

Short communication

Electrochemical performance of VOMoO₄ as negative electrode material for Li ion batteries

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Abstract

Polycrystalline samples of VOMoO₄ are prepared by a solid-state reaction method and their electrochemical properties are examined in the voltage window 0.005–3 V versus lithium. The reaction mechanism of a VOMoO₄ electrode for Li insertion/extraction is followed by ex situ X-ray diffraction analysis. During initial discharge, a large capacity (1280 mAh g⁻¹) is observed and corresponds to the reaction of ~10.3 Li. The ex situ XRD patterns indicate the formation of the crystalline phase Li₄MoO₅ during the initial stages of discharge, which transforms irreversibly to amorphous phases on further discharge to 0.005 V. On cycling, the reversible capacity is due to the extraction/insertion of lithium from the amorphous phases. A discharge capacity of 320 mAh g⁻¹ is obtained after 80 cycles when cycling is performed at a current density of 120 mA g⁻¹. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Graphite has been used as the negative electrode (anode) material in commercial lithium-ion batteries. Although it exhibits good reversibility with Li⁺, the main drawback is a low specific capacity (~370 mAh g⁻¹). The increasing energy demands of Li-ion batteries in electronic devices requires of higher performance and hence the need for materials that offer greater gravimetric and volumetric energy density. Towards this end, tin composite oxides (TCO) have been shown to be promising negative electrode materials [1]. The disadvantage with tin-based oxides is the formation of inactive Li₂O during initial discharge, which minimizes the energy density. On the other hand, the reversibility of Li₂O has been demonstrated in nanophase transitional metal oxides [2]. This has generated interest in the search for transition metal oxides as anode materials for Li-ion batteries. A great number of structurally different vanadates containing transition metals, such as LiMVO₄

(M = Ni, Co, Zn, Cu, Cd and Mg) [3–5], MVO₄ (M = Fe, Cr, In, Al, Y) [6], MV₂O₆ (M = Mn, Ni, Zn and Cd) [7,8], M₂V₂O₇ (M = Co, Ni, Zn and Cd) [4,8], M₃V₂O₈ (M = Ni, Zn) [8] have been explored as anode materials. Vanadium-based oxides react with large amounts of Li at low voltage, which leads to high specific capacities. Unfortunately, these materials exhibit poor capacity retention and also the reaction mechanism varies with composition and/or structure. For example, in LiMVO₄ (M = Ni, Co), X-ray absorption spectroscopy studies have shown that during initial discharge vanadium is reduced to the +2 oxidation state and the transition metal to the metallic state [9,10]. During charge, vanadium is oxidized to the +5 state, whereas the transition metal is not oxidized. On the other hand, Mössbauer spectroscopic studies of FeVO₄ have shown that nanoparticles of Fe metal that are formed during initial discharge are re-oxidized on charge [11]. For MnV₂O₆, the reversible capacity is enhanced with Mo substitution [12]. Several other molybdates, such as MoO₂ [13], solid solutions of MoO₂–SnO₂ [14], Na_{0.25}MoO₃ [15,16] and MMoO₄ (M = Mn, Cu, Ni, Zn, Fe and Ca) [17,18], CaMoO₄ [19] have also been examined as anode materials. The presence of two electrochemically active species, viz. V and Mo, in a single lattice can lead to high specific

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capacity. In this context, the mechanism of lithium insertion into LiVMO_6 has been reported [20]. The present study, involves an investigation of the electrochemical properties of the compound VOMoO_4 . Furthermore, the structural changes that accompany lithium insertion/extraction are evaluated by means of ex situ X-ray diffraction (XRD).

2. Experimental

The starting materials for the synthesis of VOMoO_4 are VO_2 and MoO_3 . The VO_2 was synthesized by heating stoichiometric amounts of V_2O_5 and V_2O_3 in an evacuated and sealed quartz tube at 800°C for 36 h with intermittent grinding. The resulting VO_2 was mixed with MoO_3 in a 1:1 mole ratio and pressed into pellets. The pellets were annealed in an evacuated and sealed quartz tube at 650°C for 2 days with intermittent grinding.

Powder X-ray diffraction patterns were recorded in the 2θ range $5\text{--}100^\circ$ (Cu $K\alpha$ radiation) by using a Philips X'pert diffractometer with Bragg-Brentano geometry. Rietveld refinement was carried out with the FULLPROF program.

