



Hybrid-Ion

A Lithium-Ion Cell Based on a Sodium Insertion Material

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This communication describes the performance characteristics of a graphite/Li⁺ electrolyte/Na₃V₂(PO₄)₂F₃ hybrid-ion cell. The properties of this system compare favorably with commercial lithium ion cells. During the initial charging of this cell, sodium ions are extracted from the fluorophosphate while concurrent lithium ion intercalation occurs at the graphite counter electrode. During subsequent cell cycling the cathode reaction is likely based on a mixed Li/Na insertion mechanism. Importantly we find that highly lithiated graphite is electrochemically stable in the presence of Na⁺ in the electrolyte phase, presumably due to the presence of the carbon passivation layer.

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Conventional lithium-ion batteries are normally fabricated using a combination of a lithium-containing cathode phase and a suitable carbon-based (typically graphite) anode electrode.¹ During the charging of these cells, lithium ions are extracted from the cathode material while concurrent lithium insertion occurs at the negative electrode, such that when fully charged most of the active lithium resides within the anode structure. During the subsequent cell charge-discharge process the active lithium ions are then shuttled between the two insertion electrodes.² In the work presented here we describe the first details of a hybrid-ion battery concept whereby a nonlithium containing cathode material is used in conjunction with a conventional graphite anode material. To complete the electrochemical configuration a traditional lithium-based nonaqueous electrolyte is used. The cathode material employed in this particular study is the sodium vanadium fluorophosphate phase, Na₃V₂(PO₄)₂F₃, although we believe that other suitable sodium-based insertion materials may also be utilized. The alkali ion insertion properties of the Na₃V₂(PO₄)₂F₃ phase (as well as the structurally related NaVPO₄F phase), have been described previously by this group.³⁻⁵

Experimental

The Na₃V₂(PO₄)₂F₃ was prepared using a two-step process involving the orthorhombic vanadium(III) phosphate, VPO₄, as the reaction intermediate. The VPO₄ was prepared from V₂O₅ and (NH₄)₂HPO₄ using a carbothermal reduction process.^{6,7} In the second step, the vanadium phosphate was reacted with a stoichiometric quantity of NaF to yield the Na₃V₂(PO₄)₂F₃ fluorophosphate product phase. Structural and crystallographic analyses of the active phase were provided from powder diffraction data obtained using a Siemens D5000 X-ray diffractometer equipped with Cu K α radiation.

For electrochemical testing, composite electrodes were fabricated using 84 wt % active material, 5 wt % Super P (conductive carbon), and 11 wt % polyvinylidene fluoride (PVDF-HFP) copolymer (Elf Atochem) binder. The electrolyte comprised a 1 M LiPF₆ solution in ethylene carbonate/dimethyl carbonate (EC/DMC, 2:1 by weight) while a dried glass fiber filter (Whatman, Grade GF/A) was used as the electrode separator. A commercial crystalline graphite was used as the anode active material. High-resolution electrochemical measurements were provided using the electrochemical voltage spectroscopy (EVS) technique.⁸ EVS is a voltage step method, which provides a high-resolution approximation to the open circuit voltage curve for the electrochemical system under investigation. The EVS experimental conditions of limiting current density of <100 μ A/cm² and 10 mV voltage increments were roughly

equivalent to a C/15 rate for charge and discharge. Cycling tests of the hybrid-ion cells were performed using a commercial battery cycler (Maccor Inc., Tulsa, OK, USA).

Results and Discussion

X-ray powder diffraction (XRD) analysis for the Na₃V₂(PO₄)₂F₃ indicated the material to be single-phase with a tetragonal structure, space group *P*₄₂/*mnm*. The unit cell parameters (*a* = 9.0304(5) Å, *c* = 10.6891(9) Å) were calculated from a least squares refinement procedure, in fair agreement with the structural analysis for β -Na₃V₂(PO₄)₂F₃ described by Meins et al., i.e., *a* = 9.047(2) Å, *c* = 10.705(2) Å.⁹ The fluorophosphate phase is expected to demonstrate facile sodium-ion diffusion through an extended three-dimensional framework built up from [M₂O₈F₃] bi-octahedra and [PO₄] tetrahedra.¹⁰ The [M₂O₈F₃] bi-octahedra are bridged by one fluorine atom while the sodium ions are statistically distributed in two channels within the resultant network. Figure 1 depicts a schematic representation of the fluorophosphate structure, clearly indicating the two crystallographic positions of the Na ions. A similar structural model has also been proposed for the tetragonal Na₃Fe₂(PO₄)₂(OH)₂F phase, in which the alkali ions are distributed over two structural sites.¹¹

