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$\text{Li}_5\text{VF}_4(\text{SO}_4)_2$: A Prototype High Voltage Li-ion Cathode

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Abstract

A Li-rich polyanionic compound based on V^{3+} with a previously unknown structure: $Li_5VF_4(SO_4)_2$, has been developed as a candidate high voltage cathode material for Li-ion batteries. The solvothermal preparation of this material, crystal structure solution, and initial electrochemical characterization are presented. An analysis based on density functional theory electronic structure calculations suggest that a high voltage close to 5 V is required to extract 2 Li and to reach an oxidation state of V^{5+} . However, the use of conventional carbonate-based electrolytes, which exhibit increasing degradation above a potential of 4.3 V, does not permit the full capacity of this compound to be achieved at this time.

Keywords

cathode material, lithium-ion battery, $Li_5VF_4(SO_4)_2$, fluoride, sulfate, electrochemistry

Introduction

Lithium-ion batteries play a critical role in modern society, ranging in applications from lightweight and powerful portable electronics all the way to electric vehicles, electrically-powered aircrafts, and even grid storage. A practical battery metric for these applications is energy density, which is the energy storage capacity per unit volume or mass of a material. Since the energy density is the product of the average voltage and the charge storage capacity, maximizing it requires cathode materials operating at high voltages.¹ In the design of cathode materials, the judicious choice of redox-active metal center and counter ions all contribute to both the high voltage and high capacity. The more ionic in nature the metal-anion interaction is, the higher the voltage of the $M^{(n-1)+}/M^{n+}$ couple in a compound will be versus Li.²⁻⁵ The incorporation of highly electronegative F into the compound should increase its operating voltage. Furthermore, sulphates exhibit higher voltages than oxides

for the same redox couples, which can be explained by an inductive effect. Sulfur atoms share a common oxygen with the transition metal M through an M -O-S link, which influences the covalency of the M -O bond. The electronegative S attracts electrons from the oxygen and weakens the covalent metal to oxygen bond, or in other words the M -O bond becomes more ionic.³

Vanadium makes for an effective redox-active metal for high capacity cathodes, as one of the lightest transition metals with many stable oxidation states. This means that multiple electrons can be transferred between the cathode and the anode per transition metal atom.⁶ To achieve multielectron redox, the structure must also accommodate multiple Li per transition metal, so a Li-rich structure is desirable. V-containing compounds have been previously shown to exhibit multielectron redox in a variety of structures, for example, in LiVOPO_4 ,^{7,8} $\text{Li}_3\text{V}_2(\text{PO}_4)_3$,⁹ $\text{VNb}_9\text{O}_{25}$,^{10,11} and V_2O_5 .^{12,13} The successful use of several polymorphs of LiVOPO_4 as cathode materials also indicates precedence for high gravimetric energy density and reversible cycling in V-containing polyanionic structures.¹⁴⁻¹⁶

To be able to charge and discharge a battery at useful rates, electrodes must have acceptable ionic and electronic conductivity.¹⁷ It has been suggested that incorporating F into a structure may enhance cation mobility by reducing electrostatic interactions along conduction channels.¹⁸ However, the increased bond polarity which boosts the voltage of the cathode compound also increases the electron localization, which reduces the electronic conductivity of the material. Further characterization of these high voltage polyanionic compounds and the compromise between operating voltage and conductivity is critical to the field. In order to combat poor conductivity in some of these polyanionic materials, several methods are employed such as nanoscaling and templating.¹⁹⁻²¹ This has been explored extensively, for example, with the widely commercially-available compound LiFePO_4 .²²⁻²⁴

Here we report a new high voltage material, the prototype compound $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$, based around V^{3+} . Two Li can, in principle, be removed per V to reach the stable V^{5+}

state. Reversible cycling of 2 Li would result in a moderately high gravimetric capacity of 151.5 mAh g^{-1} associated with high energy density due to the possibility of high voltage operation above 4 V. Computational studies presented here indeed predict high voltages as being required to reach the theoretical capacity. However, these are near the operating limit of conventional carbonate-based electrolytes.

