PDF Analysis of Disordered Rock-Salt-Type Li_2VO_2F

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Motivation and Aim

- The measured capacity of disordered rock-salt type Li_2VO_2F intercalation anode material is 420 mAh/g at ~2.5V *vs* Li/Li^+.
- ~1.8 Li^+ can be stored in the structure.
- Volume changes is about 3% during electrochemical cycling.
- $Li_2VO_3 \rightleftharpoons Li^+ + e^- + LiVO_3$ (V^{4+}/V^{5+})

Theoretical specific capacity : 237 mAh/g

- $Li_2VO_2F \rightleftharpoons 2Li^+ + 2e^- + VO_2F$ (V^{3+}/V^{5+})

Theoretical specific capacity : 462 mAh/g

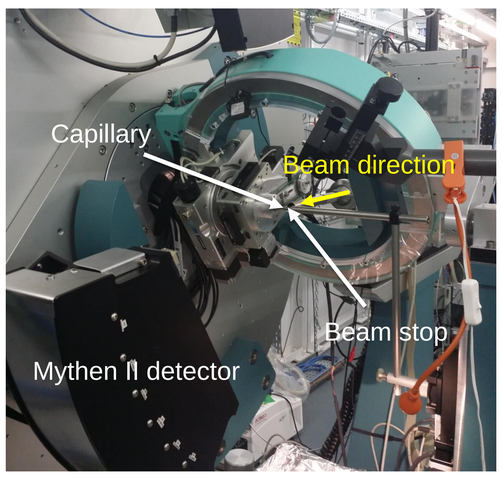
- Changing the oxidation state of V increases the total capacity.

Aim:

- Investigate local ordering and average structure of the new Lithium-Rich Oxyfluoride

Experimental

- The powders were loaded into 0.7mm capillaries in an argon-filled glovebox
- PDF measurements were performed using a Mythen II detector at beamline BL04, MSPD at the ALBA Synchrotron Light Source, Spain.
- The energy is 30 keV (λ=0.413Å)
- Data was collected using a monochromatic beam in the angular range 0-120° with 0.006° resolution.
- Q_{max} is 26.1 $Å^{-1}$
- To obtain good counting statistic at high Q-values longer exposure time was used at high scattering angles (~7min per pattern).



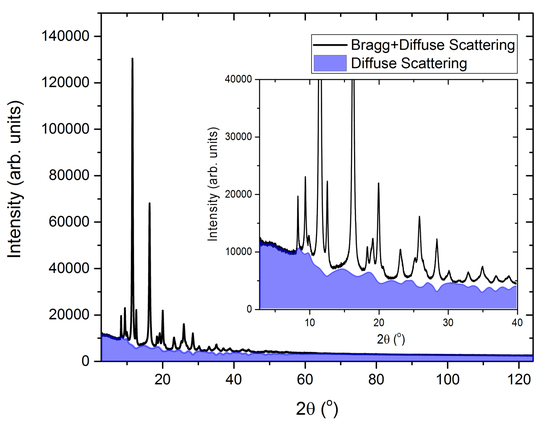


Figure : XRD pattern of and diffuse scattering Li_2VO_2F.

PDF Refinement

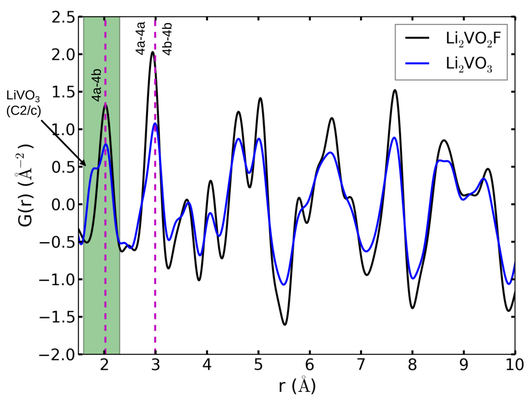


Figure : Comparison of Li_2VO_2F and Li_2VO_3 PDF

- Fluorine substitution suppresses the impurity phase of $LiVO_3$.

