**Lithium Vanadium Phosphate as a viable cathode for Lithium-ion Batteries**

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Transition metal oxides and chalcogenides with layered and three-dimensional frameworks have been the focus of a wide development effort as cathodes for lithium rechargeable batteries [1-3]. Recently, considerable study has also been given to lithium conducting phosphates and materials based on these compounds [4,5]. Their structural types allow for various isomorphous replacements, which are of importance in increasing the concentration of lithium or selecting the optimal dimensions of the conductivity channels for example. A general study of phosphates, in particular vanadates with the general formula $Li_3M_2(PO_4)_3$ will be presented. Such framework structures containing an interconnected interstitial space are potentially fast ionic conductors, especially if the energetically equivalent sites are connected. The substitution of the larger poly-anion in a open three dimensional framework helps to stabilize the structure and the 3D tunnel network and allows for fast ion migration. Furthermore, anion substitution can alter the voltage through two effects; the first is an inductive one due to changes in the metal ion energy levels because of the changed anion group. The second effect is possibly achieved by providing fewer or more electrons, thereby shifting the lithium concentration at which a given redox reaction takes place.

Previously, we have shown that 2 lithiums could be reversibly inserted into $Li_xV_2(PO_4)_3$ over the range 3-4.3V [6]. It has also been shown that the third lithium could be extracted at a relatively higher voltage[7,8]. Because of the energetics involved, the inercalation-extraction reactions exhibit an interesting profile whereby a single phase behavior is observed upon discharge for the composition, $V_2(PO_4)_3$ $Li_2V_2(PO_4)_3$, Fig. 2

Although, the reversibility when extracting the third lithium is less efficient, overall, the cycling characteristics in the full composition range is very good for rocking-chair cells @ C/2 rate with 20mg/cm$^2$ active material loading., Fig. 3. The rate capability of $Li_xV_2(PO_4)_3$ has also been found to exceed that of $LiCoO_2$ and capacity retentions greater than 70% have been achieved for 300mAh lithium ion cells at rates as high as 10C (23C), Fig.4.

**References:**

[1] S. Megahed, B. Scrosati, *J. Power Sources* **51,** 79 (1994)

[2] M. Armand in: *Materials for Advanced Batteries*, eds. D.W. Murphy, J. Broadhead and B.C.H. Steele (Plenum Press, NY, 1980. p145)

[3] R. Koksbang, J. Barker, H Shi, MY Saidi, *Solid State Ionics*, **84,** 1 (1996).

[4] S. Okada, K.S. Nanjundaswamy, A. Manthiram, J.B. Goodenough, H. Arai and J. Yamaki, *Proc. of 36th Power Sources Conf*., 110 (1994).

[5] A.B. Bykov, A.P. Chirkin, L.N. Demyanets, S.N. Doronin, *Solid St. Ionics*, **38,** 31 (1990).

[6] J. Barker, MY Saidi, *US Patent* 5,871,866

[7] L.F. Nazar, H. Huang, S.C. Yin and T. Kerr
IMLB meeting abstracts (#212), 2002

[8] M.Y. Saidi, J. Barker, H. Huang, J. Swoyer and G.Adamson, *J. Power Sources* (in press) 2002

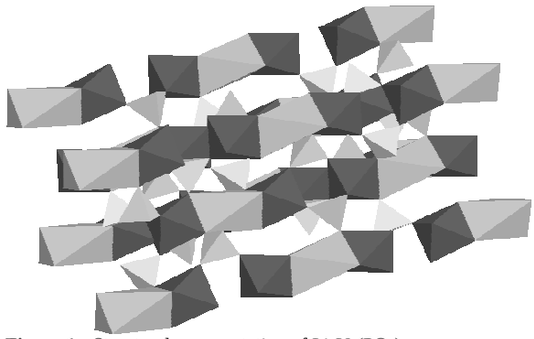

**Figure 1:** Structural representation of $Li_3V_2(PO_4)_3$

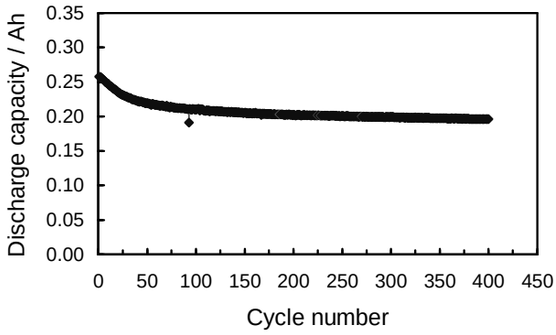


**Figure 2:** Cycling for $Li_3V_2(PO_4)_3$ based Li-ion batteries (C/2 , 20 mg/cm$^2$ active material loading).

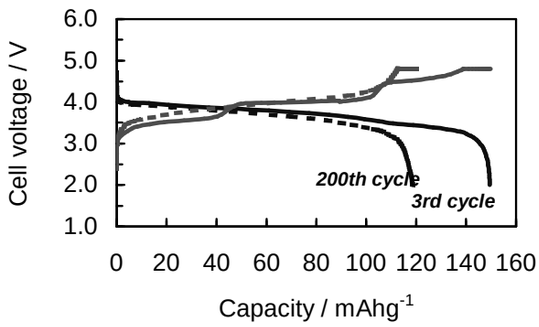


**Figure 3:** Voltage Profile for $Li_{3+x}V_2(PO_4)_3$ Rocking chair batteries cycled between 2.0–4.80V.

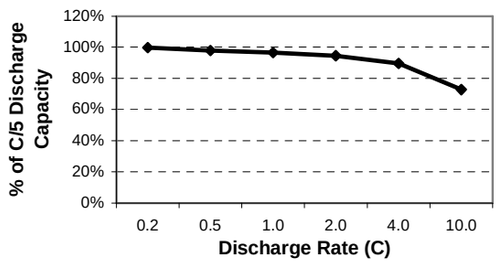


**Fig. 4:** Rate capability performance of $Li_{3+x}V_2(PO_4)_3$ lithium-ion batteries.