Computational tools were used to help determine the operating voltage. The procedure for predicting the physical properties of cathode materials from first principles is already mature.²⁵ However, these predictions typically require a database with many materials in a particular materials system at different degrees of lithiation, in this case $\text{Li}_x\text{VF}_4(\text{SO}_4)_2$, in order to make quantitatively meaningful predictions of the voltage and stability. Using the data available from the Materials Project²⁶ and newly generated structures obtained by both removing Li atoms from $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ and inserting Li based on our new Li insertion algorithm,²⁷ we were able to obtain the thermodynamic properties of $\text{Li}_x\text{VF}_4(\text{SO}_4)_2$ at many distinct Li configurations and arrive at a more reliable prediction of the voltage.

Several compounds similar to $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ have been previously examined.²⁸ Lithium transition metal fluoride-sulfates in the form of LiMSO_4F ($M = \text{Fe}, \text{Mn}, \text{Zn}$) and crystallizing in the tavorite, triplite, and sillimanite structures have been accessed using solvothermal methods.^{29,30} While triplite LiMnSO_4F and LiZnSO_4F are electrochemically inactive, substituting Mn and Zn for some of the Fe in LiFeSO_4F showed higher accessible capacity and voltage than in galvanostatic cycling of the pure LiFeSO_4F .^{30–33}

Lithium vanadium fluoride-phosphates have also been investigated as Li-ion battery cathodes. LiVPO_4F with the tavorite mineral structure can be intercalated with Li at 1.8 V versus Li to give $\text{Li}_2\text{VPO}_4\text{F}$ and deintercalated at about 4.2 V to give VPO_4F .^{34–37} Both redox reactions are two-phase and yield clear voltage plateaux during charge and discharge which is a promising sign for reversibility in these compounds, however only one of the two transitions occurs at a competitive voltage.³⁶ Tuning the ratio of oxygen to F in a similar sodium compound, and then ion exchanging Na for Li resulted in a pseudo-layered

structure with a composition of $\text{Li}_{1.1}\text{Na}_{0.4}\text{VPO}_{4.8}\text{F}_{0.7}$ and an ideal operating voltage of 4 V.³⁸

$\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ has a similar layered structure to $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$, and one Li can be reversibly extracted from it at 4.15 V with very little voltage hysteresis between charge and discharge.^{39,40} A second Li ion could be extracted at about 4.7 V, however this process was not as reversible, perhaps due to oxidation of the carbonate electrolyte at this high voltage.^{39,40} Most recently, the Li-rich compound $\text{Li}_5\text{V}_2\text{PO}_4\text{F}_8$ was reported, which also has a similar structure to $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$.⁴¹ With twice the V per formula unit, a capacity of 285 mAh g^{-1} can be utilized going from V^{3+} to V^{5+} . Experimentally, the $\text{V}^{3+}/\text{V}^{4+}$ plateau occurs reversibly around 4.5 V, and the $\text{V}^{4+}/\text{V}^{5+}$ reaction happens around 4.8 V but is not reversible.⁴¹

The sodium vanadium fluoride-sulfate $\text{Na}_3\text{VF}_2(\text{SO}_4)_2$ adopts a two dimensional layered structure and has been investigated as a sodium ion battery cathode.⁴² The same group also investigated $\text{Na}_2\text{VF}_3\text{SO}_4$ and inspired the solvothermal preparation described here.¹⁸

$\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ was prepared by a low temperature solvothermal procedure and its structure determined using single crystal X-ray diffraction. $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ crystallizes in a salt-like structure in a monoclinic space group, $P2_1/c$, with $a = 5.1496(9) \text{ \AA}$, $b = 13.045(2) \text{ \AA}$, $c = 7.1182(12) \text{ \AA}$, $\beta = 110.335(4)^\circ$, and $V = 448.36(13) \text{ \AA}^3$. As a Li-ion battery cathode, it has a theoretical capacity of 151 mAh g^{-1} . Experimentally, when charged to 4.5 V, 100 mAh g^{-1} was accessed, which would correspond to the extraction of 1.25 Li per formula unit. However, due to oxidation of the carbonate-based electrolyte at this high voltage, it is difficult to determine how much of this capacity is measured from oxidation of the active material in the cathode versus irreversible oxidation of the electrolyte. When only charged to 4.3 V, reversible cycling of 0.25 Li per formula unit was achieved.

