Tailoring a fluorophosphate as a novel 4 V cathode for lithium-ion batteries

Young-Uk Park1, Dong-Hwa Seo1, Byoungkook Kim2, Kun-Pyo Hong3,4, Hyungsub Kim1, Seongsu Lee3, Rana A. Shakoor5, Keiichi Miyasaka5, Jean-Marie Tarascon6 & Kisuk Kang1,7

1Department of Materials Science and Engineering, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul 151-742, Korea, 2Research Analysis Center, KAIST, Daehak-ro 291, Yuseong-gu, Daejeon 305-701, Korea, 3Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong-gu, Daejeon 305-600, Korea, 4Graduate School of Green Energy Technology, Chungnam National University, Daehak-ro 99, Yuseong-gu, Daejeon 305-764, Korea, 5Graduate School of EEW (WCU), KAIST, Daehak-ro 291, Yuseong-gu, Daejeon 305-701, Korea, 6Université de Picardie Jules Verne, CNRS UMR 7314, 33 rue Saint Leu, 80039 Amiens, France, 7Research Institute of Advanced Materials (RIAM), Department of Materials Science and Engineering, Seoul National University, Gwanak-ro 599, Gwanak-gu, Seoul 151-742, Korea.

Lithium-ion batteries, which have been widely used to power portable electronic devices, are on the verge of being applied to new automobile applications. To expand this emerging market, however, an electrode that combines fast charging capability, long-term cycle stability, and high energy density is needed. Herein, we report a novel layered lithium vanadium fluorophosphate, Li1.1Na0.4VPO4.8F0.7, as a promising positive electrode contender. This new material has two-dimensional lithium pathways and is capable of reversibly releasing and reinserting ~1.1 Li+ ions at an ideal 4 V (versus Li+/Li) to give a capacity of ~156 mAh g−1 (energy density of 624 Wh kg−1). Moreover, outstanding capacity retentions of 98% and 96% after 100 cycles were achieved at 60 °C and room temperature, respectively. Unexpectedly high rate capability was delivered for both charge and discharge despite the large particle size (a few microns), which promises further enhancement of power density with proper nano-engineering.

Rapidly-growing demand for better-performing lithium-ion batteries has driven researchers and engineers to intensively search for new materials having enhanced electrochemical properties. As the key technology for further development of hybrid or all-electric vehicles, lithium-ion batteries having higher power and energy density, safety, and cycle stability need to be developed. With this goal in mind, several groups of new polyanionic compounds have been discovered, including fluorosulfates, pyrophosphates, silicates, borates, and fluorophosphates. The diverse electrochemical properties of these compounds are critically affected by the species of polyanion and how they, as the building blocks, are arranged in the crystal lattice. The presence of polymorphism with one-, two-, or three-dimensional diffusional frameworks along with tunable redox potentials from the varying inductive effects of the polyanions offers great flexibility in designing new electrode materials.

Extensive research has been reported recently on polyanion-based cathodes. Earlier studies on sodium super ionic conductors (NASICONs) have shown that their open framework is exceedingly advantageous for fast diffusion of mobile ions; they can be used as the electrode for rechargeable batteries and even as the solid-state electrolyte. However, despite their fast ionic conduction, the heavy framework of typical NASICON-type compounds significantly lowers the energy density and makes them less attractive as an electrode. Rapid ionic conduction could be combined with multivalent transition metals that can contribute more than one-electron transfer during lithiation and delithiation, which would result in a strong contender to commercially available electrodes. While attempts have been made to use two-electron redox couples such as V3+/V5+ in (fluoro)phosphates, the additional capacity from V3+/V5+ has been only partially accessible, even at slow rates, and other drawbacks such as high polarization and poor reversibility have been reported as well.

