Li$_5$VF$_4$(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$_5$VF$_4$(SO$_4$)$_2$, has been developed as a 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 suggests that a high voltage close to 5 V is required to extract two Li ions and to reach the 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$_5$VF$_4$(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 aircraft, 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. Because energy density is the product of average voltage and 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 counterions all contribute to both the high voltage and high capacity. The more ionic in nature the metal-oxygen bond, or in other words, the more ionic the metal-fluoride, sulfate, electrochemistry

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$_4$.\(^{22–24}\)

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Here, we report a new high-voltage material, the prototype compound Li$_5$VF$_4$(SO$_4$)$_2$ based on V$^{3+}$. Two Li ions can, in principle, be removed per V to reach the stable V$^{5+}$ state. Reversible cycling of two Li ions would result in a moderately high gravimetric capacity of 151 mA h g$^{-1}$ associated with high energy density because of 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. However, these predictions typically require a database with many materials in a particular materials system at different degrees of lithiation, in this case, Li$_5$VF$_4$(SO$_4$)$_2$, in order to make quantitatively meaningful predictions of voltage and stability. Using the data available from the Materials Project and newly generated structures obtained by both first-principles calculations and experimental observations, we were able to obtain the thermodynamic properties of Li$_5$VF$_4$(SO$_4$)$_2$ at many distinct Li configurations and arrive at a more reliable prediction of voltage.

Several compounds similar to Li$_5$VF$_4$(SO$_4$)$_2$ have been previously examined. Lithium transition-metal fluoride–sulfates in the form of LiM(SO$_4$)$_x$F$_{3-x}$, where M = Fe, Mn, and Zn, and crystallizing in the tetragonal, triclinic, and sillimanite structures have been accessed using solvothermal methods. While tritile Li$_3$Mn$_2$SO$_4$F$_6$ and Li$_2$Zn$_2$SO$_4$F$_6$ are electrochemically inactive, substituting Mn and Zn for some of the Fe in LiFe$_2$(SO$_4$)$_2$ showed higher accessible capacity and voltage than in galvanostatic cycling of the pure LiFe$_2$(SO$_4$)$_2$.

Lithium vanadium fluoride–phosphates have also been investigated as Li-ion battery cathodes. LiPO$_4$F$_2$ with the lithium amount of lithium in the cathode structure can be intercalated with Li byplacing Li$_4$VPO$_4$F and deintercalated at about 4.2 V to afford VPO$_4$F. 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. Tuning the ratio of oxygen to fluorine in a similar niobium compound and then exchanging Na for Li resulted in a pseudo-layered structure with a composition of Li$_{1-x}$Na$_x$VPO$_4$F$_2$, and an ideal operating voltage of 4 V. Li$_5$V(P(O)$^n$)$_4$F$_2$ has a similar layered structure to Li$_5$VF$_4$(SO$_4$)$_2$, and one Li ion can be reversibly extracted from it at 4.15 V with very little voltage hysteresis between charge and discharge. A second Li ion could be extracted at about 4.7 V; however, this process was not as reversible, perhaps because of the oxidation of the carbonate electrolyte at this high voltage. Most recently, the Li-rich compound Li$_5$VPO$_4$F$_2$ was reported, which also has a similar structure to Li$_5$VF$_4$(SO$_4$)$_2$. With twice the V per formula unit, a capacity of 285 mA h g$^{-1}$ can be utilized going from V$^{3+}$ to V$^{5+}$. Experimentally, the V$^{3+}$/V$^{4+}$ plateau occurs reversibly around 4.5 V, and the V$^{4+}$/V$^{5+}$ reaction happens around 4.8 V but is not reversible.

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

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

### EXPERIMENTAL METHODS

**Solvothermal Preparation of Li$_5$VF$_4$(SO$_4$)$_2$**

LiOH (0.215 g, 9.0 mmol), 0.431 g (4.0 mmol) of V$_2$O$_5$, and 0.215 g (12 mmol) of H$_2$O$_2$ were ground using an agate mortar and pestle. The mixture was transferred to a 23 cm$^3$ Teflon vial and 0.316 g (6.0 mmol) of concentrated H$_2$SO$_4$ was added to it. The reactants were heated at 190 °C for 48 h in an autoclave. Green crystals of Li$_5$VF$_4$(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 Li$_5$VF$_4$(SO$_4$)$_2$ were collected on a Bruker KAPPA APEX II diffractometer which is equipped with a TROUHPH (graphite) monochromator to produce Mo K$_\alpha$ X-rays of wavelength $\lambda = 0.71073$ Å and an APEX II CCD detector. APEX2 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. Crystal structures are depicted using VESTA.

**Powder X-ray Diffraction.** Laboratory powder X-ray diffraction data were collected using a PANalytical Empyrean diffractometer with Cu K$_\alpha$ radiation. Rietveld analysis was performed using Topas Academic 6.

**Raman Spectroscopy.** Raman spectroscopic measurements were performed using a HORIBA Jobin Yvon T64000 confocal microscope. Data were collected on Li$_5$VF$_4$(SO$_4$)$_2$ powder with a 480 nm laser, 300 μm pinhole, 500 μm slt, 1800 grooves mm$^{-1}$ grating, and 10 s exposure. Three spectra were averaged, centered at 470 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) imaging was carried out on an FEI Nova Nano 650 FEG SEM at a 5 kV acceleration voltage. The as-prepared crystals were sputter-coated with approximately 10 nm of gold. Li$_5$VF$_4$(SO$_4$)$_2$ that was ball-milled with carbon was not gold-coated before imaging.

