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

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The microporous $\text{Mo}_{2.5+y}\text{V}_z$ molecular sieve with seven-membered ring microchannels of corner-sharing MO6 (M = Mo5+/6+ or V4+/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 $\text{Mo}_{2.5+y}\text{V}_z$ phase, we have investigated these materials as rechargeable intercalation electrodes with promise for application as the positive electrode in Li-based batteries.

Microcrystalline $\text{Mo}_{2.5+y}\text{V}_z$ has been synthesized by hydrothermal reactions between ammonium heptamolybdate (NH4)$_6$Mo$_7$O$_{24}$·4H$_2$O and vanadyl sulfate VOSO$_4$· nH$_2$O 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 $\text{Mo}_{2.5+y}\text{V}_z$ 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$^2$ (1st cycle) 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$_x$Mo$_{2.5+y}\text{V}_z$ (0 ≤ x ≤ 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 $\text{Mo}_{2.5+y}\text{V}_z$ phase with orthorhombic Pba2 symmetry. Lithium cells of $\text{Mo}_{2.5+y}\text{V}_z$ are rechargeable and exhibit a reversible charge capacity exceeding 300 mAh/g making $\text{Mo}_{2.5+y}\text{V}_z$ a potential positive electrode material for secondary lithium batteries.

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References


