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$Li_{2-x}Fe_{0.5}(VO)_{0.5}(PO_4)F_{0.5}$, a New Mixed Metal Phosphate Cathode Material

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A new Fe-V mixed metal phosphate of the composition, $Li_{2-x}Fe_{0.5}(VO)_{0.5}(PO_4)F_{0.5}$, has been synthesized and characterized as a single phase Li insertion/extraction cathode material for rechargeable lithium batteries. Its tetragonal crystal structure revealed from X-ray diffraction and absorption spectral data exhibits little change with Li extraction and subsequent Li insertion. The charge/discharge cycling capacities obtained from Li cells is consistent with the structure. The presence of F in the material is essential to prepare a mixed metal phosphate with equal amounts of Fe and V in the crystal structure and is probably the key to our success in preparing a single phase metal phosphate cathode material.

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The olivine $LiFePO_4$, developed into a power dense Li insertion cathode for Li-ion batteries, has found commercial success over the last decade. Several features inherent in the material are responsible for this, including low cost, non-toxicity, and an iron redox center. From an energy density perspective, $LiVOPO_4$, which exists in various crystallographic phases, is also an attractive polyanionic material offering a two-phase discharge plateau several hundred millivolts higher than $LiFePO_4$. But unlike $LiFePO_4$, the vanadyl phosphates have not yet overcome rate limiting processes related to poor electronic conductivities and/or low Li^+ diffusion which confine them to low rate charge/discharge cycling.

Even more recently, fluorinated derivatives of Fe and V phosphates have also received attention. For example, the $LiMPO_4F$ (M = Fe,V) phases crystallize in a triclinic P-1 space group, isostructural to tavorite and amblygonite.[1,2] These phases exhibit Li extraction voltages of 2.8V for ($Fe^{2+}/^{3+}$) and 4.1V ($V^{3}/^{4+}$) as well as large three dimensional Li pathways for good ionic conductivity. An orthorhombic Li_2FePO_4F phase also forms via ion exchange with its sodium analog, and results in a solid solution single phase cycling profile, unique to metal phosphate materials.[3] It is this electrochemical feature which brought to our attention the mixed metal (fluoro)phosphate presented here.

Combining features of the three phosphate moieties, V = O, FeO_x, and $Fe\text{-}F_y$ into a single phase material, $Li_2Fe_{0.5}(VO)_{0.5}(PO_4)F_{0.5}$, was the focus of this work. Synthetic attempts involved typical solid state techniques. The Fe-V mixed metal flourophosphate synthesized here responds electrochemically as having a single phase material with Li extraction/insertion processes at V and Fe redox active sites.

Experimental

Synthesis of the Fe/V compound was carried out using a two-step heat-treatment preceded by intimate mixing of the precursors. In an acetone slurry, appropriate amounts of iron (II) oxalate (Alfa Aesar, 99.999%), ammonium metavanadate (Aldrich, 99.999%), lithium fluoride (Aldrich, 99.98%), and ammonium dihydrogenphosphate (Aldrich, 99.999%) were mixed in a zirconium vial for five hours with a Spex ball mill. The resultant mixture was dried, pressed in to a pellet at 3000 psi, and heated for 350°C for 3 hours under argon. The Fe/V phase formed following the second 4 hour heat-treatment at 600°C under a 5% H_2/Argon blend of purge gas.

X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV diffractometer (Cu $K\alpha_{1,2}$ radiation). Unit cell constants of the powder pattern were refined with Expgui[4] and GSAS[5] using Lebail pattern matching. Prior to XRD measurements, extracted T-cell electrodes were disassembled in a glove box and washed with ethyl methyl carbonate (EMC) to remove excess salts. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were contracted out to Galbraith Laboratories, Inc. (Knoxville, TN) to determine elemental composition.

Compression fitted Li half-cells (T-cells) with 1 M $LiPF_6$ 1:1.2 EC/DMC electrolyte were utilized to collect galvanostatic cycling data on an Arbin battery cycler. Pressed cathodes consisted of 77% active material, 20% carbon black, and 3% PVDF binder resulting in active material loadings of approximately $5 mg/cm^2$. Active material and carbon black was mixed in a Spex stainless steel vial for 3 hours. The in-situ spectroelectrochemical half-cell which was used for the X-ray absorption near edge structure (XANES) study consisted of a Li anode, Whatman glass microfiber separator, and the cathode mix, painted onto a substrate (Al or grafoil). The cell was housed between two steel plates with polyester protected windows to allow for X-ray transmission along with a silicon gasket to provide a hermetic seal.

X-ray absorption measurements were collected in transmission mode at the V K-edge (5465 eV) and Fe K-edge (7112 eV) at beam line X-18a of the National Synchrotron Light Source at Brookhaven National Laboratory, with a Si 111 crystal detuned 35% to reject higher harmonics. Grafoil was used as the positive electrode substrate to increase transmission signal at the V edge and Al was utilized at the Fe edge to avoid Fe contamination originating from grafoil. Preparation of triclinic $\alpha\text{-}Li_xVOPO_4$ and collection of XAS data for this phase is described elsewhere.[6] Data processing was done in Athena, version 8.056 developed by Ravel and Newville.[7]

Discussion

Initial efforts at synthesizing lithiated Fe-V mixed metal phosphates without F led to mixtures of $LiFePO_4$, $Li_3Fe_2(PO_4)_3$, Li_3PO_4, and V_2O_3 when Li acetate or Li_2CO_3 were used as Li sources. The synthesis conditions were not favorable, possibly due to structural differences between the $LiFePO_4$ and $LiVOPO_4$ frameworks. Olivine $LiFePO_4$, which does share the same space group as orthorhombic $\beta\text{-}LiVOPO_4$ (Pnma) has recently been shown to substitute up to 0.25 moles of Fe with V using a low temperature microwave synthetic route.[8]

We succeeded in synthesizing the Fe-V mixed metal compound, $Li_{2-x}Fe_{0.5}(VO)_{0.5}(PO_4)F_{0.5}$, by incorporating fluorine into its crystal structure. We can see that by including LiF along with the V, Fe and P starting materials in atomic ratios proportional to the two lithiated metal phosphates, Li_2FePO_4F (Fe^{2+}) and Li_2VOPO_4 (V^{3+}), the mixed metal phase is formed as represented in scheme 1.

Scheme 1

$$Li_2FePO_4F \cdot Li_2VOPO_4 \rightarrow Li_4Fe(VO)(PO_4)_2F$$

$$\text{(i.e.) } Li_2Fe_{0.5}(VO)_{0.5}(PO_4)F_{0.5}$$

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