Experimental Methods

Solvothermal preparation of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ 0.215 g (9.0 mmol) of LiOH, 0.431 g (4.0 mmol) of VF_3 , and 0.215 g (12 mmol) of H_2O were ground using an agate mortar and pestle. The mixture was transferred to a 23 cm³ Teflon vial and 0.316 g (6.0 mmol) of concentrated H_2SO_4 was added to it. The reactants were heated at 190 °C for 48 h in an autoclave. Green crystals of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ were obtained, washed with water and ethanol, and dried in a vacuum oven at 60 °C.

Single crystal X-ray diffraction Single-crystal X-ray diffraction data for $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ were collected on a Bruker Kappa Apex II diffractometer which is equipped a TRIUMPH (graphite) monochromator to produce Mo- $\text{K}\alpha$ X-rays of wavelength $\lambda = 0.71073 \text{ \AA}$ and an APEX II CCD detector. The APEX3 software was used for the data collection, unit cell determination, data integration, data scaling, and structure solution. The structure was solved by direct methods and refined by full-matrix least-squares on F_2 using the SHELXL-2014 program package.⁴³ Crystal structures are depicted using VESTA.⁴⁴

Powder X-ray diffraction Laboratory powder X-ray diffraction data was collected using a PANalytical Empyrean diffractometer with Cu- $\text{K}\alpha$ radiation. Rietveld analysis was performed using Topas Academic v6.⁴⁵

Raman spectroscopy Raman spectroscopic measurements were performed using a Horiba Jobin Yvon T64000 confocal microscope. Data were collected on $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ powder with a 480 nm laser, 300 μm pinhole, 500 μm slit, a 1800 grooves mm⁻¹ grating, and 10 s exposure. Three spectra were averaged, centered at 470 cm⁻¹ and 1150 cm⁻¹. A background spectrum was taken with the same conditions on the glass slide background and subtracted from the sample data.

Microscopy Scanning electron microscopy (SEM) was carried out on an FEI Nova Nano 650 FEG SEM at 5 kV acceleration voltage. The as-prepared crystals were sputter coated with approximately 10 nm of gold. $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ that was ball milled with carbon was not gold-coated before imaging.

Electrochemical characterization The electrochemical performance of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ was characterized using Swagelok-type cells assembled in an argon-filled glovebox using polished Li foil as a combined counter and reference electrode. $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ was ball milled with carbon black (TIMCAL Super P) for 20 min. in a 7 cm³ stainless steel ball mill canister. The ball milled mixture was then ground with polytetrafluoroethylene (PTFE with average particle size of 1 μm) such that the final electrode composition was 60 % active material, 30 % carbon black, and 10 % PTFE binder. Thick film electrodes 10 mm in diameter were prepared by pressing pellets from this mixture using a hydrostatic pressure of 1.5 tons. Whatman GF/D glass microfiber filters were used as the separator. The electrolyte was 1 M LiPF_6 in ethylene carbonate and dimethylcarbonate (EC/DMC 50/50 v/v from Sigma Aldrich).

Potentiostatic electrochemical impedance spectroscopy Samples were prepared by ball milling the single-crystalline material for 30 min. to reduce the particle size, then pressing approximately 60 mg into a blocking electrode setup inside an Ar-filled glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm). The spacer is electronically insulating Delrin and the two cylindrical plunger blocking electrodes are 316 stainless steel. A full description of the cell and setup has been previously reported.⁴⁶ The material was densified in situ to reduce empty space between particles by applying an average pressure of 175 MPa over 2 days at 363.15 K (90 °C). Since the material is hygroscopic, the setup was maintained air-free. Once densification stabilized (pressure was not dropping), measurements were recorded every 10 K from 303.15 K to 353.15 K (30 °C to 80 °C) using a Bio-Logic VMP3 potentiostat in a two-electrode blocking configuration. The frequency was scanned from 1 MHz to

10 mHz with 10 points per decade and an amplitude of 500 mV. Each measurement was averaged 15 times per frequency. Spectra were fit to an equivalent circuit using ZFit in the EC-Lab software.

