

Supporting Information

Li⁺ intercalation in isostructural Li₂VO₃ and Li₂VO₂F with O²⁻ and mixed O²⁻/F⁻ anions

Ruiyong Chen,* Shuhua Ren, Murat Yavuz, Alexander A. Guda, Viktor Shapovalov,
Raiker Witter, Maximilian Fichtner and Horst Hahn

* E-Mail: ruiyong.chen@kit.edu; hc18chen@gmail.com

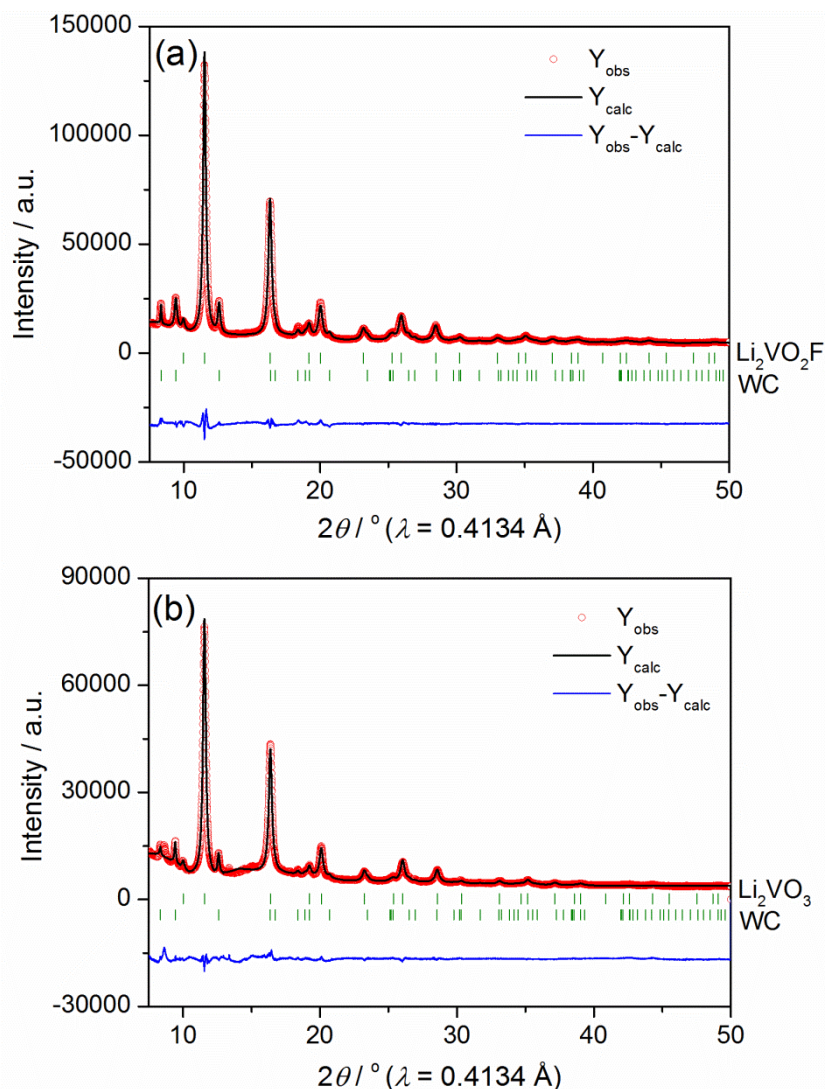


Fig. S1 Synchrotron XRD patterns ($\lambda = 0.4134 \text{ \AA}$) and Rietveld refinement ($Fm-3m$ space group) for (a) $\text{Li}_2\text{VO}_2\text{F}$, $a = 4.1178 \text{ \AA}$, $R_p = 7.83$, $R_{wp} = 7.82$, $R_e = 2.38$, $B_{\text{iso}}(\text{O},\text{F}) = 1.186$, $B_{\text{iso}}(\text{Li},\text{V}) = 0.467$; (b) Li_2VO_3 , $a = 4.1044 \text{ \AA}$, $R_p = 11.6$, $R_{wp} = 10.8$, $R_e = 3.08$. The phase fractions for the $Fm-3m$ phase are 99% for both materials.