**Electrochemical Characterization.** The electrochemical performance of Li$_5$VF$_4$(SO$_4$)$_2$ was characterized using Swagelok-type cells assembled in an argon-filled glovebox using a polished Li foil as a combined counter and reference electrode. Li$_5$VF$_4$(SO$_4$)$_2$ was ball-milled with carbon black (TIMCAL Super P) for 20 min in a 7 cm$^3$ stainless steel ball mill canister. The ball-milled mixture was then ground with polytetrafluoroethylene (PTFE) with an average particle size of 1 μm from Sigma Aldrich) such that the final electrode composition was 60% active material, 30% carbon black, and 10% PTFE binder. Thick-film electrodes of 10 mm 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 (O₂ < 0.1 ppm, H₂O < 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. The material was densified in situ to reduce the empty space between particles by applying an average pressure of 175 MPa over 2 days at 363.15 K (90 °C). Because 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 to 353.15 K (30–80 °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. The spectra were fitted to an equivalent circuit using ZFit in the EC-Lab software.

**Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) of Li₅VF₄(SO₄)₂ was carried out on a Discovery TGA instrument (TA Instruments) under a continuous flow of nitrogen gas at a flow rate of 25 cm³ min⁻¹. The crystals were ground in a mortar and pestle and about 13 mg was placed in an aluminum crucible. The temperature ramp rate was 5 °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 with the generalized gradient approximation (GGA) functional of Perdew–Burke–Ernzerhof, as implemented in the Vienna Ab Initio Simulation Package (VASP). 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 energies from the two types of calculation methodologies using the procedure from Jain et al. Structural relaxation was performed until the maximum force on each atom was less than 0.05 eV Å⁻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 Li₅VF₄(SO₄)₂ are provided in Table 1 and bond distances and angles in the structure are provided in the Supporting Information in Table S1. A representation of the monoclinic crystal structure is provided in Figure 1. The crystal is best described as a salt of Li⁺ with the complex anion VF₄(SO₄)₂⁻ (the complex anion is depicted alongside the unit cell in Figure 1). More specifically, isolated V⁵⁺F₃O₃ 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.

Prior to electrochemical characterization, crystals of Li₅VF₄(SO₄)₂ were ground and characterized by powder X-ray diffraction. The fit pattern is shown in Figure 2a. By Rietveld analysis, approximately 8 wt % of the powder was determined to be a Li₁ VF₆ 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 2b) shows crystal size on the order of 200 μm. After ball milling the Li₅VF₄(SO₄)₂ crystals with carbon black to reduce particle size and increase the electronic conductivity of the cathode, Li₅VF₄(SO₄)₂ particles were on the order of 2 μm in size, as shown in Figure 2c.

To verify that a significant amount of water was not adsorbed onto the sample following preparation and washing (which would interfere with electrochemical testing), TGA was

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<th>Table 1. Crystallographic Data and Structure Refinement for Li₅VF₄(SO₄)₂</th>
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**Figure 1.** Crystal structure of the solvothermally prepared compound Li₅VF₄(SO₄)₂ solved from single-crystal X-ray diffraction data and projected almost down the c axis. On the right is a single VF₄(SO₄)₂⁻ anion. The unconnected gray atoms are the Li⁺. All atoms are depicted using the refined anisotropic atomic displacement parameters with probabilities of 95%.
performed on the sample. The TGA curve showing mass versus temperature is provided in the Supporting Information in Figure S2. No weight loss was observed up to 200 °C, which suggests that the sample did not contain adsorbed water.

Figure 3a shows the predicted stability of delithiating Li$_5$VF$_4$(SO$_4$)$_2$ while charging a cell. At most, it is expected that two Li ions 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 extracted. Figure 3b 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 the plot), the predicted voltages appear to be slightly lower than the experimentally observed oxidation and reduction voltages found in this study.

The cyclic voltammogram (Figure 4a) 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 is achieved at a very slow rate of C/60 (rate calculated for two Li ions cycling per formula unit) between 4.3 and 1.5 V, and reversible cycling of 0.25 Li per formula unit is achieved, as shown in Figure 4b. When charged to 4.5 V (Figure 4c), 100 mA h g$^{-1}$ was accessed, which would correspond to the extraction of 1.25 Li per formula unit. However, because of 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 mA h g$^{-1}$. While increased polarity of the V–F bond increases the voltage, it also decreases the electronic bandwidth, which contributes to the low electronic conductivity of the material. The electronic conductivity is likely the largest barrier to overcome, as Li$_5$VF$_4$(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. Although 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 the electrolyte, the conductivity of the pure

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

Figure 3. (a) Computed stability of the experimentally determined structure of Li$_5$VF$_4$(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 Li$_5$VF$_4$(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 4. (a) Cyclic voltammetry was performed at a rate of 0.1 mV s$^{-1}$ from 5 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 material studied here highlights the inherent trade-off between high voltage and electronic conductivity in cathode materials. Although 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 LiFePO₄, nanoscaling the active material and improving the conductive carbon coating could reveal significantly higher cycling performance in Li₅VF₄(SO₄)₂.²²⁻²⁴

An aspect that has not been discussed so far is the ability of a saltlike material such as Li₅VF₄(SO₄)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.³⁵ Tetrahedral moieties centered around a high-charge cation such as S⁶⁺ 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 valency. This is depicted schematically in Figure 6, where plausible structural networks

between an octahedrally coordinated metal M⁴⁺ cation with anions X⁻⁻ are depicted for anions such as F⁻, O²⁻, and C⁴⁻. 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 M⁴⁺, 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.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c14781.

Crystallographic data of Li5VF4(SO4)2 (CIF) Bond distances and bond angles from the single crystal X-ray structure analysis of Li5VF4(SO4)2; Raman spectroscopy results from Li5VF4(SO4)2 powder; and TGA of Li5VF4(SO4)2 crystals to show that water was not adsorbed onto samples (PDF)

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Notes

The authors declare no competing financial interest.

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