To combine the high ionic conduction of an open framework with a multivalent redox center, we focused on a vanadium-containing fluorophosphate compound in this study. Although sodium vanadium fluorophosphate, Na1.5VPO5F0.5, has shown unsatisfactory electrochemical performance, we chose it as a starting material because of its many attractive features: (i) it contains 1.5 mobile ions (Na+ and Na+) per transition metal, (ii) it possesses a multivalent transition metal ion, (iii) it has an open crystal structure, and (iv) it has a relatively high voltage of ca. 3.8 V (vs. Na+/Na). However, the multivalency of the vanadium ion (from +3 to +5) is counterbalanced by the initial valence of +4 in the material. Cathode operation of this material in rechargeable batteries contributes only one electron via the V4+/V5+ redox reaction, and results in limited capacity (ca. 130 mAh g−1), even though more...
Chimie Douce
ion-exchange (here that the lithium derivative of this sodium phase obtained from polyanion groups in the structure could compensate for the low V\(^{3+}\)). Moreover, a higher inductive effect with more fluorine-containing ions by tens of ppm\(^{31,32}\). We believe that two paramagnetic sources could lower the initial valence of the vanadium ion. Evidence for reduced oxidation state of vanadium in Na\(_{1.5}\)VO\(_{2.8}\)F\(_{0.7}\). By altering the polyanion group from \([\text{PO}_3\text{F}_{0.5}]^{5-}\) to \([\text{PO}_4\text{F}_{1.5}]^{4-}\), we could effectively reduce the overall oxidation state of vanadium while maintaining structural integrity. \(^{23}\)Na magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of the three samples (Figure 2a) supported our claim. The \(^{23}\)Na MAS NMR spectrum of our sample (middle spectrum) shows two major Fermi contact shifts at 70 and 112 ppm, whereas the others exhibit a single contact shift at 136 ppm (Figure 1b). By plotting unit cell volumes of two samples having extreme degrees of fluorination (\(\delta = 0\) and 1) and our sample (\(\delta = 0.2\)), we found a linear relationship between \(\delta\) and cell volume (Figure 1c). This suggests that our sample is a solid-solution phase between Na\(_{1.5}\)V\(^{4+}\)PO\(_4\)F\(_{0.5}\) and Na\(_{1.5}\)V\(^{5+}\)PO\(_4\)F\(_{1.5}\). More detailed NMR studies are in progress.

**Results**

**Fluorination of the pristine Na phase.** Na\(_{1.5}\)VPO\(_3\)F\(_{0.5}\) has a pseudo-layered structure in which the sodium and vanadium layers are roughly separated in an alternate manner along c direction (Figure 1a). The framework is made up of VO\(_2\)F octahedra and PO\(_4\) tetrahedral units, where two VO\(_2\)F octahedra are linked by a bridging fluorine ion to form a V\(_2\)O\(_{10}\)F biocathedron\(^{20}\). The V\(_2\)O\(_{10}\)F biocathedral units are repeatedly connected in \(ab\) plane via PO\(_4\) tetrahedral sharing oxygen atoms to thereby construct an open framework having a layer-like spacing into which Na\(^+\) ions are intercalated. Our synthesis strategy was to create an appropriate stoichiometric ratio of fluorine and oxygen in Na\(_{1.5}\)VPO\(_4\)F\(_{0.5}\) so that the redox range of vanadium ions was widened below +4 at a reasonably high potential. Starting from Na\(_{1.5}\)VPO\(_4\)F\(_{0.5}\), we tried to increase the degree of fluorination (\(\delta\)) in Na\(_{1.5}\)VPO\(_4\)F\(_{0.5-\delta}\) by increasing the portion of V\(^{3+}\) precursor with a sufficient amount of fluorine-containing precursor, as described in the Methods section. We found that V\(^{3+}\) ions prefer F\(^-\) ions as the anions constituting the V\(_2\)O\(_{10}\)F biocathedron than V\(^{4+}\) ions due to the charge balance. Hence, by changing the ratio of V\(^{3+}\) to V\(^{4+}\) precursors, we could control \(\delta\). Here, we describe the results of the sample that was shown to have an optimum degree of fluorination, \(\delta = 0.2\) (see Chapter 1 in the Supplementary Information for details on stoichiometry optimization).

