

A novel fluoro-polyanionic cathode $\text{LiV}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$ for lithium ion batteries

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Development of high performance cathode materials is one of the greatest interesting in the academic and industrial research realms of rechargeable energy storage systems, such as lithium, sodium and magnesium ion batteries. Prime attentions have also been paid to understand the basic information of cathode materials, such crystal structure variation, the electrochemical behaviour and the mechanism behind.¹⁻³ Fluoro-polyanionic cathodes, such LiFeSO_4F ¹, LiFePO_4F ² and LiVPO_4F ³, they have attracted great attention as promising alternative cathode materials for lithium-ion batteries, on the basis of their 3-dimensional (3D) framework, good thermal stability, remarkable electrochemical properties. However, the two phase electrochemical behaviour of these fluorophosphates may limit their practical application due to the marked flat voltage-capacity profiles and the slow kinetics of phase transition⁴.

In this study, a novel fluoro-polyanionic cathode $\text{LiV}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$ is designed and successfully synthesized via a wet ball-milling-assisted solid state method, as clarified by the X-ray diffraction pattern shown in Fig. 1. This newly confected fluorophosphate with ordered cations of V^{3+} and Fe^{3+} exhibits a single-phase solid-solution behavior over the entire lithium composition range of $\text{Li}_{1-x}\text{V}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$ ($0 < x < 0.5$) with two alternatively electrochemical active regions centered at ~4.3 and ~2.76 V, see the sloping charge/discharge profile. Cationic order of V^{3+} and Fe^{3+} is responsible for the single phase behaviour over the lithium composition range of $\text{Li}_{1-x}\text{V}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$ ($0 < x < 0.5$) as revealed by X-ray diffraction and X-ray absorption near edge spectra analysis results and electrochemical test results.

The main issue is that tuning the stoichiometry of cationic transition metal in LiVPO_4F (in this case, $\text{LiV}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$) triggers a transition in the chemical reactivity path, that is, two-to single-phase (de) lithiation mechanism. Moreover, the feasibility of having a single-phase mechanism (for instance, a sloping voltage curve) presents some intrinsic advantages with regards to applications such as an easier monitoring of the state of charge / discharge of a battery as compared with a flat voltage curve (characteristic of a two-phase mechanism). Nevertheless, these findings offer numerous possibilities of introducing single-phase solid-solution behaviour in promising polyanionic compounds that only exhibit two-phase mechanisms. Future work is underway to investigate the temperature and particle size effects on the electrochemical performances of $\text{LiV}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$.

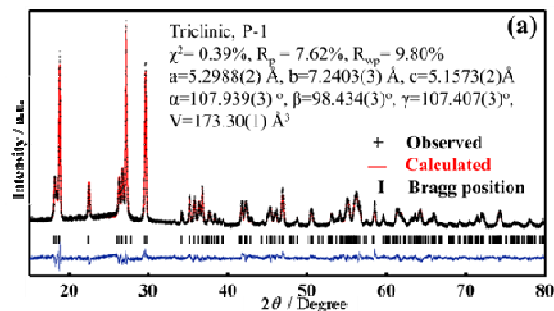


Fig. 1. Rietveld refined X-ray diffraction results of $\text{LiV}_{0.5}\text{Fe}_{0.5}\text{PO}_4\text{F}$.

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