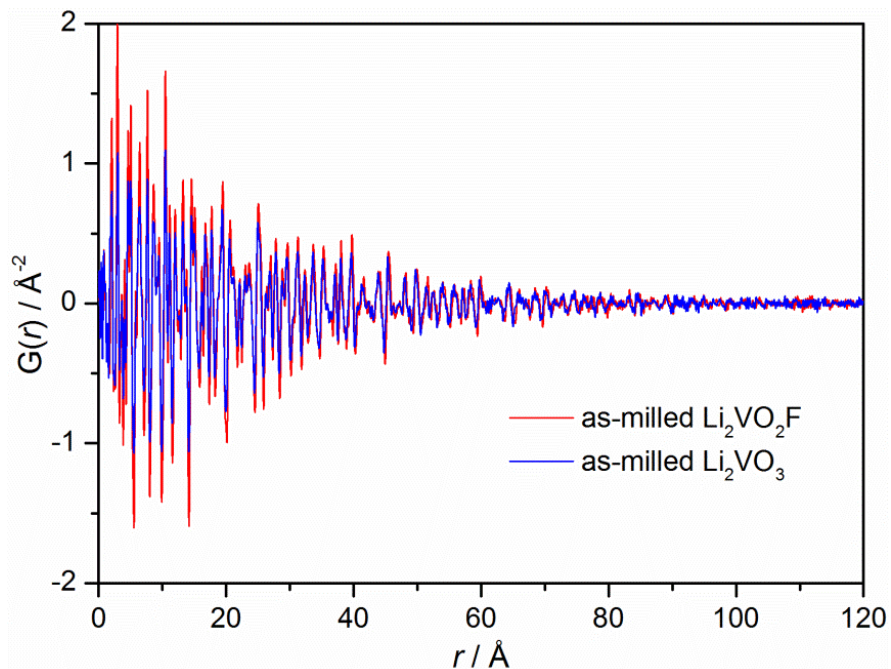


Fig. S2 Experimental atomic PDF profiles, $G(r)$, for the as-milled $\text{Li}_2\text{VO}_2\text{F}$ and Li_2VO_3 . The primary crystallite sizes for both materials are about 10 nm.