The phase-pure Na\(_{1.5}\)VPO\(_{4}\)F\(_{0.5-\delta}\) was successfully obtained, and all reflections in its neutron diffraction (ND) pattern were completely indexed with a space group of P4\(_2\)/mm, as shown in Figure 1b (see Chapter 2 in the Supplementary Information for details on the structural refinement). Elemental analysis of the micron-sized Na phase (inset of Figure 1b) by inductively coupled plasma (ICP) and energy-dispersive X-ray spectroscopy (EDS) revealed the detailed composition, i.e., Na\(_{1.48(\pm0.02)}\)V\(_{3.8(\pm0.1)}\)PO\(_{4.8(\pm0.1)}\)F\(_{0.8(\pm0.1)}\), hereafter called Na\(_{1.5}\)VPO\(_{4}\)F\(_{0.7}\) for convenience (see Chapter 1 in the Supplementary Information for details). Both the decreased O/V ratio and the increased F/V ratio suggested partial replacement of fluorine ions (F\(^-\)) for oxygen ions (O\(^2-\)), which led to a less negatively charged anion group in the structure. X-ray photoelectron spectroscopy (XPS) results (see Supplementary Figure S4) suggested that the fluorine ions replaced those oxygen ions that lie in the two terminal positions of the V\(_2\)O\(_4\)F biocathedra (denoted by arrows in Figure 1a). By plotting unit cell volumes of two samples having extreme degrees of fluorination (\(\delta = 0\) and 1) and our sample (\(\delta = 0.2\)), we found a linear relationship between \(\delta\) and cell volume (Figure 1c). This suggests that our sample is a solid-solution phase between Na\(_{1.5}\)V\(^{4+}\)PO\(_4\)F\(_{0.5}\) and Na\(_{1.5}\)V\(^{5+}\)PO\(_4\)F\(_{1.5}\) with a ratio of 4:1.

than one Na\(^+\) ion per transition metal exists in the structure. Further utilization of the vanadium redox reaction below +4 by inserting additional Na\(^+\) ions into the structure has led to a substantially lower voltage that is practically unacceptable. Instead, we adjusted the stoichiometric ratio of oxygen and fluorine in the material and kept the original structure intact. The difference in the oxidation states of F\(^-\) vs. O\(^2-\) could lower the initial valence of the vanadium ion. Moreover, a higher inductive effect with more fluorine-containing polyanion groups in the structure could compensate for the low V\(^{3+}\)/V\(^{4+}\) redox potential and offer a higher average voltage. We report here that the lithium derivative of this sodium phase obtained from ion-exchange (Chimie Douce) between Na\(^+\) and Li\(^+\) has excellent performance as a cathode material, reversibly releasing and reinserting ca. 1.1 Li\(^+\) ions with the V\(^{4+}\)/V\(^{3+}\) redox reaction at an ideal 4 V in the lithium cell.
To further probe the substitution, we carried out electron paramagnetic resonance (EPR) experiments (Figure 2b) on those three samples. The EPR spectrum of Na$_{1.5}$V$_4$PO$_4$.8F$_{0.7}$ was very intense, and the shape was in good agreement with a previous report.$^{13}$ However, the EPR signal of Na$_{1.5}$V$_3^+$PO$_{4.8}$F$_{0.7}$ was negligible, which can be explained by the fact that V$^{3+}$, a non-Kramers’ ion with integral J in LS coupling$^{14}$, is silent under conventional EPR experimental conditions$^{12}$. On the contrary, the EPR spectrum of our sample, Na$_{1.5}$V$_{1.8}$PO$_{4.8}$F$_{0.7}$, showed a broad peak, unlike that of Na$_{1.5}$V$_3^+$PO$_{4.8}$F$_{0.7}$ or Na$_{1.5}$V$_3^+$PO$_{4.5}$F$_{1.5}$. It resembles the EPR spectra of Li$_x$V$_2$(PO$_4$)$_3$ phases ($x = 2.0$ and 2.5) in which V$^{3+}$ and V$^{4+}$ ions coexist$^{15}$, implying the coexistence of V$^{3+}$/V$^{4+}$ ions in our sample.

Na$^+$/Li$^+$ ion-exchange for lithium derivative of Na$_{1.5}$VPO$_4$.8F$_{0.7}$. Ion exchange is an effective way to synthesize a new metastable phase without causing much structural change to the pristine structure$^{28,39}$. Using a Na$^+$/Li$^+$ ion-exchange method, we successfully prepared an isostructural lithium derivative of Na$_{1.5}$VPO$_4$.8F$_{0.7}$ (see Supplementary Table S4 for details). According to ICP elemental analysis, ca. 1.1 Na$^+$ ions were replaced by Li$^+$ ions without affecting the other elements; the overall composition was Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$.

