REGULAR ARTICLE

Electrochemical study of two structurally related compounds FeVMoO₇ and CrVMoO₇ synthesized by sol–gel method

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Abstract. FeVMoO₇ and CrVMoO₇ phases were synthesized by sol–gel method for the first time and used as promising cathode materials for Lithium ion batteries. Effortless and flexible procedure for the preparation of FeVMoO₇ and CrVMoO₇ via a facile sol–gel method was developed. The structure, morphology and the electrochemical properties have been studied by X-ray diffraction (XRD), scanning electronic microscope (SEM) and galvanostatic charge-discharge test measurements. Study of these compounds as electrode materials was motivated by the three-dimensional structure and the redox couples of Fe, V and Mo. The first cycle discharge capacity values for FeVMoO₇ and CrVMoO₇ phases were 284 mAhg^{−1} and 264 mAhg^{−1}, respectively, in the voltage range of 3.2–1.5 V. The discharge capacity of FeVMoO₇ was 160 mAhg^{−1} after 20 cycles.

Keywords. 3D structure; FeVMoO₇; CrVMoO₇; electrochemical Li insertion; Li batteries; polyanions.

1. Introduction

Vanadates/Molybdates are extensively used as catalysts for selective oxidation of hydrocarbons. Numerous polyanionic compounds have been considered as alternatives to the positive electrode materials, layered LiCoO₂ type and spinel LiMn₂O₄, for Lithium batteries.¹ Vanadate and molybdate groups behave structurally like PO_x and SO_x polyanions. But vanadium and molybdenum are electrochemically active, and therefore contribute to theoretical capacity when compared to sulphate and phosphate groups. These oxides have attracted attention as positive electrodes because of the possibility of using the redox couples of V/Mo and the three-dimensional structure.^{2–7}

Vanadium and Molybdenum oxides are well studied in the literature. Denis *et al.*, studied amorphous RVO₄ (R = In, Cr, Al, Y and Fe) as electrodes for lithium insertion.^{8–12} Transition metal vanadates show realistic capacity and enhanced cycling behavior compared to the pure vanadium oxides for lithium insertion.^{13–15} Capacity retention in iron vanadates such as FeVO₄, Fe₂V₄O₁₃ and Fe₄(V₂O₇)₃·3H₂O is good.¹⁶ Li₂MoO₃ and Li₄Mo₅O₁₂ are shown to exhibit interesting cycling capacities.^{17–21} Nasicon-type Li₂Ni₂(MoO₄)₃ and Li₂Co₂(MoO₄)₃, Fe₂(MoO₄)₃ have been tested as positive electrodes.^{2,22,23} Ternary oxides MMoO₄ (M = 3d

transition metal) have been studied as cathode materials but the capacity observed to fade in these compounds.³ Vanadium and molybdenum-based mixed oxides MoV₂O₈, bannerette-type LiVMoO₆, VoMoO₄ have been studied for lithium insertion.^{24–27} Positive electrode materials based on Mo–O and V–O polyanions have been investigated in order to obtain high capacity.^{24–27} In this article, we decided to explore FeVMoO₇ and CrVMoO₇ compounds as electrode materials for batteries.

FeVMoO₇ and CrVMoO₇ compounds crystallize in the triclinic system and both are isostructural.¹⁶ The structures consist of corner-shared tetrahedral anions of V and Mo in the form of V₂O₇ and Mo₂O₇. It is coordinated to Fe³⁺ or Cr³⁺ to form isolated edge-shared M₂O₁₀ octahedral dimers (M) (Figure 1). It would be exciting to compare the electrochemical behavior of the two structurally related compounds FeVMoO₇, CrVMoO₇ and the influence of trivalent cation such as Fe³⁺, Cr³⁺ on the structural and electrochemical properties of the corresponding FeVMoO₇ and CrVMoO₇ compounds.

2. Experimental

2.1 Sol–gel synthesis (SG)

In the SG synthesis method, a clear solution (A) was obtained by dissolving MoO₃ powder (Cerac, 99.9%) in a mixture of

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Figure 1. Crystal structure of FeVMoO₇ (and CrVMoO₇) along ab-plane.¹⁶

40 mL of 30% H₂O₂ and 10 mL of NH₄OH. It was carried out in an ice bath because the reaction is exothermic. NH₄VO₃ was dissolved in hot water. Fe(NO₃)₃ solution (B) was added to the above solution (A). A solution of citric acid was added to the mixed solution of A and B with constant stirring to acquire a sol. Citric acid to metal ion ratio was 3:1. 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 for 12 h. The final heat treatment data for the compounds FeVMoO₇, CrVMoO₇ is given in Table 1.