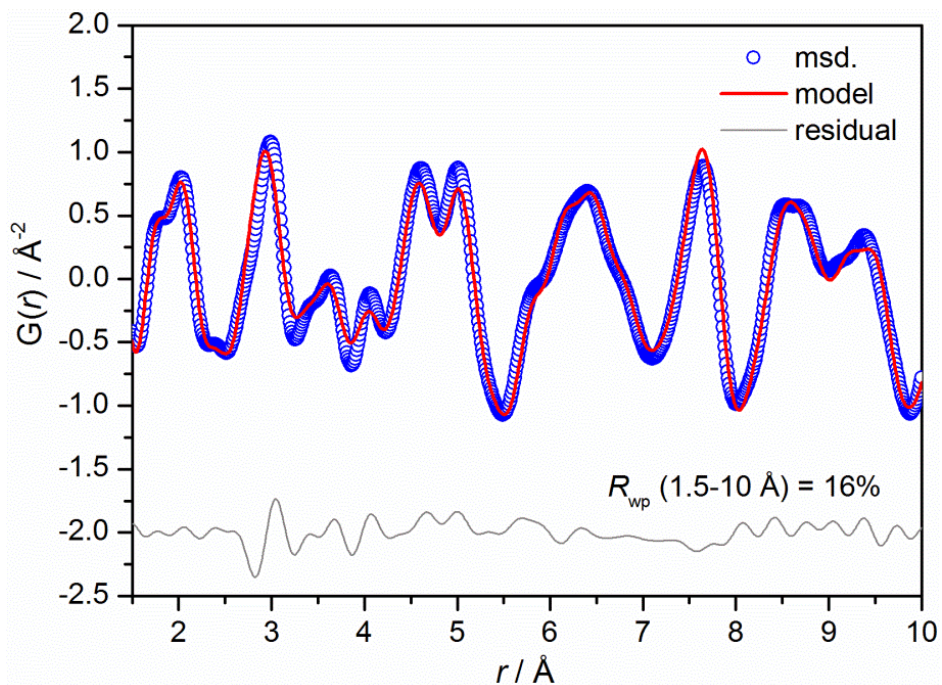


Fig. S3 Experimental and calculated atomic PDF profile, $G(r)$, for the as-milled Li_2VO_3 . The fitting was performed using a three-phase model: Li_2VO_3 ($Fm-3m$), LiVO_3 ($C2/c$) and WC. For the Li_2VO_3 $Fm-3m$ phase, $U_{\text{iso, Li}} = 0.091\text{\AA}^2$, $U_{\text{iso, V}} = 0.010\text{\AA}^2$ and $U_{\text{iso, O}} = 0.019\text{\AA}^2$.

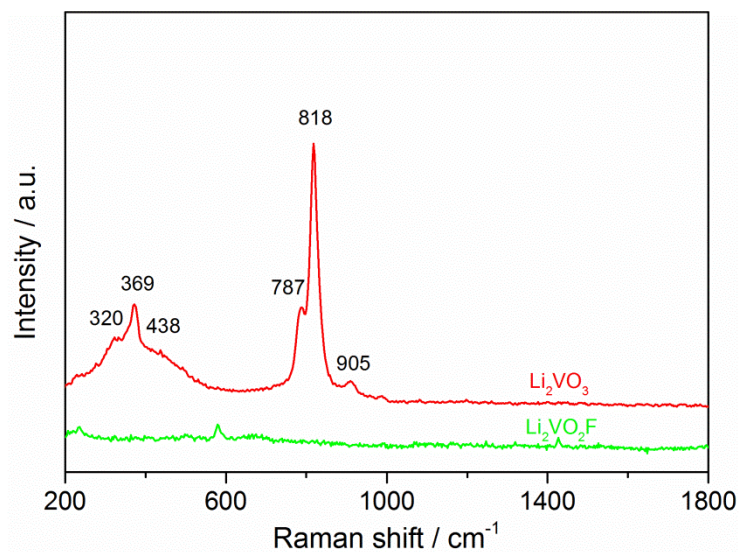


Fig. S4 Raman spectra of the as-milled Li₂VO₂F and Li₂VO₃.

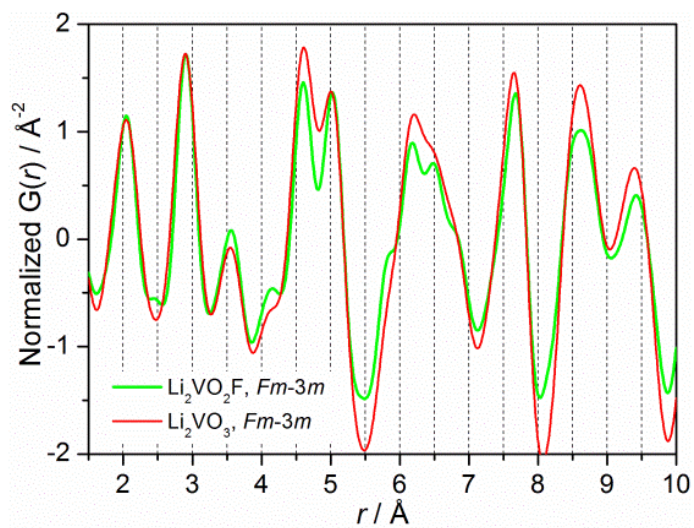


Fig. S5 Modelled PDF profiles for the major *Fm-3m* phases of Li₂VO₂F and Li₂VO₃ extracted from the multiple-phase PDF files.

