Microporous Molybdenum-Vanadium-Based Oxide: a High Capacity Electrode Material for Rechargeable Lithium Batteries

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The microporous $Mo_{2.5+y}VO_z$ molecular sieve with seven-membered ring microchannels of corner-sharing MO_6 (M = $Mo^{5+/6+}$ or $V^{4+/5+}$) (see Fig.1) belongs to the family of isostructural MoVNbTeO compounds, which are very active, selective and by far the most promising oxidation catalysts for light alkanes.[1-4] Due to the large open channels along the crystallographic c-axis which can accommodate small guest molecules such as Li^+ ions, and the redox properties of this $Mo_{2.5+y}VO_z$ phase, we have investigated these materials as rechargeable intercalation electrodes with promise for application as the positive electrode in Li-based batteries.

Microcrystalline $Mo_{2.5+y}VO_z$ has been synthesized by hydrothermal reactions between ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and vanadyl sulfate $VOSO_4\cdot nH_2O$ and found to have a range of composition rather than a single composition as reported.[1-4] Figure 2 shows an SEM image of the rod-like $Mo_{2.5+y}VO_z$ crystals with the size of up to tens of microns in length and 200 nm in diameter. The electrochemical properties of the compound as a positive electrode material have been investigated by using Li metal as the negative electrode and 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) solution (1/1 by volume) as the electrolyte. The discharge/recharge behavior when a cell was cycled with a current density of 0.3 mA/cm^2 is shown in Fig. 3. According to our studies, it is found that when the cells are cycled between 1.5 and 3.9 V vs. Li/Li^+, the electropositive Li^+ species can be electrochemically inserted into the framework up to 6 Li^+ per formula unit and almost all the lithium can be extracted with minimal structural rearrangement (only 2% expansion of the cell volume.) We also describe the chemical lithiation and characterization of $Li_xMo_{2.5+y}VO_z$ ($0 < x \leq 6$) phases formed at room temperature by treatment with a solution of n-butyllithium. Unit cell dimensions for all the phases have been determined by powder X-ray analysis and are closely related to those of the parent $Mo_{2.5+y}VO_z$ phase with orthorhombic Pba2 symmetry. Lithium cells of $Mo_{2.5+y}VO_z$ are rechargeable and exhibit a reversible charge capacity exceeding 300 mAh/g making $Mo_{2.5+y}VO_z$ a potential positive electrode material for secondary lithium batteries.

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References

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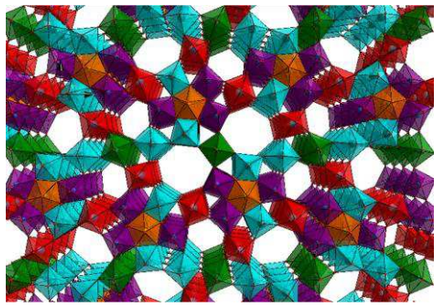

Figure 1. Structure of the $Mo_{2.5+y}VO_z$ framework projecting the cross-section of a rod-like crystal (a-b plane) showing large open channels that can accommodate Li^+ diffusion.

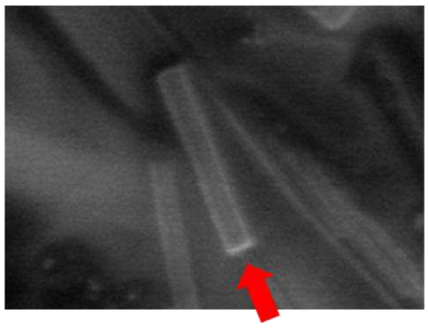

Figure 2. SEM image of the rod-like orthorhombic $Mo_{2.5+y}VO_z$ crystals (200 nm in diameter). Red arrow pointing along the length of the crystal which is the c direction.

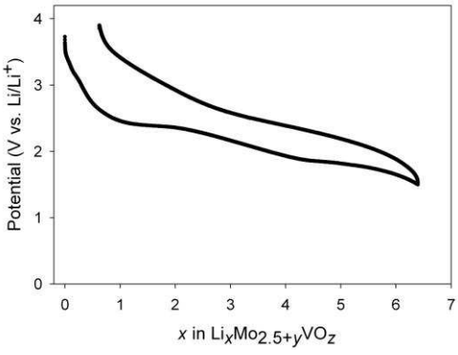

Figure 3. Voltage-composition profile of a Li/1 M $LiPF_6$, EC-DMC/$Mo_{2.5+y}VO_z$ cell when the cell was cycled with a current density of 0.3 mA/cm^2 (1st cycle).