In previous communications we have reported the electrochemical insertion behavior for Na₃V₂(PO₄)₂F₃, as well as for the structurally related NaVPO₄F.³⁻⁵ In one of these investigations the NaVPO₄F phase was capacity-matched with a hard carbon anode material and a sodium-based electrolyte to fabricate a fully functional sodium-ion cell.³ This work clearly established NaVPO₄F as a reversible insertion host. In Fig. 2 we show the first cycle EVS response for a typical Li/1 M LiPF₆ (EC/DMC)/Na₃V₂(PO₄)₂F₃ test cell. Electrochemical testing was undertaken immediately following cell fabrication (typically within 5 min) thereby removing the possibility of appreciable ion-exchange taking place between the Na₃V₂(PO₄)₂F₃ and Li⁺ electrolyte phase. During the initial charging process sodium is extracted from the fluorophosphate phase and enters the electrolyte phase to create a mixed Li-Na electrolyte. On subsequent discharge it is presently unclear what precise insertion mechanism is occurring, although the generally symmetrical nature of the differential capacity profile depicted in Fig. 2 supports a predominant sodium insertion process. A reversible specific capacity [calculated from the initial mass of the Na₃V₂(PO₄)₂F₃] is 126 mAh/g, representing 98% of the theoretical material utilization, based on the assumption of cycling two alkali ions per formula unit. From closer inspection of this figure it appears that sodium is extracted from the Na₃V₂(PO₄)₂F₃ in two processes centered around 3.80 V vs Li and 4.30 V vs Li while the subsequent alkali ion insertion processes are positioned at about 4.25 V vs Li and 3.75 V vs Li. These data support the structural model previously identified for the fluorophosphate phase in which the alkali ions are evenly dis-

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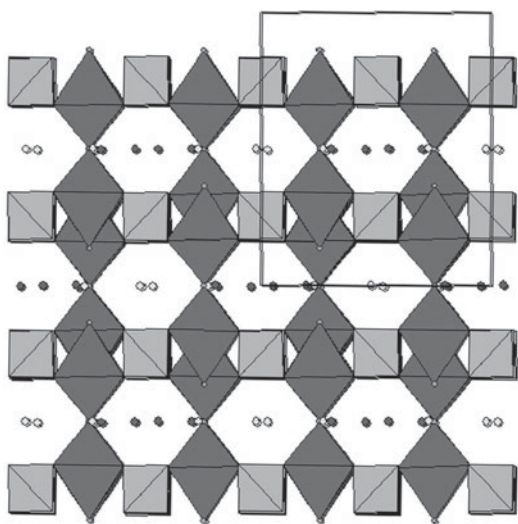


Figure 1. Structural representation of the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ structure projected along the a direction. The unit cell is shown outlined by the box.

tributed between two crystallographic sites. Attempts to extract the remaining one Na ion from the fluorophosphate structure by excursions to higher charge voltages, proved inconclusive. Although an

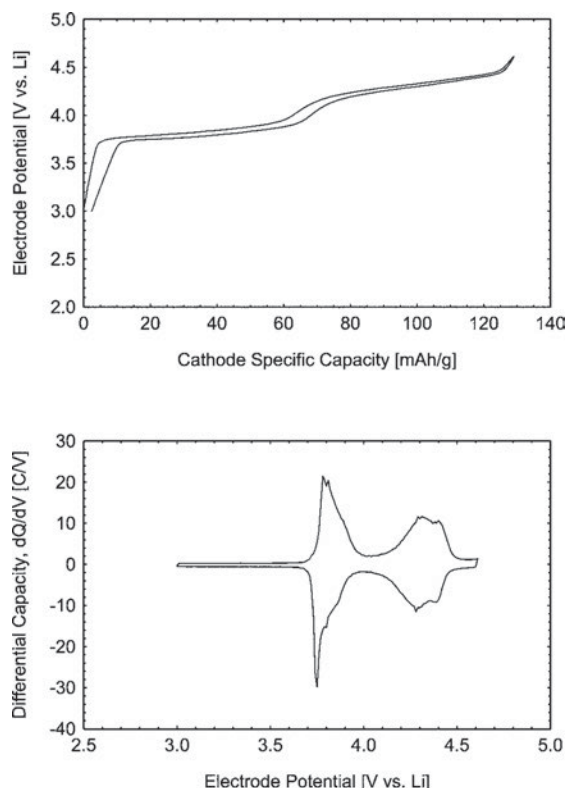


Figure 2. EVS data for a typical $\text{Li}/\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cell cycled between 3.00–4.60 V vs Li. The data shown were collected at 23°C and are for the first cycle. The electrolyte comprised a 1 M LiPF_6 solution in EC/DMC (2:1 by weight) Top: EVS voltage profile; bottom: EVS differential capacity profile.