Detailed structural analysis of the new lithium phase was carried out using ND and solid-state ‘Li and 23Na NMR spectroscopies. All reflections of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ observed in the ND pattern (Figure 3a) could be indexed in the space group P4$_2/mnm$. All Miller indices (hkl) of the structure matched those of Na$_{1.5}$VPO$_4$.8F$_{0.7}$, indicating that the isostructural lithium derivative was obtained (see Chapter 3 in the Supplementary Information for details on the refinement). Na$_{1.5}$VPO$_4$.8F$_{0.7}$ and Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ particles had similar morphology, with sizes in the range of ca. 1–5 μm (inset of Figure 3a). Figure 3b shows that the observed micron-sized crystallites were single crystals rather than agglomerates of nanocrystals [see Figure S7 in the Supplementary Information for more transmission electron microscopy (TEM) images].

The local lithium environments in Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ were investigated by ‘Li MAS NMR (see Chapter 7 in the Supplementary Information for more information on “Na MAS NMR”). The ‘Li MAS NMR spectrum (Figure 3c) suggests the existence of two types of local environments for lithium in the structure, reminiscent of the two kinds of sodium sites in the parent sodium phase. The signal at 25.5 ppm is significantly more intense than the signal at 0 ppm, indicating that one of two crystallographic sites for alkali ions is preferentially occupied by Li$^+$ ions. This preferential occupation of Li$^+$ ions in one alkali-metal site is consistent with the ND refinement result (see Figure 3d).

The thermal phase stability of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ was evaluated by temperature-controlled X-ray diffraction (XRD) (Figure 3d). Increasing temperature above 600°C triggered phase separation into a sodium phase (Na$_{1.5}$VPO$_4$.8F$_{0.7}$) and lithium phase (tavorite LiVOPO$_4$ or triclinic α-LiVOPO$_4$). This suggests that sodium and lithium phases crystalize in different structures having dissimilar stoichiometries in the “Na(Li)–V–P–O–F” system under conventional high-temperature synthesis conditions. Metastable phases obtained from low-temperature Chimie Douce routes are often susceptible to thermal degradation upon slight heat treatment. However, we found that the Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ phase was thermally stable up to 550°C, which indicates that various low-temperature synthesis techniques, such as ionothermal processes$^{5,8,9}$, can be applied to the synthesis of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$.

**Electrochemical performance of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$**. The electrochemical properties of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ were examined in a Li cell. The quasi-equilibrium profile obtained by the galvanostatic intermittent titration technique (GITT) at 60°C shown in Figure 4a exhibited an average voltage of ca. 3.95 V. The low-current charge and discharge via the GITT mode exhibited a low polarization and yielded a capacity approaching the theoretical capacity for Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$, 156 mAh g$^{-1}$ (equivalent to insertion/deinsertion of 1.1 Li$^+$ ions per formula unit). This clearly indicates more than one lithium ion contributes to the capacity through the widened V$^{3+}$/V$^{4+}$ redox

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**Figure 2**: NMR and EPR spectra of the fluorinated Na$_{1.5}$VPO$_4$.8F$_{0.7}$. (a) 23Na MAS NMR spectra of Na$_{1.5}$V$_4^+$PO$_{4.5}$F$_{0.7}$ (bottom), Na$_{1.5}$V$_3^+$PO$_{4.5}$F$_{0.7}$ (middle), and Na$_{1.5}$V$_3^+$PO$_{4.1}$F$_{1.5}$ (top). Spinning sidebands are marked with asterisks. Small isotropic peaks (denoted as ◆) could not be assigned. (b) EPR spectra of Na$_{1.5}$V$_4^+$PO$_{4.5}$F$_{0.7}$ (black dashed line), Na$_{1.5}$V$_3^+$PO$_{4.5}$F$_{0.7}$ (red solid line), and Na$_{1.5}$V$_3^+$PO$_{4.1}$F$_{1.5}$ (blue dotted line).