For electrochemical studies, electrodes were fabricated by mixing the active material, acetylene black (Denka Singapore Pvt. Ltd) and polyvinylidene fluoride (PVDF) in a weight ratio of 75:15:10. *N*-Methyl-2-pyrrolidinone was added to the mixture to form a slurry, which was then spread on a stainless-steel foil and dried in an oven at 100°C for 12 h. Swagelok cells were fabricated in an Argon-filled glove-box (mBraun, Germany, <5 ppm H_2O) with a lithium foil (Aldrich) as the anode, Teklon (Anatek, USA) was employed as the separator and 1 M LiPF_6 in 1:1 EC + DMC (Chiel industries Ltd., Korea) as the electrolyte (EC = ethylene carbonate; DMC = dimethyl carbonate). Cells were allowed to equilibrate for 24 h at room temperature (RT). Charge–discharge cycling of the cells was performed at RT in a galvanostatic mode at 120 mA g^{-1} (Arbin battery cycling unit BT2000, USA). For ex situ XRD studies of the electrodes, the cells were discharged and charged to various states and then disassembled inside the glove-box. The XRD patterns were taken by covering the electrodes with a Mylar film to avoid exposure to air and moisture.

3. Results and discussion

The Rietveld refined powder XRD pattern of VOMoO_4 is presented in Fig. 1. The presence of sharp peaks indicates the formation of a well-crystalline phase. All the peaks are indexed on the basis of a tetragonal system with the space group $P4/n$. The refined lattice parameters are $a = b = 6.6110(5)\text{ \AA}$ and $c = 4.2675(4)\text{ \AA}$. The values match well with those reported by Eick and Kihlberg [21]. The inset of Fig. 1 shows the structure of VOMoO_4 viewed in the ab plane. In VOMoO_4 , vanadium and molybdenum are in the $4+$ and $6+$ oxidation states, respectively. The structure is built up of corner connecting VO_5 square pyramids and MoO_4 tetrahedra.

The electrochemical charge–discharge curves of VOMoO_4 are shown in Fig. 2(a). The corresponding differential capacity plots are presented in Fig. 2(b). The initial discharge curve reveals a sharp drop in voltage to 1.2 V, followed by two

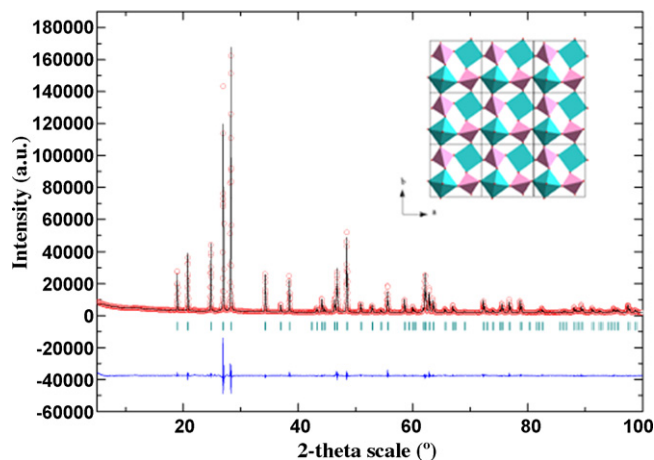


Fig. 1. Rietveld refinement pattern of powder X-ray diffraction data for VOMoO_4 . Inset shows crystal structure of VOMoO_4 .

plateaux at 0.5 and 0.2 V. The plateau at 0.5 V corresponds to the reaction of 4.0 Li. On complete discharge to 0.05 V, ~ 10.3 Li are reacted and this corresponds to a capacity of $\sim 1230\text{ mAh g}^{-1}$. During charge, no plateau is observed, and

