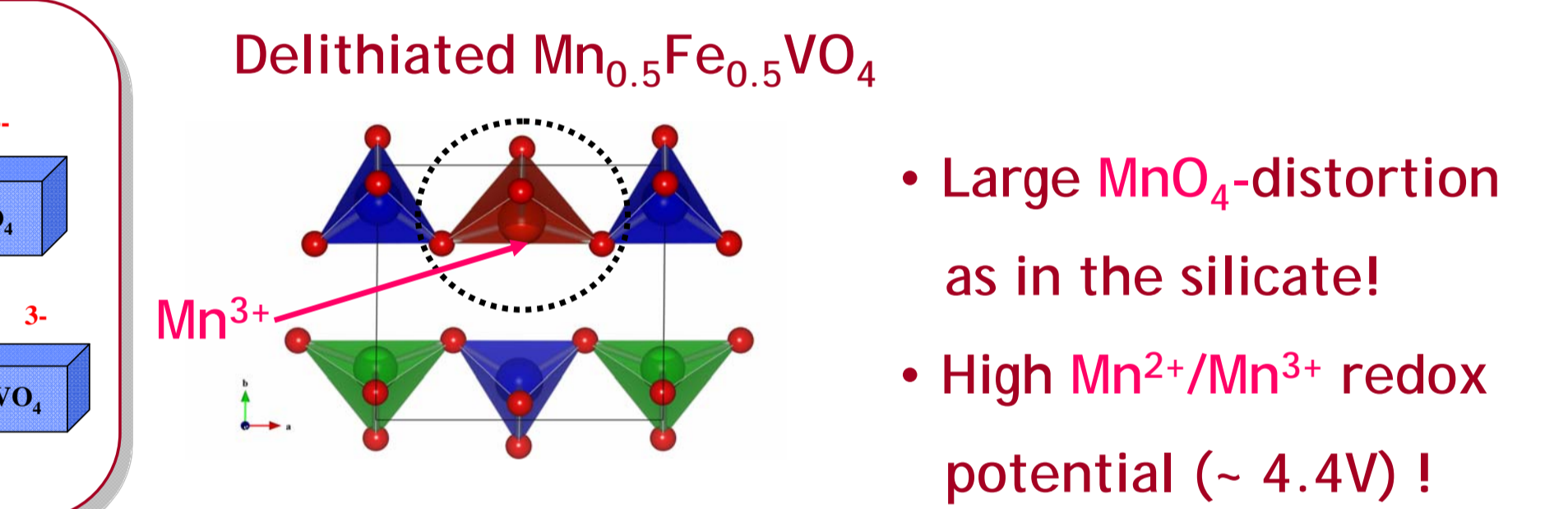
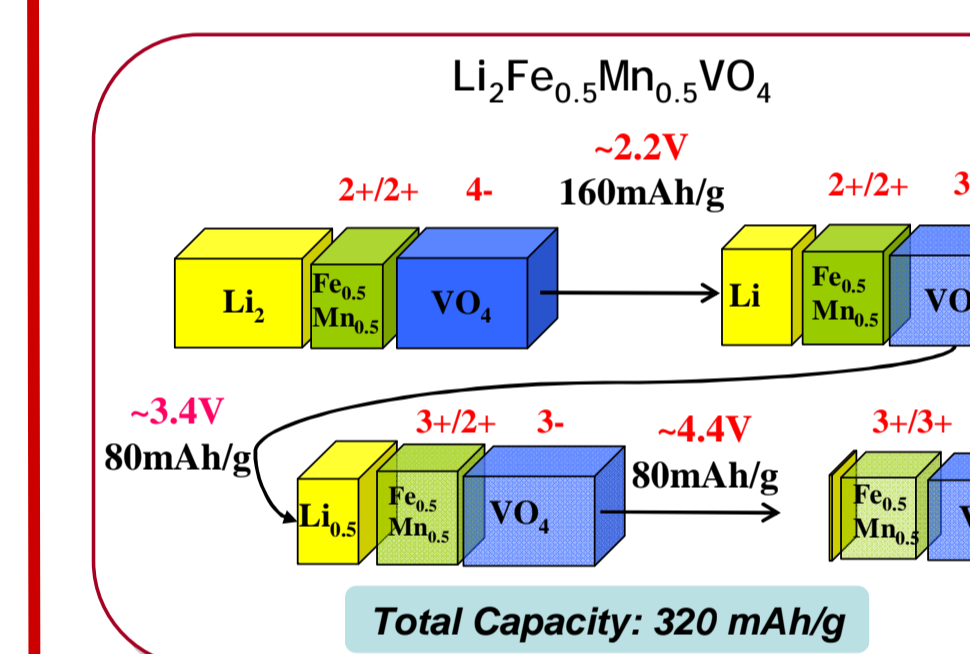
Density of States (DOS) for $\text{Li}_{1.9}\text{Fe}_{0.9}\text{V}_{0.1}\text{SiO}_4$

Polyanion substitution

DFT modelling of substitution of redox-active $\text{VO}_4^{3-}/\text{VO}_4^{4-}$ at the SiO_4^{4-} -site



50% Fe/50% Mn system



Conclusions

- Mn-doped systems: structural instability!
- V-doped systems: higher σ_{el} , increased capacity - and higher $\text{V}^{4+}/\text{V}^{5+}$ voltage (~4.1V)
- Fe-systems: capacities of ~ 300mAh/g attainable with redox-active $\text{VO}_4^{4-}/\text{VO}_4^{3-}$ instead of SiO_4^{4-}
- Energy-density needs optimal $(\text{VO}_4^{4-}/\text{VO}_4^{3-})\text{:SiO}_4^{4-}$ ratio (to raise the $\text{V}^{4+}/\text{V}^{5+}$ voltage)

References

- Ensling, D., Stjern Dahl, M., Nyttén, A., Rensmo, H., Gustafsson, T. and Thomas, J.O., A comparative XPS surface study of $\text{Li}_2\text{FeSiO}_4$ cycled with LiTFSI- and LiPF₆-based electrolytes. Accepted in *J. Mater. Chem.*
- Larsson, P., Liivat, A., Rajeev, A., Nyttén, A. and Thomas, J.O., Structural and electrochemical aspects of Mn-substitution into $\text{Li}_2\text{FeSiO}_4$: DFT calculations and experiment. Submitted to *Chem. Mater.*