**Figure 3**: Material characterization of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$. (a) ND pattern of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$ and its Rietveld refinement in the P4$_2/mnm$ space group with observed data points (red dots), calculated pattern (black line), difference curve (blue line), and Bragg positions (green bars); lattice parameters are a = b = 8.9836(6) Å, c = 10.4483(8) Å, and V = 843.24(9) Å$^3$. The unit cell volume was significantly reduced from 867.37(2) Å$^3$ for Na$_{1.5}$VPO$_4$.8F$_{0.7}$ to 843.24(9) Å$^3$ for the new lithium phase because of the smaller ionic radius of Li$^+$ ion. The inset shows a scanning electron microscopy (SEM) image (magnification: ×5,000). (b) A bright-field TEM image of a micron-sized particle (top) and its corresponding SAED pattern (bottom). (c) ‘Li MAS NMR spectrum of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$. (d) Temperature-controlled XRD patterns of Li$_{1.1}$Na$_{0.4}$VPO$_4$.8F$_{0.7}$. A reflection denoted as ◆ could not be identified. Supplementary Table S6 and demonstrates that most Li$^+$ ions reside in the original Na1 site, while the Na2 sites remained mainly occupied by Na$^+$ ions.
reaction achieved by tailoring the pristine Na1.5VPO5F0.5 and its lithium derivative (LiNa0.5V4PO4F1.5) with a V4+/V3+ redox couple can theoretically deliver only ca. 130 mAh g−1 and 141 mAh g−1, respectively. Tailoring the pristine fluorophosphate material as the 4 V electrode with the capacity of 156 mAh g−1 makes this material a strong alternative to other known cathode materials: LiCoO2 (4 V, ca. 160 mAh g−1), LiFePO4 (3.45 V, ca. 170 mAh g−1), LiNi0.5Mn1.5O4 (4.7 V, ca. 130 mAh g−1), LiMn2O4 (4 V, ca. 120 mAh g−1), and LiNi0.5Mn1.5O4 (4.7 V, ca. 130 mAh g−1).

Galvanostatic cycling at a rate of C/20 (Figure 4b) could deliver ca. 140 mAh g−1 reversibly without a noticeable change in the shape of the charge/discharge profile. At a faster rate of 1C, ca. 87% of the theoretical capacity of Li1.1Na0.4VPO4.8F0.7 could be retained after the first cycle. After 100 full charge–discharge cycles at 1C at room temperature, no significant capacity loss occurred (i.e., a capacity retention of 96%), as shown in the bottom panel of Figure 4c. Moreover, the cyclability at 60°C was observed between redox potentials of V3+/V4+ and V4+/V5+ in this material. In fact, the redox potential of V4+/V3+ in V2O10F6 (left inset) is ca. 3.9 V vs. Na+/Na (ref. 50) and that of V4+/V5+ in V2O10F6 of Na1.5V4PO4F1.5 (right inset) is ca. 3.8 V vs. Na+/Na (ref. 29). We believe that the larger inductive effect in the V2O10F6 biocathahedron having more fluorine atoms increased the redox potential of V4+/V3+ up to that of V4+/V5+.

(a) GITT curve in charge and discharge modes at 60°C. Note that no clear separation was observed between redox potentials of V3+/V4+ and V4+/V5+ in this material. (b) Galvanostatic charge/discharge curves for the first two cycles at the C/20 rate. 1C corresponds to 156 mA g−1. The inset shows the corresponding dQ/dV curve. Two major peaks were reversibly detected at ca. 3.8 and 4.1 V, whose origin is under investigation. (c) Cyclability over 100 cycles of galvanostatic charge/discharge at the 1C rate at room temperature (bottom) and at an elevated temperature of 60°C (top). (d) The charge and (e) discharge curves for various C rates.

Discussion

We believe that the unexpected capacity retention (see Figure 4c) is due to the small difference in the cell volumes between lithiated and delithiated phases. The cell volumes of the pristine Li1.1Na0.4VPO4.8F0.7 and Na0.4VPO4.8F0.7 (i.e., fully charged state) calculated from XRD experiments revealed that the change in volume between the two is ca. 0.7% (see Supplementary Figure S10 and Table S7). This unusually small volume change of Li1.1Na0.4VPO4.8F0.7 upon cycling is comparable to the lowest volume change reported for triplite Li(Fe1–xMnx)SO4F (ca. 0.6%)4. First-principles structure calculations also confirmed the small volume difference between two simple models of Li0.5VPO3.5F1.5 and Na0.5VPO3.5F1.5 (see Chapter 9 in the Supplementary Information for calculation details). The structural investigation of Li1.1Na0.4VPO4.8F0.7 after 100 cycles at a rate of 1C rate showed no change in the XRD pattern (see Supplementary Figure S12).

