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Synthesis and electrochemical analysis of $AlVMoO_7$ oxide prepared via sol–gel method

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Abstract. In this study, $AlVMoO_7$ phase was fruitfully synthesized by sol–gel method and investigated as electrode material. The role of trivalent cation Al on the position of V and Mo redox couples in a three-dimensional framework of $AlVMoO_7$ promoted us to use this compound. The electrochemical insertion of Li in this phase was characterized by both solid solution and two-phase regimes. In the voltage range of 3.2–1.5, the first cycle discharge capacity value was found to be 310 mAh g^{-1}. It showed very good capacity of 180 mAh g^{-1} even after 20 cycles.

Keywords. 3D structure; $AlVMoO_7$; electrochemical Li insertion.

1. Introduction

Polyanionic compounds are more favourable as positive electrode materials than the currently used ones, owing to their superior electrochemical features, environmental easiness and low-cost for lithium batteries (layered $LiCoO_2$ and spinel $LiMn_2O_4$) [1]. Among these compounds, olivine $LiFePO_4$, amorphous $FePO_4$ and nasicon $Li_3Fe_2(PO_4)_3$ were broadly studied [1]. The phosphate $(PO_4)^{3-}$ framework present in these compounds acts as the structural stabilizer during the electrochemical reactions. The specific capacity of these electrodes is limited due to the electrochemical inertness of these electrodes compared to the vanadium- and molybdenum-based polyanions [2]. The vanadium- and molybdenum-based polyanions provide numerous metal oxidation states, structural stability as well as a high theoretical specific capacity which could be replaced by phosphate- and sulphate-based polyanion groups. These oxides were recognized as positive electrode materials [2–7]. Based on the advantages associated with them, the present work was focussed on polyanion compound $AlVMoO_7$, which contains both vanadium and molybdenum as electroactive species.

There are several studies on vanadium- and molybdenum-based oxides in the literature. Vanadium containing phases, such as VO_2 (B), V_2O_5, V_6O_{13}, LiV_3O_8 and $LiNaV_2O_5$ were found to show superior electrochemical properties [8–16]. It is feasible to insert reversibly about 2.2 Li per molybdenum in molybdenum oxides [17]. Molybdenum-containing compounds exhibit a large reversible capacity when employed as negative electrodes [18–23]. Based on all these observations, it is concluded that vanadium- and molybdenum-containing oxides offer better electrochemical activity due to V and Mo in contrast to phosphates and sulphates. MoV_2O_8, brannerite-type $LiVMoO_6$ and $VoMoO_4$ were recently explored for lithium insertion [24–26].

$AlVMoO_7$ crystallizes in the orthorhombic system and the structure is composed of corner-shared tetrahedral polyanionic groups. It forms isolated edge-shared Al_2O_{10} octahedral dimers when coordinated to Al^{3+} (figure 1). The columns of both edge-shared Al_2O_{10} octahedral dimers and corner-shared $(Mo/V)_2O_7$ tetrahedral clusters run parallel to the *c*-axis. These columns share the corners to form a three-dimensional network. One oxygen per formula unit [O (1)] is bonded to one Mo/V atom forming (Mo/V) = O oxo-linkage [27].

The present work investigates electrochemical insertion of lithium on a sol–gel synthesized $AlVMoO_7$ sample. The redox couples of V/Mo and the cavities present in the structure were investigated to determine the facile insertion/extraction of Li in $AlVMoO_7$.

2. Experimental

2.1 *Synthesis*

2.1a *Sol–gel synthesis (SG)*: In SG synthesis method, MoO_3 powder (Cerac, 99.9%) was dissolved in a mixture of 40 ml of 30% H_2O_2 and 10 ml of NH_4OH, resulting in a clear solution (A). Since the reaction is exothermic; it was carried out in an ice bath. NH_4VO_3 was dissolved in hot water and subsequently, $Al(NO_3)_3$ was added to this solution (B). A solution of citric acid at 3:1 molar ratio was added to a mixture of solutions A and B under constant stirring; this led to the formation of a sol and then ethylene glycol was added to this for gel formation. After stirring for 5 h, a transparent gel was obtained. The gel was decomposed by heating at 90°C

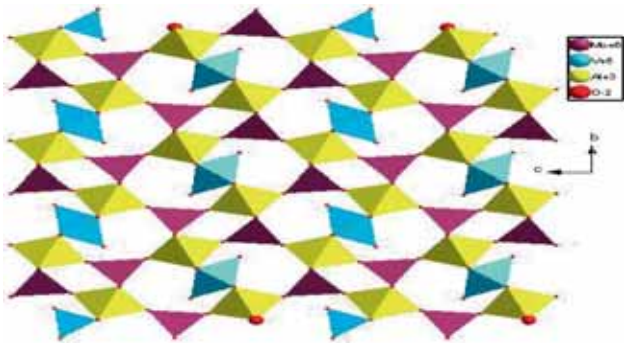

Figure 1. Crystal structure of $AlVMoO_7$ along bc-plane [27].