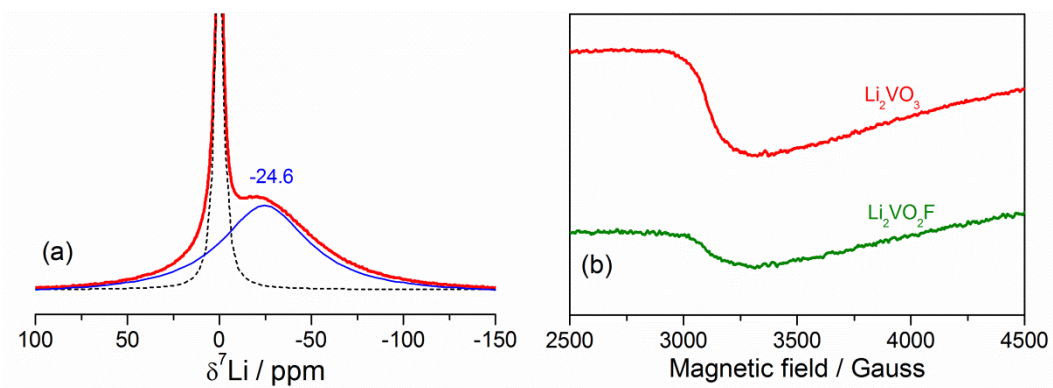


Fig. S6 (a) ^7Li MAS NMR for Li_2VO_3 , (b) EPR spectra for $\text{Li}_2\text{VO}_2\text{F}$ and Li_2VO_3 .

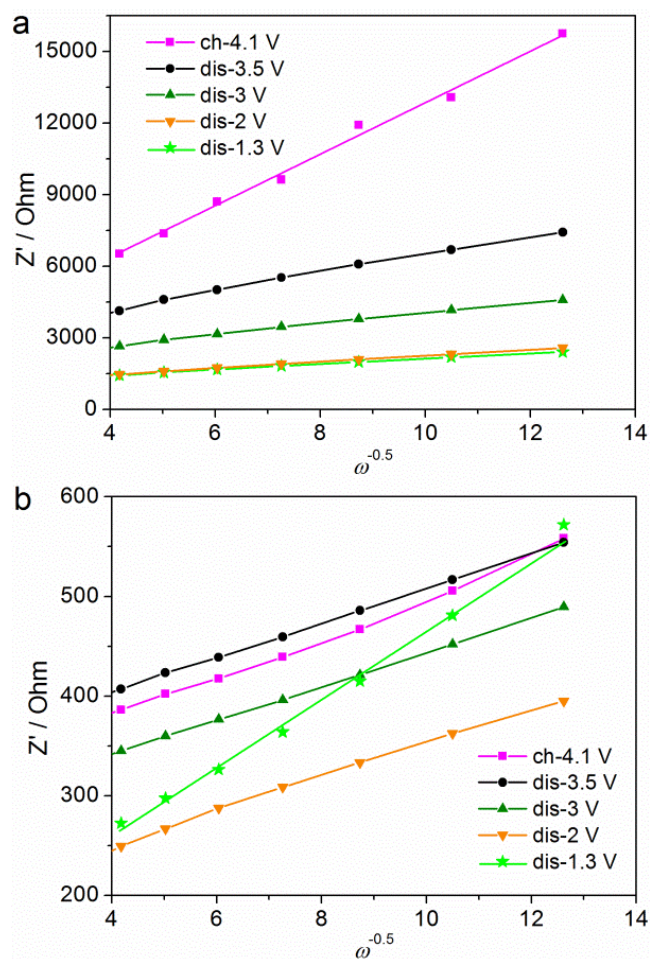


Fig. S7 Real parts of the complex impedance versus $\omega^{-1/2}$ at different voltages for (a) Li_2VO_3 and (b) $\text{Li}_2\text{VO}_2\text{F}$.