The high rate capability of Li1.1Na0.4VPO4.8F0.7 (see Figure 4d) is attributable to fast Li+ ion transport in the open crystal lattice.
Figure 5 | NEB calculations for Na\(^+\) and Li\(^+\) diffusion in Na\(_{1.5}\)VPO\(_5\)F\(_{0.5}\) and LiNa\(_{0.5}\)VPO\(_5\)F\(_{0.5}\). (a) Top view (ab plane) of the alkali metal layer in Li\(_{1.1}\)Na\(_{0.4}\)VPO\(_{4.8}\)F\(_{0.7}\), representing two types of diffusion paths for Li\(^+\) ions (indicated by arrows). This illustration was based on the refinement results. Li, Na, O, and F atoms are represented in blue, yellow, red, and green, respectively. (b) Trajectories and (c) the corresponding activation barriers for Na hopping in diffusion path 2 in Na\(_{1.5}\)VPO\(_5\)F\(_{0.5}\) as predicted by the NEB method. (d) Trajectories and (e) the corresponding activation barriers for Li hopping in diffusion path 2 in LiNa\(_{0.5}\)VPO\(_5\)F\(_{0.5}\) as predicted by the NEB method. The Li\(^+\) ion trajectory along path 2 is quite different from that of Na\(^+\). While the Na\(^+\) ions, whose site energy strongly affects the activation barrier, migrate with a sinusoidal motion (Figure 5b) along path 2 due to the small intermediate space in the middle of the path, the Li\(^+\) ions travel in a nearly straight line (Figure 5d). The energy trajectory in Figure 5e indicates the metastability at the intermediate space. This is because the presence of Na\(^+\) ions in the structure provides a larger empty space for Li\(^+\) ions.
investigation of polyanion-based compounds as frameworks for new cathode materials and offers exciting opportunities for the development of new compounds.

Methods

Synthesis. A stoichiometric amount of VO2 (Sigma-Aldrich, 99%) and NH4H2PO4 (Sigma-Aldrich, 99%) was blended by high-energy ball-milling (HEBM) at 300 rpm for 24 hours. The mixture was then pelletized and heat-treated at 750 °C for 4 hours in air to provide yellowish VOPO4 (or V5+ over 24 hours). The mixture was then pelletized and heat-treated at 750 °C for 2 hours under an Ar atmosphere. The precursor combination used to synthesize Na1.5VPO5F0.5 was dried overnight at 70 °C.

Electrochemistry. For the electrochemical test, a slurry of 88 wt% carbon-coated Li0.5Na0.5VPO4F0.5 (70.4 wt% total active material), 2 wt% black carbon (19.6 wt% total carbon), and 10 wt% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrroldione (NMP) was prepared and cast on aluminum foil (see Chapter 13 in the Supplementary Information for details on the coating-process coating). The electrode was dried overnight at 70 °C under vacuum. The loading of the active material on the electrode was referenced to 5–6 mg cm⁻². Electrochemical cells were assembled in an Ar-filled glove box into CR2016-type coin cells consisting of a counter electrode (lithium metal, separator (Celgard 2400; Celgard, USA), and electrolyte (1 M LiPF6 solution) in a mixture of ethyl carbonate/dimethyl carbonate (EC/DMC, 1:1 v/v). All the electrochemical tests were carried out using a WBCS 3000 potentiostat (WanAtech, Korea). For the GITT measurements, the electrochemical cells were rested for 2 hours after each hour-long charging or discharging at the C/20 rate (voltage window: 2.2–4.5 V) at 60 °C. 1T corresponds to 156 ma g⁻¹. To acquire the charge curves for various C rates, the cells were cycled once at the rate of C/20 and then charged to 4.5 V at different rates. To obtain the discharge curves for various C rates, the cells were charged at the same rate of C/20 to 4.5 V and then discharged to 2.5 V at different rates. Unless otherwise noted, all cells were cycled between 2.5 and 4.5 V at room temperature.