Thermogravimetric analysis Thermogravimetric analysis (TGA) of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ was carried out on a Discovery TGA instrument (TA Instruments) under a continuous flow of nitrogen gas at a flow rate of $25\text{ cm}^3\text{ min}^{-1}$. The crystals were ground in a mortar and pestle and about 13 mg were placed in an aluminum crucible. The temperature ramp rate was $5\text{ }^\circ\text{C min}^{-1}$.

Computational methods The total energies of the atomic structures at each level of lithiation were calculated using first principles density functional theory (DFT)⁴⁷ with the generalized-gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE),⁴⁸ as implemented in the Vienna Ab initio Simulation Package (VASP).⁴⁹ To obtain sufficiently accurate and directly comparable energies across chemical systems, we use GGA when appropriate, and GGA with a Hubbard U correction (GGA+ U) otherwise, and mix i energies from the two types of calculations methodologies using the procedure from Jain *et al.*⁵⁰ Structural relaxation was performed until the maximum force on each atom was less than $0.05\text{ eV \AA}^{-1}$. Initial guesses of the structures with intermediate Li content are obtained from the charged, delithiated, structure using a charge-density-based cation insertion algorithm.

Results and discussion

Crystal structure refinement parameters of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ are provided in Table 1 and bond distances and angles in the structure are provided in the Supporting Information (SI) in Table S1. A representation of the monoclinic crystal structure is shown in Figure 1. The structure is best described as a salt of Li^+ with the complex anion $\text{VF}_4(\text{SO}_4)_2^{5-}$ (the

Table 1: Crystallographic data and structure refinement for $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$.

Chemical formula	$\text{Li}_5\text{VF}_4(\text{SO}_4)_2$
Empirical formula	$\text{Li}_5\text{VF}_4\text{S}_2\text{O}_8$
Formula weight	$353.76 \text{ g mol}^{-1}$
Temperature	$299(2) \text{ K}$
Wavelength	$0.71073 \text{ \AA}$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a	$5.1496(9) \text{ \AA}$
b	$13.045(2) \text{ \AA}$
c	$7.1182(12) \text{ \AA}$
α	90°
β	$110.335(4)^\circ$
γ	90°
Volume	$448.36(13) \text{ \AA}^3$
Z	2
Density (calculated)	2.620 Mg m^{-3}
Absorption coefficient	1.669 mm^{-1}
Crystal size	$0.150 \times 0.100 \times 0.100 \text{ mm}^3$
θ range for data collection	3.123° to 26.443°
Reflections collected	4609
Independent reflections	925 [$R(\text{int}) = 0.0866$]
Completeness to $\theta = 25.242^\circ$	100.0%
Max. and min. transmission	0.7454 and 0.3474
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	925 / 0 / 92
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0508$, $wR_2 = 0.1256$
R indices (all data)	$R_1 = 0.0716$, $wR_2 = 0.1384$
Largest diff. peak and hole	1.151 and $-0.852 \text{ e.\AA}^{-3}$

Figure 1: Crystal structure of the solvothermally prepared compound $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ as solved from single crystal X-ray diffraction data, and projected almost down the c axis. On the right is a single $\text{VF}_4(\text{SO}_4)_2^{5-}$ anion. The unconnected grey atoms are the Li^+ . All atoms are depicted using the refined anisotropic Atomic Displacement Parameters (ADP) with probabilities of 95 %.

complex anion is depicted alongside the unit cell in Figure 1). More specifically, isolated $\text{V}^{3+}\text{F}_2\text{O}_4$ octahedra are arranged into planes parallel to the (010) crystal plane. Within the planes, rows of octahedra are alternating with rows of Li ions which are oriented along the [100] direction. In alternating planes, the octahedra are tilted. Octahedra are angled such that the sulfate tetrahedra with which they corner-share dip into the interplanar spacing. There appears to be enough space between the octahedral planes for Li diffusion, perhaps preferentially in the [001] direction. To better understand the local bonding environment, Raman spectroscopy was performed on the sample, and the Raman spectrum is given in Figure S1.