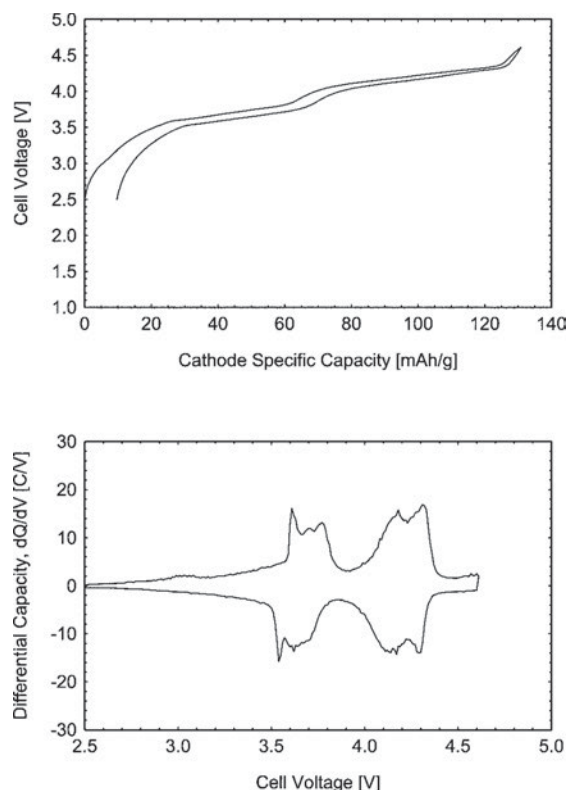


Figure 3. EVS data for a typical graphite/ $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ hybrid-ion cell cycled between 2.50–4.60 V. The data shown were collected at 23°C and are for the first cycle. The electrolyte comprised a 1 M LiPF_6 solution in EC/DMC (2:1 by weight) Top: EVS voltage profile; bottom: EVS differential capacity profile.

additional voltage plateau was found to be present at around 4.9 V vs Li, only a small percentage of the associated oxidation charge was found to be reversible. Based on the electrochemical stability window of the EC/DMC electrolyte system, this observation may be consistent with electrolyte decomposition rather than some inherent active material limitation.

To establish the stability of the ion insertion reactions in the active material $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ long-term testing of the $\text{Li}/\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ was carried out. These results (not shown here) confirmed several hundred charge-discharge cycles with low capacity fade. Clearly the fluorophosphate material shows encouraging electrochemical stability, characterized by the reversibility of the alkali-ion insertion reactions over this extended cycling regimen. In addition, over the course of this cycling regimen it was noted that the shape of the differential capacity profile changed significantly, presumably indicating an alteration in the overall ion insertion mechanism.

Next, the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ material was capacity-matched (using a 2:1 cathode to anode mass balance) with a crystalline graphite anode material to form a graphite/1 M LiPF_6 (EC/DMC)/ $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ rocking chair cell. In this configuration the only available Li in the system originates from the LiPF_6 -based electrolyte phase. Based on a cathode-limited system, the actual volume of electrolyte used was carefully controlled so as to allow charging of the graphite active material to an approximate utilization limit of 300 mAh/g or $\text{Li}_{0.81}\text{C}_6$. In Fig. 3 we show the first cycle EVS response for one representative test cell, and it is clear from inspection that the voltage profile and differential capacity data are qualitatively similar to those depicted in Fig. 2 for the metallic

lithium cell. During the initial charge process, sodium ions are extracted from the fluorophosphate cathode, while lithium ions (from the electrolyte) are intercalated into the graphite anode. The relatively low first cycle charge inefficiency (<7%), compares favorably with commercial graphite/LiCoO₂ lithium-ion cells and is presumably associated with the creation of a stable, lithium-based solid electrolyte interphase (SEI) passivation layer on the carbon anode. Moreover, during this first cycle, the cell operates with low voltage polarization, indicative of the favorable rate capability of the system.