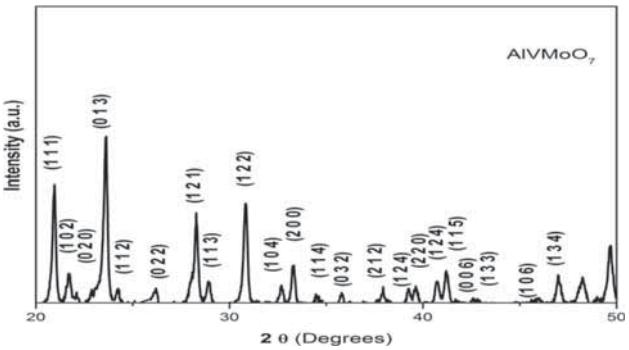

Figure 2. PXRD pattern of $AlVMoO_7$.

for 12 h. The final heat treatment for the compound $AlVMoO_7$ was 550°C for 12 h.

2.2 *Characterization*

Powder X-ray diffraction patterns (PXRD) were analysed using a Rigaku MiniFlex X-ray diffractometer with CuK_α radiation. The morphology of the sample was analysed using scanning electron microscope (SEM, FEI Quanta 200). Galvanostatic charge/discharge cycling was determined using an Arbin battery cycling unit (Arbin Instruments, BT 2000, USA). *Ex situ* XRD characterization was carried out by using Rigaku miniflex X-ray diffractometer in the 2θ range of 10°–70°.

The Swagelok cells (Swagelok India, Bangalore) were dismantled in the glove box. In addition to this, the electrodes were covered with a Mylar film and the obtained XRD patterns were used for the *ex situ* XRD studies. Swagelok cells were used to analyse electrochemical lithium insertion/extraction. The electrodes were fabricated by dispersing a blend of 70 wt% active material, 20 wt% acetylene black (Denka Singapore Pvt. Ltd.) with 10 wt% PVDF in N-methyl-2-pyrrolidinone on a stainless steel foil (as a disc of 14 mm diameter) and dried in an oven at 100°C for 12 h. An argon-filled glove box (mBraun, 120G, Germany) was used to assemble the Swagelok cells. Lithium metal (Aldrich, 99.9%) was used as the counter electrode and Teklon (Anatek, USA) as the separator. All the tests were performed using 1 M $LiPF_6$ dissolved in the mixture of 1:1 ethylene carbonate + dimethyl carbonate (Chile Industries Ltd., Korea) as the electrolyte. For the electrochemical experiments, the cells were equilibrated for 12 h at room temperature. *Ex situ* XRD description of the electrodes was processed in the 2θ range of 10°–70° by covering the electrodes with a Mylar film.

3. Results and discussion

3.1 *Phase formation*

The PXRD pattern of $AlVMoO_7$ is shown in figure 2. The pattern is indexed based on JCPDS file no. 89–0871 for

Table 1. Cell parameters for the three samples: $AlVMoO_7$, $Li_{0.5}AlVMoO_7$ and $Na_{0.5}AlVMoO_7$.

Lattice parameters	$AlVMoO_7$	$Li_{0.5}AlVMoO_7$	$Na_{0.5}AlVMoO_7$
a (Å)	5.3760(0)	5.3600	5.3760(0)
b (Å)	8.1600(1)	8.1580	8.1580(1)
c (Å)	12.7211(3)	12.7100	12.7100(3)
α (°)	90.000(1)	90.000(1)	90.000
β (°)	90.000	90.000	90.000(1)
γ (°)	90.000(2)	90.000(2)	90.000
Cell volume ($Å^3$)	558.1(2)	558.8(2)	555.6