Figure 2: (a) Rietveld refinement of a powder X-ray diffraction pattern of the solvothermally prepared $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$. (b) SEM image of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ crystals. (c) SEM image of the crystals after being ball milled with carbon black.

Prior to electrochemical characterization, crystals of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ were ground and characterized by powder X-ray diffraction. The fit pattern is shown in Figure 2(a). By

Rietveld analysis, approximately 8 wt% of the powder was determined to be a Li_3VF_6 impurity taking the form of small light blue crystals which could be visually separated from the desired green product. A scanning electron micrograph of the as-prepared crystals [Figure 2(b)] shows crystal size on the order of $200\text{ }\mu\text{m}$. After ball milling the $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ crystals with carbon black to reduce particle size and increase electronic conductivity of the cathode, $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ particles were on the order of $2\text{ }\mu\text{m}$ in size, as shown in Figure 2(c).

Primarily to verify that a significant amount of water was not adsorbed to the sample following preparation and washing (which would interfere with electrochemical testing), TGA was performed on the sample. The TGA curve showing mass loss versus temperature is provided in the SI in Figure S2. No weight loss was observed up to 200°C , which suggests that the sample did not contain adsorbed water.

Figure 3: (a) Computed stability of the experimentally determined structure of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ with varying amounts of Li compared to the lowest energy structure calculated for the same compositions using the Materials Project. The Materials Project convex hull considers the decomposition of each compound into two to four other compounds. (b) Predicted voltage of redox reactions in $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$. The shaded region indicates the approximate voltage stability window of the electrolyte used in the electrochemical measurements (EC/DMC 50/50 v/v).

Figure 3(a) shows the predicted stability of delithiating $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ while charging

a cell. At most, it is expected that two Li can be extracted from the material per V atom, corresponding to a change in the oxidation state from V^{3+} to V^{5+} , and the structure is calculated to become less stable the more Li is extracted. Figure 3(b) shows the corresponding calculated voltage at which each Li can be extracted and inserted into the structure. In the range of cycling voltages that could be reached experimentally (shaded region on plot), the predicted voltages appear to be slightly lower than the experimentally observed oxidation and reduction voltages found in this study.

Figure 4: (a) Cyclic voltammetry was performed at a rate of 0.1 mVs^{-1} from 5 V to 1.5 V. (b) Galvanostatic cycling at a rate of $C/60$ first charging to 4.3 V and then discharging to 1.5 V. (c) Galvanostatic cycling at a rate of $C/60$ first charging to 4.5 V and then discharging to 1.5 V. Irreversibility shown at high voltage could be due to decomposition of the electrolyte.

The cyclic voltammogram [Figure 4(a)] reveals a reversible oxidation peak appearing at approximately 4.4 V and a reversible reduction peak at approximately 4.15 V. This moderate voltage polarization can mostly be attributed to the electronic resistance of the active material. Galvanostatic cycling at a very slow rate of $C/60$ (rate calculated for 2 Li cycling) between 4.3 V and 1.5 V, reversible cycling of 0.25 Li per formula unit is achieved, as shown in Figure 4(b). When charged to 4.5 V [Figure 4(c)], 100 mAh g^{-1} was accessed,

which would correspond to the extraction of 1.25 Li per formula unit. However, due to the likelihood of electrolyte oxidation at this high voltage, it is difficult to determine how much of this capacity is measured from oxidation of the active material in the cathode versus irreversible oxidation of the electrolyte. Furthermore, the irreversibility of the high voltage cycling could indicate surface decomposition of the active material, or other detrimental phenomena, not just electrolyte decomposition.