- Data reduction : PDFGetX3
- Structure model from DISCUS (2x2x2 and 3x3x3 supercells)
- PDF refinement : PDFGui

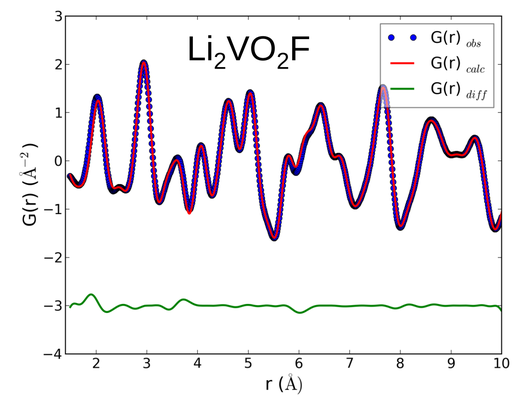


Figure : PDF refinement of Li_2VO_2F

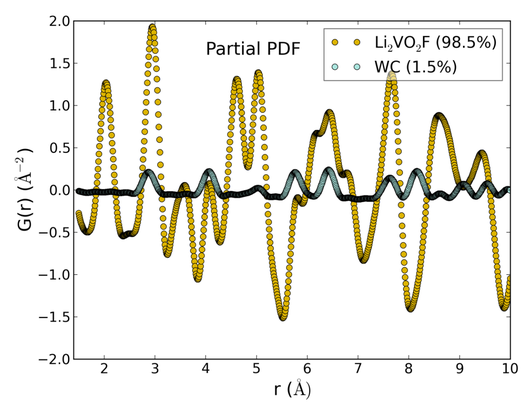


Figure : Partial PDF of Li_2VO_2F

- Rietveld and PDF refinement of Li_2VO_2F resulted in very similar structure parameters but with very large ADP for fluorine in the Rietveld refinement.
- Best PDF fit was obtained with fractional atomic coordinates of F refined and (small) ADP constrained with O atoms.

PDFs of Li_2VO_2F at different Li-content

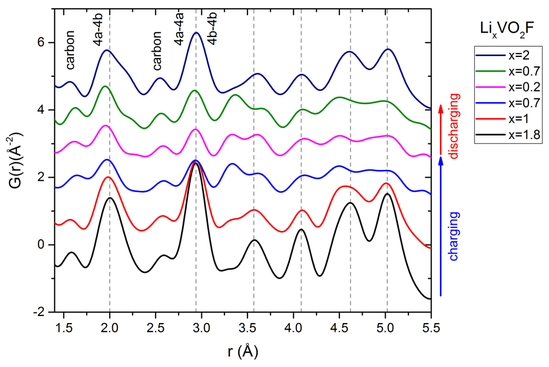
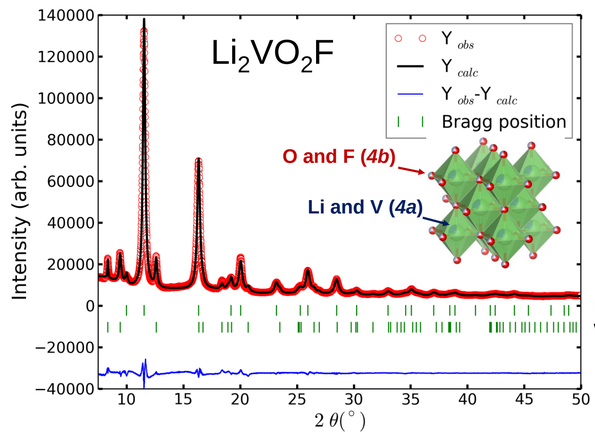


Figure : PDFs of Li_2VO_2F at different Li-content during cycling. Dashed lines represent the peak position for main phase at 1.8 mol of Li-content.

- Electrochemically cycled samples contain Super Carbon P which can be seen in the PDFs (at 1.56Å and 2.55Å).
- New peak occurs around 3.3Å at intermediate step.
- The structure is reversible after electrochemical cycling.

Rietveld Refinement-Li_2VO_2F



- Space group : $Fm\bar{3}m$
- Cell parameter : 4.1177(9) Å
- B_{iso} for F and O : 1.2(2)
- B_{iso} for Li and V : 0.4(1)
- WC phase of 0.97 %

Conventional Rietveld method is not sensitive to local structure distortion

Summary

- PDF shows that F-substitution suppress the monoclinic impurity phase in the as-prepared sample.
- F atoms have positional disorder as shown by large B_{iso} in Rietveld refinement.
- During electrochemical cycling new peak appears (around 3.3Å).
- The structure is almost reversible.