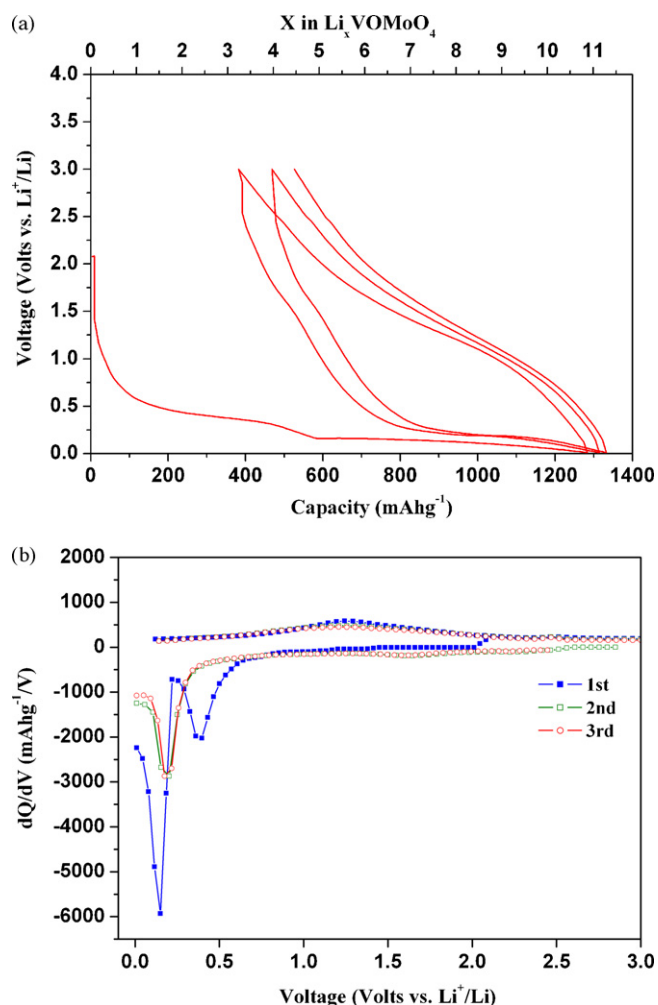
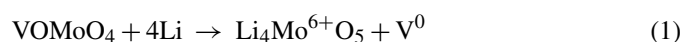


Fig. 2. (a) Charge–discharge profiles of VOMoO_4/Li cell and (b) differential capacity plots of VOMoO_4 electrode for first 3 cycles.

the voltage gradually increases to 3.0 V (cut-off voltage) with large polarization. The initial charge capacity is 880 mAh g^{-1} , which indicates the extraction of 7.5 Li. The plateau developed in the charge–discharge curves can be clearly seen in the differential capacity plots (Fig. 2(b)). During the second discharge, the plateau at $\sim 0.5 \text{ V}$ disappears, which is clearly evident from the differential capacity plots. This indicates that the reaction mechanism of VOMoO_4 with Li during initial discharge is different from that on subsequent cycling.

To investigate the structural changes during lithium insertion/extraction, ex situ XRD patterns were obtained for the electrodes at various stages of charge/discharge (Fig. 3). The XRD pattern (Fig. 3(b)) taken after the reaction of one Li with VOMoO_4 shows no change in the peak positions compared with the parent phase (Fig. 3(a)). This indicates that there is no intercalation of Li into the structure. Also, the attempts to intercalate Li by using *n*-BuLi proved not to be successful. Further reaction of Li results in the appearance of new peaks, which are marked as asterisk (*) in Fig. 4(c). The peaks are characteristic of the Li_4MoO_5 phase and are indexed based on the JCPDS card number 33-0806. In addition to the Li_4MoO_5 phase, weak reflections which correspond to an unidentified phase are observed at lower 2θ (Fig. 3(c and d)). The intensity of the peaks for the parent phase gradually decrease with simultaneous increase in the intensities of peaks for the Li_4MoO_5 phase. The peaks due to the VOMoO_4 phase completely disappear after reaction of 4Li (end of first plateau). Thus, it is concluded that the initial discharge capacity is mainly due to the reduction of V^{4+} with simultaneous formation of the Li_4MoO_5 phase that can be written as follows:



Recently, the formation of crystalline intermediate phases, such as Li_2MoO_4 and Li_2MoO_3 have been identified during the electrochemical lithiation of CuMoO_4 and ZnMoO_4 , respectively [17]. On further discharge of VOMoO_4 to a lower voltage,

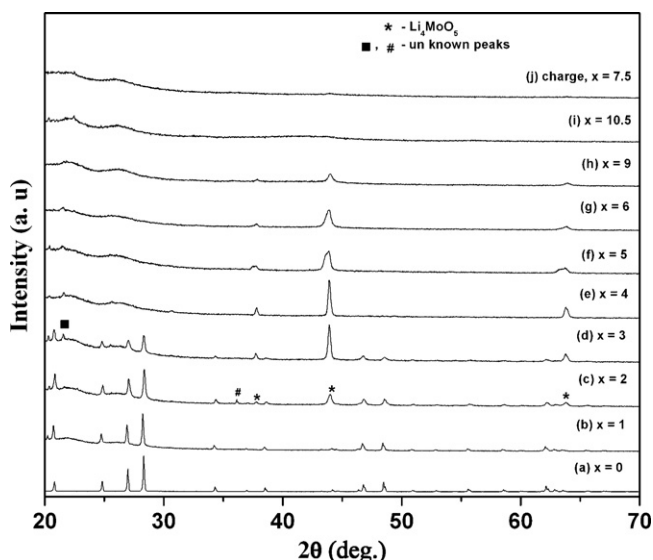


Fig. 3. Ex situ XRD patterns of $\text{Li}_x\text{VOMoO}_4$ electrode during initial cycle at different Li content (*x*).