These voltage limitations, in addition to the poor electronic conductivity of this insulating material, contribute to not being able to experimentally access the theoretical capacity of 151 mAh g^{-1} . While increased polarity of the V-F bond increases voltage, it also decreases the electronic bandwidth which contributes to the low electronic conductivity of the material.

Figure 5: Potentiostatic electrochemical impedance spectroscopy results every 10 K from 303.15 K to 353.15 K also showing the fits and the equivalent circuit employed.

The electronic conductivity is likely the largest barrier to overcome, as $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ has reasonable ionic conductivity as measured directly using potentiostatic electrochemical impedance spectroscopy [Figure 5]. Densified powder was used to measure the intrinsic conductivity of the material between two blocking electrodes. While it is important to

note that these values will change in the setting of an assembled cell, in which the material will be mixed with carbon and soaked in electrolyte, conductivity of the pure material still lends valuable insight into Li conduction in a cell configuration. Since there is no measurable evidence of a low resistance contribution to the Nyquist plots, the resistance values extracted from fitting modified Debye circuits are assumed to be from ionic conduction. The activation energy was extracted from the data shown in Table 2 using the following modified Arrhenius relationship: $\sigma T = A \exp[-E_A/(k_B T)]$ where σ is the conductivity, A is a pre-factor, E_A is activation energy, and k_B is the Boltzmann constant. The Meyer-Neldel compensation was applied to account for thermally activated Li hopping in an intrinsic Li conductor.^{51,52}

Table 2: Potentiostatic electrochemical impedance spectroscopy results recorded every 10 K from 303.15 K to 353.15 K.

T (K)	bulk R (M Ω)	σ (mS/cm)	$\ln(\sigma T)$
303.15	9.48	2.24×10^{-2}	-11.90
313.15	6.06	3.51×10^{-2}	-11.42
323.15	3.06	6.94×10^{-2}	-10.70
333.15	2.28	9.30×10^{-2}	-10.38
343.15	1.57	1.35×10^{-1}	-9.980
353.15	0.573	3.70×10^{-1}	-8.942

The activation energy calculated from the Arrhenius-type equation is 482 meV, which is even within range of some solid electrolytes.⁵³ This is not surprising given that the structure is Li-rich and rather open. The room temperature conductivity value of 2.2×10^{-2} mS cm⁻¹ is similar to the value of Li ion conductivity value reported for LiFePO₄ using similar measurement methods.⁵⁴ Therefore, similar processing employed for LiFePO₄ particles and electrodes that have led to its widespread use could also be applied to Li₅VF₄(SO₄)₂ to achieve higher capacity and better rate capabilities.

Conclusions

Li₅VF₄(SO₄)₂, a high-voltage Li-ion battery cathode candidate, has been prepared and

characterized for the first time, and its single-crystal X-ray structure has been determined. The material has a decently high ionic conductivity of $2.2 \times 10^{-2} \text{ mS cm}^{-1}$ at room temperature. $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ has a theoretical capacity of 151 mAh g^{-1} , associated with the two-electron process of converting V^{3+} to V^{5+} . This high capacity was not reached experimentally, in part due to high-voltage limitations of the carbonate electrolyte used. Further testing performed using, for example, ionic liquid electrolytes that are reported to be more electrochemically stable at high voltages⁵⁵ could be a promising continuation of this work.

The material studied here highlights the inherent trade-off between high voltage and electronic conductivity in cathode materials. While high-voltage redox occurs when cycling this material, it is electronically insulating, which hinders its rate capability. As shown from the study and commercialization of LiFePO_4 , nanoscaling the active material and improving the conductive carbon coating could reveal significantly higher cycling performance in $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$.^{22–24}

Figure 6: Electrostatic valence maps associated with plausible structures of an octahedrally coordinated M^{4+} cation with anions X^{n-} . (a) An acceptable structural network for MX_4 with only two of four X^- sharing features (forming an extended chain, for example). (b) An acceptable structural network for MX_2 as seen in the rutile structure, or the structure of layered CoO_2 . (c) An acceptable structural network for MX exemplified by the rock-salt structure of TiC .