Computational details. First-principles calculations were made using the Perdew–Burke–Ernzerhof exchange-correlation parameterization to density functional theory (DFT) with the spin-polarized generalized gradient approximation (GGA). We used a plane-wave basis set and the projector-augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP). The Hubbard parameters (GGA+U) were added to correct the incomplete cancellation of the self-interaction of GGA. A U value of 5.0 eV (the on-site coulomb term) and J value of 1.0 eV (the exchange term) were used for the vanadium ions in Na1.5VPO4F5. LiNa0.5VPO4F5, and Na0.5VPO4F5. Activation barriers for lithium and sodium diffusion in the two model systems of Na1.5VPO4F5 and LiNa0.5VPO4F5 were calculated using the nudged-elastic-band (NEB) method. In those calculations, the Li and Na ions were allowed to move in Na231VPO4F5 and Li115Na0.5VPO4F5. Seven replicas of the systems were used as a starting point fixed with linear interpolation between the initial and final states of the path. All lattice parameters were fixed at the Na231VPO4F5 and Li115Na0.5VPO4F5 states, but all the internal degrees of freedom were relaxed during the NEB calculations.

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X-ray photoelectron spectroscopy. XPS spectra were obtained by electron spectroscopy for chemical analysis (ESCA) (Sigma Probe; Thermo VG Scientific, UK) with a pass energy of 30 eV and a step size of 0.1 eV. Binding energies were referenced to the Cls peak at 284.6 eV.

Diffraction. ND data were collected over a 20 range of 0–180 ° with a step size of 0.05° and λ = 1.83429 Å supplied by a Ge(311) single-crystal monochromator on a high-resolution powder diffractometer (HRPD) at the Hanaro facility of the Korea Atomic Energy Research Institute. XRD was carried out using an X-ray diffractometer (D8 Advance; Bruker, Germany) using Ni-filtered Cu-Kα radiation (λ = 1.5406 Å) in the 2θ range of 10–80 °. The room-temperature XRD data were refined using the Rietveld method and Fullprof software. Temperature-controlled XRD measurements were carried out under vacuum using an X-ray diffractometer (D/MAX-2500 diffractometer; Rigaku, Japan) with Cu-Kα radiation (λ = 1.5406 Å) and step scanning (0.01° s⁻¹ in the 2θ range of 10–60 ° with a scan speed of 2° min⁻¹). The heating rate was 5 °C min⁻¹. Each measurement was taken after stabilizing at the desired temperature for 5 min. The XRD data were collected at room temperature at the beam line of BL02B2 in SPring-8 (Japan) with an average wavelength of ca. 0.9988 Å calibrated using the NIST silicon fine powder (SRM640d).

NMR and EPR spectroscopy. Solid-state 'Li and 'Na MAS NMR spectroscopy experiments were performed using a Bruker Avance 400 MHz 9.4 T Wide Bore spectrometer at Larmor frequencies of 58.9 and 162 MHz, respectively. All experiments were performed with a Bruker 4-mm probe at a MAS frequency of 15 kHz at room temperature. For the 'Na MAS NMR measurements, all spectra were obtained using a 90° pulse of 1 μs and a recycle delay of 0.5 s. The 'Li MAS NMR spectra were collected using a 90° pulse of 2 μs and a recycle delay of 1 s. The 'Na and 'Li NMR shifts were referenced to 0.1 M NaCl (0 ppm) and 1 M LiCl (0 ppm) respectively. EPR spectra were recorded using a JES-TE200 electron resonance spectrometer (JEOL, Japan) at room temperature with 4-mm quartz tubes. The magnetic field was varied from 2000 to 5000 Gauss at a resonance frequency of 9.447 GHz.
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Author contributions

Y.-U. Park and R.A. Shakoor executed the synthesis with some advices from J.-M. Tarascon. The computational study was carried out by D.-H. Seo, and B.K. Kim carried out the NMR experiments. K.P. Hong, S. Lee, and H. Kim performed the ND analyses. Synchrotron XRD data were acquired by K. Miyasaka. K. Kang proposed the original idea and supervised the project. Y.-U. Park and K. Kang wrote the manuscript, and all authors participated in the discussion of the results and the structure of the final manuscript. Correspondence and requests for materials should be addressed to K. Kang.

Additional information

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