

Novel Battery Systems based on Advanced Fluorophosphate Active Materials

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Framework materials based on the phosphate polyanion have recently been identified as potential electroactive materials for lithium metal and lithium ion battery applications [1,2]. We have extended these investigations to include the evaluation of a series of fluorophosphate materials represented by the general formula $AMPO_4F$, where A is an alkali metal while M is a 3d transition metal [3]. The electrochemical activity in these materials is based on the reversibility and energetics of the M^{3+}/M^{4+} redox couple. These advanced materials are considered suitable for application in both lithium-ion and sodium-ion batteries.

The representative fluorophosphate compounds $LiVPO_4F$ and $NaVPO_4F$ were prepared by a simple incorporation reaction involving vanadium (III) phosphate, VPO_4 and the appropriate alkali fluoride. These materials crystallize with a triclinic structure. The electrochemical properties of the active materials were evaluated using a combination of constant current cycling and Electrochemical Voltage Spectroscopy (EVS). The electrolyte comprised either a 1M $LiPF_6$ solution in ethylene carbonate/dimethyl carbonate (2:1 by weight) or a solution of 1 M $NaClO_4$ in EC/DMC (2:1 by weight).

Figure 1 shows typical first cycle performance data for a $Li//NaVPO_4F$ cell collected at a charge-discharge current density of $\pm 0.2 \text{ mA/cm}^2$. The low level of voltage hysteresis in the figure is indicative of the small overvoltage associated with the alkali ion insertion reactions. Detailed performance characteristics of prototype carbon/ $NaVPO_4F$ sodium ion cells will be presented and discussed.

Preliminary evaluation of the $LiVPO_4F$ material indicates a reversible specific capacity close to 120 mAh/g. Elevated temperature testing suggests that the extraction process yields the novel de-lithiated phase, VPO_4F . The EVS data shown in Figure 2 reveal a structured voltage response for the lithium extraction process, characterized by two well-defined peaks in the differential capacity profile. The corresponding discharge process, centered at around 4.19 V vs. Li, indicates a two-phase insertion mechanism coupled to phase nucleation behavior. Data will be presented that suggest that $LiVPO_4F$ may be a candidate replacement for the commercial lithium-ion materials $LiCoO_2$ and $LiMn_2O_4$.

References:

- [1] J. Barker and M.Y. Saïdi, US Patent 5,871,866 (1999).
- [2] A. K. Padhi, N.S. Nanjundaswamy, C. Masquelier and J.B. Goodenough, *J. Electrochem. Soc.* 144, 2581 (1997).
- [3] J. Barker, M.Y. Saïdi and J. Swoyer, US Patent Application.

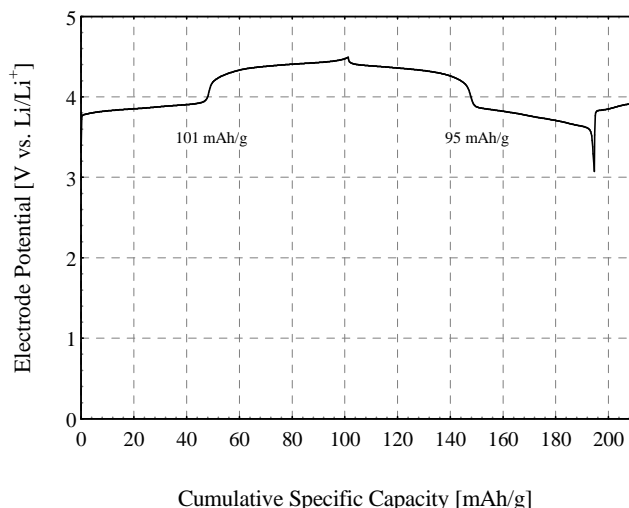


Figure 1: Constant Current Voltage Profile for a representative $Li//NaVPO_4F$ cell cycled between 3.00 – 4.40 V.

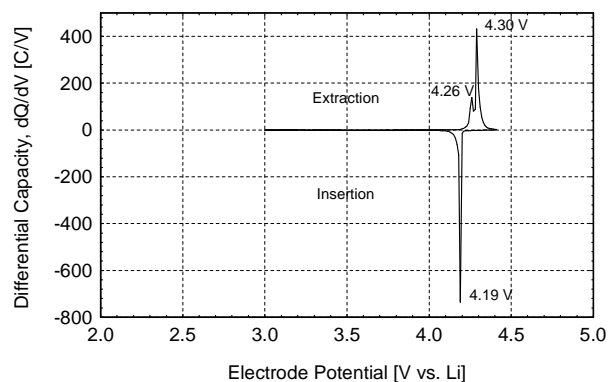
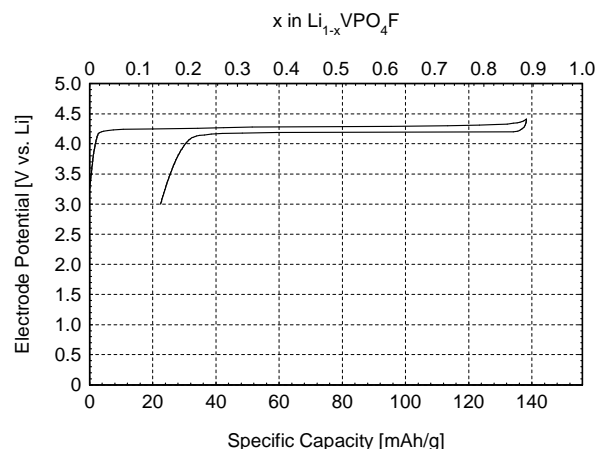


Figure 2: EVS Voltage Curve and Differential Capacity Profile for a representative $Li//LiVPO_4F$ cell cycled between 3.00 – 4.40 V.