An aspect that has not been discussed so far is the ability of a salt-like material such as $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ to robustly hold up against cycling. Compounds with polyanions, and with low-valent anions such as F^- , tend to not form dense network structures, an outcome of the application of the crystal chemical rules of Pauling.⁵⁶ Tetrahedral moieties centered around a high-charge cation such as S^{6+} tend not to share features, and hence do not favor extended networks. This is an application of the third and fourth rules of Pauling. Furthermore, fluorides and other monovalent anions also tend to prefer weaker structural networks, a consequence of the second rule, based on electrostatic valence. This is depicted schematically in Figure 6 where plausible structural networks between an octahedrally coordinated metal M^{4+} cation with anions X^{n-} are depicted for anions such as F^- , O^{2-} , and C^{4-} . In these depictions, single connections between M and X suggest a “molecular” feature that is not extended in the crystal, resulting in mechanically weaker structures that would also be poorer electrical conductors. When there are multiple connections between M and X , a network is indicated. It is seen that at least for the combination with octahedral M^{4+} , the oxide anion is in a sweet spot forming structures with robust networks that are not so dense as to completely block ion insertion. From an electronegativity viewpoint as well, O is comparatively well situated for cathode materials.

Supporting Information Available

CCDC deposit number 2016644 contains the supplementary crystallographic data. Table of bond distances and bond angles from the single crystal analysis of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$. Raman spectroscopy results from $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ powder. Thermogravimetric analysis of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ crystals to show that water was not adsorbed onto samples.

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Graphical TOC Entry

Supporting Information for

$\text{Li}_5\text{VF}_4(\text{SO}_4)_2$: A Prototype High Voltage Li-ion Cathode

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Table S1: Selected bond distances and bond angles for $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$.

Bond distances (Å)		Bond angles (°)	
V(1)-F(1)	1.916(3)	F(2)-V(1)-F(2)	180.00(14)
V(1)-F(2)	1.896(3)	F(2)-V(1)-F(1)	88.52(13)
V(1)-O(3)	2.025(3)	F(2)-V(1)-F(1)	91.48(13)
Li(1)-F(2)	1.94(2)	F(1)-V(1)-F(1)	180.0
Li(2)-F(1)	1.862(9)	F(2)-V(1)-O(3)	93.71(14)
Li(2)-F(2)	1.870(10)	F(1)-V(1)-O(3)	89.82(13)
Li(3)-F(1)	1.917(11)	O(3)-V(1)-O(3)	180.00(18)
Li(2)-O(4)	2.002(12)	F(2)-Li(1)-O(4)	96.6(9)
Li(1)-O(4)	2.01(2)	F(2)-Li(1)-O(2)	96.6(7)
Li(1)-O(4)	2.06(2)	O(4)-Li(1)-O(2)	103.6(7)
Li(3)-O(4)	2.452(11)	F(2)-Li(1)-Li	140.6(9)
Li(2)-O(1)	2.031(10)	F(1)-Li(2)-F(2)	139.4(6)
Li(3)-O(1)	2.092(12)	F(1)-Li(2)-O(4)	118.3(6)
Li(3)-O(1)	2.255(13)	F(1)-Li(2)-O(1)	105.3(4)
Li(3)-O(2)	1.899(10)	O(4)-Li(2)-O(1)	94.7(4)
Li(1)-O(2)	2.243(15)	O(2)-Li(3)-F(1)	98.1(5)
Li(3)-O(1)	2.092(12)	O(2)-Li(3)-O(1)	114.9(6)
		F(1)-Li(3)-O(1)	103.6(5)
		O(2)-Li(3)-O(1)	118.0(5)
		F(1)-Li(3)-O(1)	110.3(5)
		O(2)-Li(3)-O(4)	87.0(4)
		F(1)-Li(3)-O(4)	170.6(7)
		O(1)-Li(3)-O(4)	81.1(4)

Figure S1: Raman spectrum of $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$ powder.

Figure S2: Thermogravimetric analysis of the solvothermally synthesized $\text{Li}_5\text{VF}_4(\text{SO}_4)_2$.