2.2 Characterization

Rigaku mini flex X-ray diffractometer (Cu K α radiation) was used to record the Powder X-ray diffraction (XRD) patterns. To study the morphology of the as-synthesized sample, a scanning electron microscope (SEM, FEI Quanta 200) was used. Galvanostatic charge/discharge cycling studies were carried out with an Arbin battery cycling unit (Arbin Instruments, BT 2000, USA). Swagelok-type cells were used to execute the electrochemical studies. Electrodes were made-up by spreading a mixture of 70 wt% active material, 20 wt% acetylene black (Denka Singapore Pvt. Ltd.) and 10 wt% PVDF using N-Methyl pyrrolidinon (NMP) as a solvent on a stainless steel

foil. Argon-filled glove box (mBraun, 120G, Germany) was used to assemble the Swagelok cells. The counter electrode and the separator used was Lithium metal (Aldrich, 99.9%), Teklon (Anatek, USA), respectively. The electrolyte used was 1M LiPF₆ in 1:1EC + DMC (Chile Industries Ltd., Korea). *Ex situ* XRD characterization of the electrodes was carried out by covering the electrodes with Mylar film in the 2 θ range 10–70°.

3. Results and Discussion

3.1 Phase formation

The powder X-ray diffraction patterns of FeVMoO₇ and CrVMoO₇ are shown in Figure 2. These patterns are indexed based on JCPDS file nos: 83-1054 for FeVMoO₇, 89-0856 for CrVMoO₇. In the case of CrVMoO₇, a minor secondary phase of Cr₂O₃ is observed (indicated in XRD pattern in Figure 2). Figure 3 presents the SEM images of FeVMoO₇ and CrVMoO₇. The morphology of the synthesized phases exhibit agglomerated particles with average particle size of 1 μ m.

3.2 Electrochemical studies

3.2.1 FeVMoO₇ The voltage-capacity-composition profile of Li vs. FeVMoO₇ cell and the corresponding differential capacity plot are shown in Figure 4. The differential capacity plots for the first five cycles are shown in Figure 5. The charge-discharge curves are obtained galvanostatically at C/10 rate (reaction of one Li per formula unit in 10 h). The value of the first discharge capacity observed is 284 mAhg⁻¹. It is equivalent to the insertion of 3.3 Li per formula unit of FeVMoO₇. An irreversible capacity loss of 1.1 Li is observed in the first charge-discharge cycle, leading to a reversible capacity of 2.2 Li (185 mAhg⁻¹). The difference can be attributed to irreversible insertion of Li⁺ or due to minor structural changes that take place during the lithium insertion.^{28–31} However, on further cycling, this cell shows a reversible capacity of 160 mAhg⁻¹. During the initial discharge,

Table 1. The final heat treatments for the compounds FeVMoO₇ and CrVMoO₇.

Compound	Calcination temperature (°C)	Calcination time (h)	Space group
FeVMoO ₇	550	12	Triclinic P-1
	650	18	
CrVMoO ₇	550	12	Triclinic P-1
	800	24

Figure 2. Powder X-ray diffraction patterns of FeVMoO₇ and CrVMoO₇(*Cr₂O₃).

Figure 3. SEM pictures of (a) FeVMoO₇, (b) CrVMoO₇.

the voltage of the cell drops from the open circuit voltage (OCV) of 3.43 V to 2.3 V. Consequently, a plateau is observed at around 2.24 V. vs Li⁺/Li. This plateau can be seen evidently from the differential capacity plot (Inset in Figure 4). The redox potential of the Fe³⁺/Fe²⁺

Figure 4. Electrochemical charge-discharge curves of FeVMoO₇. The inset shows the corresponding differential capacity plot (dQ/dV).

couple varies with the crystal structure and the nature of the polyanion. Reported values for Fe³⁺/Fe²⁺ couple in various materials built up from different polyanions range from 2.55 V in LiFeAs₂O₇³², 3 V in Fe₂(MoO₄)₃,³³ 3.4 V in LiFePO₄,³⁴ 2.4 V in Li₃Fe(MoO₄)₂ and 3.6 V in Fe₂(SO₄)₃.³⁵ The observed voltage in FeVMoO₇ is 2.24 V which exactly matches with the above previous reports. Therefore, the plateau at 2.24 V is due to the reduction of Fe³⁺/Fe²⁺.

The plateau at 2.4 V corresponds to the reduction of Mo⁶⁺/Mo⁵⁺, V⁵⁺/V⁴⁺ in both the compounds LiVMoO₆ and MoV₂O₈.^{25,26} Two clearly discernible plateaus were observed at about 2.1 and 1.7 V, which could be correlated to the reduction of molybdenum in the case of Ni₂(MoO₄)₃.³⁶ According to literature reports, the redox potentials of Fe³⁺/Fe²⁺ and Mo⁶⁺/Mo⁴⁺, V⁵⁺/V⁴⁺ are very close to each other

Figure 5. Differential capacity plot (dQ/dV) of FeVMoO_7 for the first five cycles.

(~ 2.24 V vs Li^+/Li).^{23,26} Based on all these literature reports, it can be concluded that the plateau at 2.24 V is due to the reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{V}^{5+}/\text{V}^{4+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$ redox couples.