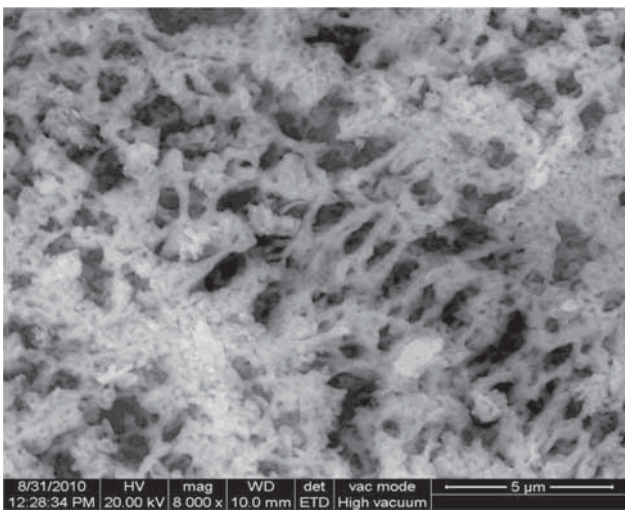

Figure 3. SEM micrograph of $AlVMoO_7$.

$AlVMoO_7$ and confirms that only a single phase is formed. The calculated lattice parameters are in agreement with those reported in earlier studies (table 1) [27]. Figure 3 presents SEM image of $AlVMoO_7$. The microstructure collaborates well with the final calcination temperature/time. The calcination temperature and time for $AlVMoO_7$ were significantly lower, thus, very porous structure was formed.

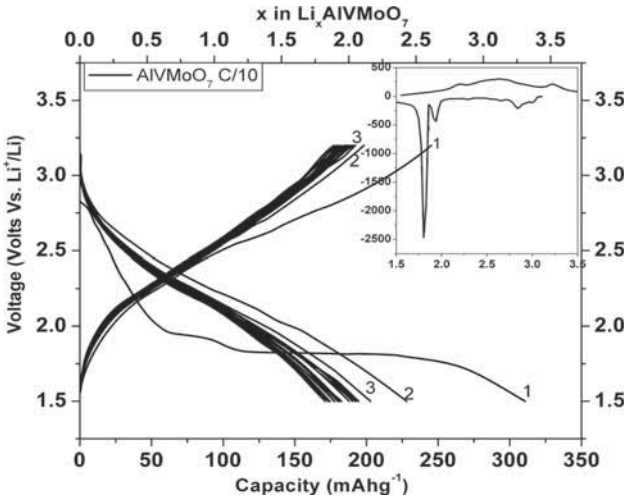

Figure 4. Electrochemical charge–discharge curves of $AlVMoO_7$. The inset shows the corresponding differential capacity plot (dQ/dV).

3.2 *Electrochemical studies*

3.2a *$AlVMoO_7$*: The voltage–capacity–composition profile of $AlVMoO_7$ *vs.* Li^+/Li cell and the corresponding differential capacity plot are shown in figure 4. The charge–discharge curves were obtained galvanostatically at C/10 rate (reaction of one Li in 10 h). During initial discharge, a drop in the voltage of the cell from the open circuit voltage of 3.1–3.07 V was noted. During the first discharge, the system showed the capacity of 310 mAh g^{-1}. This corresponds to the reaction of 3.3 Li per formula unit. The first charge capacity was found to be 245 mAh g^{-1} corresponding to the extraction of 2.6 Li. Three plateaus were observed at 2.8, 1.9 and 1.8 V in the differential capacity plot. However, the assignments of the plateaus will differ, if the phases contain both V and Mo in the same lattice. In MoV_2O_8, the major reduction progression was noted at 2.5–2 V, which could be attributed to both redox couples V^{5+}/V^{4+} and Mo^{6+}/Mo^{5+} [24] and in the case of $LiVMoO_6$, a single plateau at 2.4 V was observed attributable to the reduction of $Mo^{6+} \rightarrow Mo^{5+}$ and $V^{5+} \rightarrow V^{4+}$ [25]. Two clearly discernible plateaus were observed at about 2.1 and 1.7 V, which were attributed to Mo^{6+}/Mo^{5+}, Mo^{5+}/Mo^{4+} reduction in the case of $Ni_2(MoO_4)_3$ [28]. Thus, considering the literature reports, it can be concluded that the plateaus at 2.8 and 1.9 V can be attributed to the reduction of $V^{5+} \rightarrow V^{4+}$ and $Mo^{6+} \rightarrow Mo^{5+}$, respectively [24,25,28]. In addition, the plateau at 1.8 V can be attributed to the reduction of Mo^{5+}/Mo^{4+} [28]. Out of the 3.3 Li reacted during the first discharge in $AlVMoO_7$, the reaction of two Li can be attributed to the reduction of $V^{5+} \rightarrow V^{4+}$ and $Mo^{6+} \rightarrow Mo^{5+}$ and one Li can be ascribed to the reduction of Mo^{5+}/Mo^{4+} in the redox couple. The remaining 0.3 Li reacted was involved in the further partial reduction of V and Mo [24,25,28].