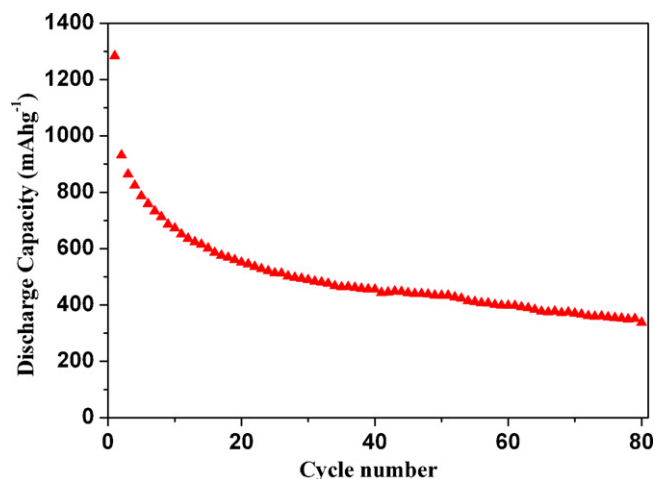
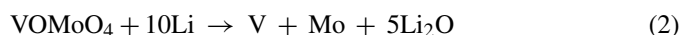


Fig. 4. Cycling performance of VOMoO_4/Li cell.

the observed capacity is due to the reaction of Li with Li_4MoO_5 (corresponds to second plateau). This leads to a gradual decrease in the intensities of the peaks corresponding to the Li_4MoO_5 phase and, consequently, the compound becomes amorphous on discharge to 0.005 V. The irreversible transformation of crystalline vanadates and molybdates to amorphous phases on discharge is known in the literature [6, 11, 16, 18]. After subtracting the capacity due to acetylene black, the amount of Li reacted at the end of initial discharge is $\sim 10.3 \text{ Li}$, which is as expected according to reaction (2), i.e.



During charge, Li^+ is extracted from Li_2O and consequently MO_x ($\text{M} = \text{Mo}, \text{V}$) may form. The observed large polarization in voltage is typical for this type of conversion reaction. Also, the high initial charge capacity (7.5 Li) suggests that both V and Mo species become oxidized during initial charge. Careful studies using X-ray absorption spectroscopy are necessary to determine the oxidation states of V and Mo after initial charge. The XRD pattern of the fully charged electrode is amorphous (Fig. 3(j)). Thus, during subsequent cycling, lithium is extracted/inserted from amorphous phases.

The cycling behaviour of a VOMoO_4/Li cell during the first 80 cycles is given in Fig. 4. A large irreversible capacity loss of 350 mAh g^{-1} occurs for the first cycle. During the first 20 cycles, the capacity fades rapidly, but this effect is less pronounced on further cycling. A discharge capacity of 320 mAh g^{-1} is observed even after 80 cycles. Since the conversion efficiency of Li_2O and M to MO_x and Li is dependent on both the nature and the size of the M particles, the initial particle size of VOMoO_4 may also play a crucial role in determining the rapid fading of capacity during initial cycles. In the present case, it is expected that the reversible capacity can be improved by decreasing the size of the VOMoO_4 particles.

4. Conclusions

VOMoO_4 has been explored as an anode material for Li-ion batteries. During initial discharge, ex-situ XRD patterns show

the conversion of VOMoO_4 to a crystalline intermediate phase Li_4MoO_5 , which transforms irreversibly to amorphous phases, viz. Li_2O , Mo and V. The initial charge capacity corresponds to extraction of ~ 7.5 Li, which suggests the extraction of lithium from Li_2O resulting in the partial oxidation of both vanadium and molybdenum. Although VOMoO_4 exhibits a high discharge capacity of about 320 mAh g^{-1} , even after 80 cycles, the irreversible capacity loss during initial cycles and large polarization limits its application in Li-ion batteries.

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