Thus, of the 3.3 Li atoms reacted during the first discharge, the reaction of one Li can be attributed to the reduction of Fe^{3+} to Fe^{2+} and that of two Li can be attributed to the reduction of two atoms of $\text{V}^{5+}/\text{V}^{4+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$. The remaining Li reacted is attributed to the further partial reduction of Mo and V. These assignments are made based on literature reports.^{25–36}

The X-ray diffraction patterns are obtained for the parent electrode and the electrode discharged up to different cut-off voltages are shown in Figure 6. The major

intensity peaks progressively decreases with lithiation and the peaks disappeared entirely after complete discharge. When the discharged electrodes were charged, we could not detect the crystalline peaks. It signifies that an irreversible phase transformation into amorphous lithiated material occurred during the first lithium insertion. This occurrence of amorphization was reported earlier in a number of vanadates and molybdates.^{34–36} It is difficult to maintain the reduced oxidation state of Mo^{4+} or Mo^{5+} and V^{4+} or V^{5+} in the tetrahedral coordination. They do not adopt tetrahedral geometry. The cause for this is that both Mo^{4+} or Mo^{5+} and V^{4+} or V^{5+} are large in size. This could possibly lead to slow structural disintegration and result in the observed capacity fading.³⁶

The electrochemical study on FeVMoO_7 with a 3D structure shows that it can react with lithium leading to the phase $\text{Li}_{3.3}\text{FeVMoO}_7$. The reversibility of this phase is good, leading to a capacity 160 mAhg^{-1} even though the charge profile is significantly differing from the discharge profile.

3.2.2 CrVMoO_7 We have studied the electrochemical properties of CrVMoO_7 containing only two redoxable species. The voltage-capacity-composition profile of the CrVMoO_7 cell and the corresponding differential capacity plot are shown in Figure 7. The differential capacity plots for the first five cycles are shown in Figure 8.

Figure 6. *Ex situ* X-ray diffraction patterns of FeVMoO_7 . (a) before discharge, (b) up to 1Li, (c) up to 2Li, (d) after first discharge, and (e) after first cycle (*represents Mylar film which covers the electrodes).

Figure 7. Electrochemical charge-discharge curves of CrVMoO_7 . Inset shows the corresponding differential capacity plot (dQ/dV).

Figure 8. Differential capacity plot (dQ/dV) of CrVMoO_7 for the first five cycles.

The charge-discharge curves were obtained galvanostatically at C/10 rate (reaction of 1 Li per formula unit in 10 h). During the first discharge, a capacity of 264 mAhg^{-1} was observed. This corresponds to the reaction of 2.5 Li per formula unit. An irreversible capacity loss of 1.2 Li was observed after the first charge, leading to a reversible capacity of 1.3 Li (118 mAhg^{-1}). The first discharge consists of two distinct plateaus at around 2.32 V and 1.94 V vs Li^+/Li . The two plateaus can be clearly seen from the differential capacity plot (Figure 7, inset). The plateaus at 2.32 V and 1.94 V confirm the redox couples of $\text{V}^{5+}/\text{V}^{4+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$.^{25,26} Depending on the 3d transition metal ion, the redox couple value of other elements will change.³⁷ Thus, of the 2.5 Li reacted during the first discharge, reaction of two Li can be attributed to the reduction of two atoms of $\text{V}^{5+}/\text{V}^{4+}$ and $\text{Mo}^{6+}/\text{Mo}^{5+}$. The remaining 0.5 Li atom per formula unit can be attributed to the further partial reduction of $\text{V}^{4+}/\text{V}^{3+}$ and $\text{Mo}^{5+}/\text{Mo}^{4+}$.^{25,26,36} The *ex situ* XRD patterns were recorded on electrodes at various stages of lithium insertion to know the structural changes. The XRD pattern of the electrode discharged to 1.5 V and upon charge to 3.2 V indicated amorphous state except two main intensity peaks (Figure 9). A constant specific capacity of 160 mAhg^{-1} was observed in FeVMoO_7 even after 20 cycles. Capacity fading with cycle number was observed in the case of CrVMoO_7 *vis-à-vis* FeVMoO_7 even though the two phases are isostructural (Figure 10). Lower Capacity fading was

Figure 9. *Ex situ* X-ray diffraction patterns of CrVMoO_7 . (a) before discharge, (b) upto 1Li, (c) upto 2Li, (d) after first discharge, and (e) after first cycle (* represents Cr_2O_3).

Figure 10. Comparison of the capacity versus cycle number for the two samples, FeVMoO₇ and CrVMoO₇ at C/10 rate.

observed in FeVMoO₇ as the sintering temperature is low compared to CrVMoO₇.

4. Conclusions

Electrochemical Li insertion studies into FeVMoO₇ and CrVMoO₇ phases have been studied for the first time. These studies reveal that FeVMoO₇ accommodates 3.3 Li per formula unit of which reaction of only 2.2 Li is reversible. CrVMoO₇ accommodates 2.5 Li per formula unit of which reaction of only 1.3 Li is reversible. Sol-gel method was adopted, for the first time, to synthesize these phases and they exhibit good electrochemical behavior. The results of cycling studies show that the FeVMoO₇ phase exhibits a reversible capacity of 160 mAhg⁻¹ without any noticeable capacity fading even after 20 cycles.

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