From these preliminary observations we may draw an important and unexpected conclusion that highly lithiated graphite is apparently chemically stable in the presence of the relatively high activity of Na ions in the electrolyte phase. This is a somewhat surprising result, since based on purely thermodynamic considerations one would predict that Na ions would be reduced to Na metal at the carbon surface (assuming no appreciable Na insertion into the crystalline graphite) during which time Li ions would be displaced from the lithiated graphite. A possible explanation for this observation is that, unlike Li ions, the Na⁺ cannot penetrate the SEI passivation layer formed on the lithiated graphite. Separate experiments carried out using highly lithiated graphite in contact with a 1 M NaPF₆ EC/DMC electrolyte confirmed the apparent stability of this couple. In summary, these observations suggest that in the charged hybrid ion cell the electrolyte would comprise both Na and Li ions and that the cathode reaction may in fact be a mixed Li/Na insertion process.

The differential capacity data shown in Fig. 3 reveal the relative complexity of the charge/discharge process as evidenced by the multiple but reversible differential capacity peaks, and may result as a consequence of the mixed insertion mechanism in the Na₃V₂(PO₄)₂F₃. XRD studies are currently underway in our laboratory to help elucidate the precise nature of these reactions.¹² In accordance with the Li half cell studies, subsequent EVS cycles show a gradual change and sharpening of the differential capacity profile, particularly in the voltage region around 3.8 V, consistent perhaps with a change in the nature of the insertion reaction. Separate tests with lower levels of Li in the electrolyte phase (i.e., sufficient to only partially lithiate the graphite) produced much higher first cycle coulombic inefficiencies (presumably due to unwanted side reactions) and consequently resulted in cells with low discharge capacities. As expected, a test carried out with a 100% Na⁺ based electrolyte (i.e., 1 M LiPF₆ in EC/DMC) resulted in virtually no reversible capacity.

In Fig. 4 we show the preliminary cycling behavior of a representative graphite/Na₃V₂(PO₄)₂F₃ cell. These data were collected at approximate charge/discharge rates of C/2 and 2C. The initial cathode reversible capacity is in the range 115–120 mAh/g, and the cells cycle with relatively low capacity fade behavior. The minor decrease in discharge capacity recorded at the two discharge rates is indicative of the excellent rate characteristics of this system. Clearly these preliminary data show the insertion stability of this novel battery configuration. They also confirm the overall stability of the lithiated graphite/Na⁺ electrolyte couple.

Conclusions

In this communication we have demonstrated the feasibility of a novel lithium-ion cell based on the application of a sodium-based

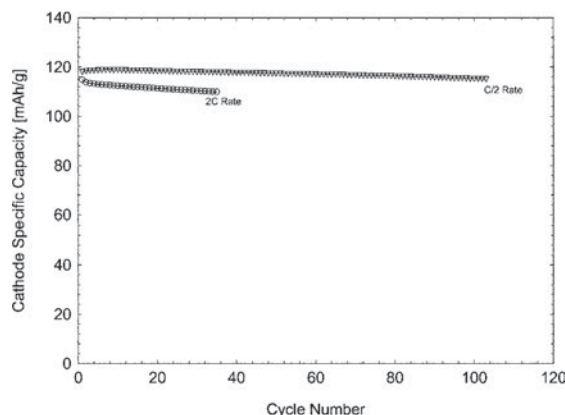


Figure 4. Lifetime cycling of representative graphite/Na₃V₂(PO₄)₂F₃ hybrid-ion cells cycled between 3.00–4.60 V at C/2 and 2C rates for charge and discharge. The data shown were collected at 23°C using an electrolyte that comprised a 1 M LiPF₆ solution in EC/DMC (2:1 by weight).

cathode phase. Conventional lithium-ion cells employ a lithium-containing cathode material used in conjunction with a suitable carbon anode. The properties of these commercial cells are thus limited by the availability and performance characteristics of these lithium-based cathode phases. In the cell configuration described here, we utilize the sodium fluorophosphate, Na₃V₂(PO₄)₂F₃, as the cathode active phase, although we believe the basic cell fabrication concept is not limited to this particular active material. During initial charging sodium ions are extracted from the fluorophosphate and enter the electrolyte, and the presence of appreciable levels of Na⁺ in the electrolyte does not appear to be detrimental to the long-term performance characteristics of the cell. The concurrent anode reaction is lithium intercalation into the graphite. During subsequent cell operation, the precise insertion reactions taking place at the cathode are presently unknown, although we believe a mixed Li/Na insertion mechanism is likely occurring.

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