The PXRD patterns recorded on the parent electrode, as well as the electrodes discharged up to different cut-off voltages, are shown in figure 5. The intensity of the main peaks progressively decreased with the lithiation and fully disappeared after the discharge. After charging the electrodes, the Bragg peaks completely vanished in the PXRD patterns. An irreversible phase transformation into amorphous lithiated phases occurred during the first discharge. The occurrence of amorphization during the first discharge was reported for various vanadates and molybdates in several studies [29–32].

In $AlVMoO_7$ phase, Mo^{6+} and V^{5+} were found to exist in the tetrahedral coordination, whereas the reduced species in the lithiated phase, viz. Mo^{5+} and V^{4+}, appeared not favouring the tetrahedral coordination. They were found generally not accepting tetrahedral geometry as both Mo^{4+} or Mo^{5+} and V^{4+} were bigger in size. This indicates the loss of structural integrity as a function of lithium reaction, which leads to the observed fading of the capacity [28].

Ex situ PXRD patterns were recorded for the electrodes at various stages of lithium reaction to monitor the structural changes (figure 6). The reaction of 1.0 Li did result in any major changes in the PXRD pattern. However, upon reaction of 3 Li, an apparent change was seen in the PXRD pattern. The phase remained 'X-ray amorphous', even after a charge cycle [29–32].

The solid solution regime was more prevalent in the case of $AlVMoO_7$ (0.5 Li). We believe that 0.5 Li is inserted and the remaining is reacted in the case of $AlVMoO_7$. To prove that the insertion is feasible in this lattice, the chemical insertion of sodium into $AlVMoO_7$ phase was carried out using the reducing agent sodium azide (NaN_3). This alkali metal azide can decompose easily at elevated temperature to the alkali metal and nitrogen, and acts as an intercalating agent. The sodium intercalated phase, $Na_{0.5}AlVMoO_7$, was prepared by heating the stoichiometric amounts of NaN_3 and $AlVMoO_7$ in an evacuated and sealed quartz tube at 350°C for 6 h (in pellet form). The intercalated phase of $Na_{0.5}AlVMoO_7$ was characterized by PXRD, which showed a single phase, where all the reflections could be indexed on the basis of the orthorhombic unit cell with space group P mcn (62). The analysis of the PXRD patterns of $Na_{0.5}AlVMoO_7$ and $Li_{0.5}AlVMoO_7$ indicated that the orthorhombic structure of the parent $AlVMoO_7$ phase is retained and the lattice parameters are decreased slightly. The calculated lattice parameters are given in table 1 [27]. The chemical insertion experiment demonstrated that the structure is stable with the insertion of alkali in the extent of 0.5 per formula unit corroborating well with the solid solution behaviour observed from the voltage–capacity–composition curves. A constant specific capacity of 180 mAh g^{-1} was observed in $AlVMoO_7$ even after 20 cycles.

4. Conclusion

In this study, we determined the effects of electrochemical insertion of Li in $AlVMoO_7$. It was observed that the voltage corresponding to the redox couples V^{5+}/V^{4+} and Mo^{6+}/Mo^{5+} were significantly different for $AlVMoO_7$. It can

