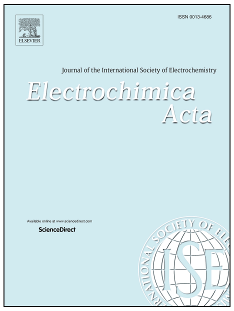

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Crystal structure and electrochemical properties of $\mathrm{LiFe_{1-\mathit{x}}V_{\mathit{x}}PO_4F_{1-\delta}O_\delta}$ cathode materials for lithium-ion batteries

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ABSTRACT:

Tavorite-structured polyanion compounds such as $LiVPO_4F$, $LiFePO_4F$ and $LiVPO_4O$ are promising cathode candidates of Li-ion batteries due to their structural stability as a result of strong covalent bonds. A few publications related to $LiVPO_4F$–$LiFePO_4F$ and $LiVPO_4F$–$LiVPO_4O$ solid solutions have been reported to date. In this work, $LiFePO_4F$–$LiVPO_4O$ solid solution, *i.e.* $\mathrm{LiFe_{1-\mathit{x}}V_{\mathit{x}}PO_4F_{1-\delta}O_\delta}$ ($0 \le x \le 1$; $0 \le \delta \le 0.36$) is first prepared by a two-step solid-state route using the pre-synthesized $FePO_4$ and VPO_4O powders. Sloping discharge profiles shown in solid-solution cells indicate a single-phase behavior which is different from the two-phase reaction of end members. The structure determination, refinement and electrochemical properties are studied. The mechanisms are concluded involved in redox energies of cations. Redox energies are tuned within a wide range 1.5–4.5 V in polyanion-type cathodes, through the inductive effect introduced by cation (V for Fe) and anion (O for F) substitution.

Keywords: $LiFePO_4F$–$LiVPO_4O$; solid solution; tavorite; polyanion-type cathode; Li-ion battery

1. Introduction

$LiVPO_4F$ [1-6], $LiFePO_4F$ [7-10] and $LiVPO_4O$ [6, 11-18] are homeotypic with a tavorite-type ($P\bar{1}$, triclinic) crystal structure. As for unit-cell volume per molecular formula ($V' = V/Z$), $V'_{\mathrm{LiV^{III}PO_4F}} > V'_{\mathrm{LiFe^{III}PO_4F}} > V'_{\mathrm{LiV^{IV}PO_4O}}$. Considering the oxidation state and octahedral ionic radii of Fe/V cations while coordination number (CN) corresponds to 6, $r_{\mathrm{Fe^{III}}}$ = 0.645 Å (in high-spin state)