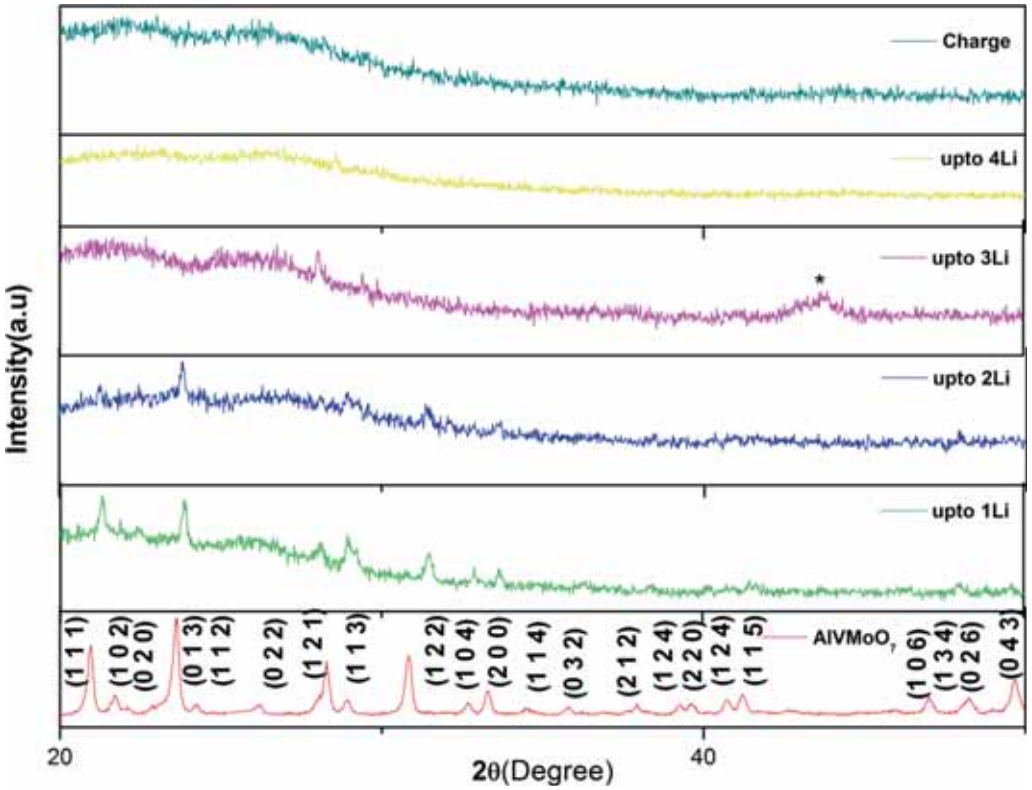

Figure 5. *Ex situ* XRD patterns of $AlVMoO_7$: (**a**) before discharge, up to (**b**) 1 Li, (**c**) 2 Li, (**d**) 3 Li, (**e**) after the first discharge and (**f**) after the first cycle.

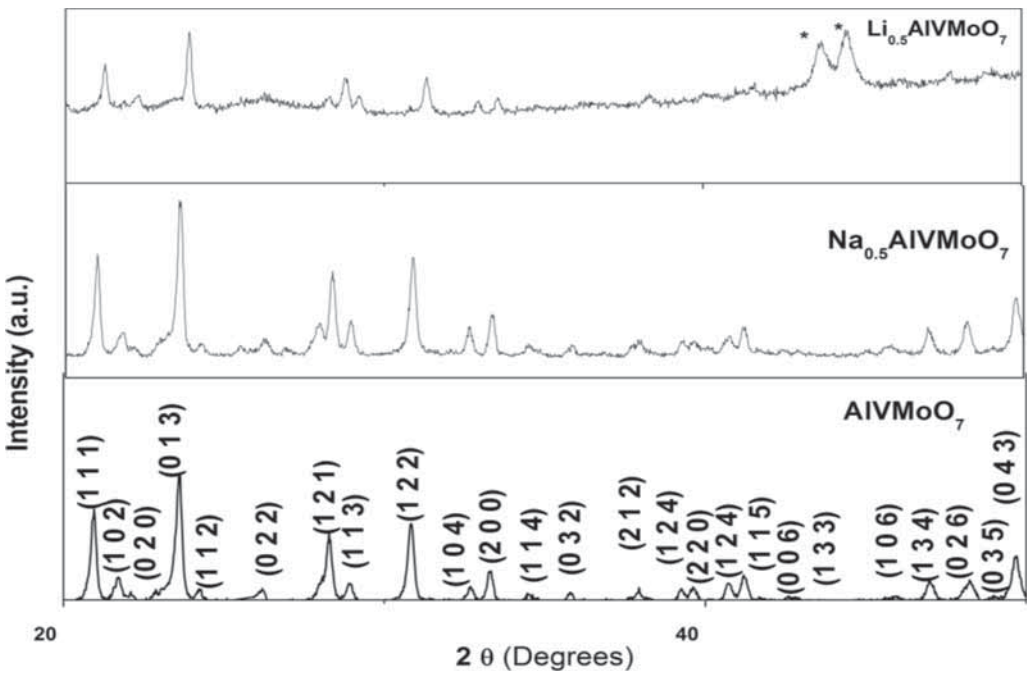

Figure 6. PXRD patterns of $AlVMoO_7$: after (**a**) 0.5 Na and (**b**) 0.5 Li.

be affirmed that sodium insertion is also possible in the lattice up to 0.5 Na. $AlVMoO_7$ can accommodate 3.3 Li per formula unit, of which the reaction of 2.6 Li only is reversible. The results of cycling studies showed that the $AlVMoO_7$ phase exhibits a reversible capacity of 180 mAh g^{-1} without any noticeable fading even after 20 cycles. The reversibility of Li reaction was more facile in $AlVMoO_7$.

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