

Study of lithium insertion into $\text{Me}^x\text{V}_2\text{O}_{5+x/2}$, Me = copper, iron or chromium

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Abstract

Transition metal vanadates, containing copper, iron or chromium, with the stoichiometry $\text{Me}^x\text{V}_2\text{O}_{5+x/2}$, where Me = Cu, Fe and/or Cr, and a monoclinic-brannerite structure were formed by thermal decomposition of hydrated metal vanadates ($\text{Me}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$) above 550 °C. Intercalation of lithium into composite electrodes containing a 85:10:5 mixture of $\text{Me}^x\text{V}_2\text{O}_{5+x/2}$, graphite and polytetrafluoroethylene gave initial specific capacities in the 0.4–0.7 Ah/g range to 1.0 V versus lithium (0.7–1.3 Wh/g). The specific capacity fade over the first few cycles was largely caused by structural changes taking place in the $\text{Me}^x\text{V}_2\text{O}_{5+x/2}$ structure. The capacity and reversibility of transition metal vanadates was related to the transition metal ion present in the order $\text{Cu} > \text{Cr} > \text{Fe}$. They had reasonable reversibility towards lithium intercalation with higher capacities compared to vanadium based oxides studied in the past. © 1997 Elsevier Science S.A.

Keywords: Lithium; Intercalation; Metal oxides; Vanadium

1. Introduction

Transition metal vanadates, such as copper vanadates, show promise for use in rechargeable lithium batteries [1–3]. These transition metal vanadates have a structure with tunnels in a three-dimensional framework in which lithium ions can move and reversibly intercalate Li^+ . The $\text{Me}^{\text{II}}\text{V}_2\text{O}_6$ vanadates (Me = Mg, Ca, Mn, Co, Ni, Zn, Cd), were found to have very poor electrochemical properties when compared with CuV_2O_6 [3]. These divalent metal vanadates are of interest because of their structural relationship to $\gamma\text{-MnO}_2$.

The good insertion capacity of CuV_2O_6 was because Cu^{2+} can be reduced to Cu^{1+} during Li insertion. Because Fe and Cr have (+III) as their most stable oxidation state and can be reduced to (+II) during Li insertion, it was expected that these metal vanadates would have better reversibility to Li insertion than the other metal vanadates examined previously [1–3]. For this reason, Cu, Fe, and Cr vanadates were thought to have potential as a reversible lithium intercalation electrode.

2. Experimental

The hydrated metal vanadates were prepared by a precipitation procedure similar to the formation of BiVO_4 [4,5].

After filtration, the air-dried precipitate was heated in a tube furnace at temperatures above 550 °C for 24 h. Electrodes were fabricated using a 85–10–5 wt.% mixture of metal vanadate, Ketjen black carbon and polytetrafluoroethylene (PTFE) binder, respectively. The composite electrodes with a surface area 0.8 to 2.0 cm^2 were pressed onto a 150 grid nickel or a stainless-steel mesh which provided conductive support.

The vanadates were examined by X-ray powder diffraction (XRD) (Scintag, XDS 2000), inductively coupled plasma spectroscopy (ICP) and chemical analysis. Capacity and reversibility to Li insertion of these composite electrodes were determined using galvanostatic or cyclic voltammetry methods at current densities from 0.5 to 2.0 mA/cm^2 . A flooded laboratory cell with Li anode and reference electrodes in 1 M LiClO_4 -propylene carbonate/ethylene carbonate (50:50) was used in a glove box.

3. Results and discussion

The hydrated metal vanadates, $\text{Me}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ where Me = Cu, Fe, or Cr, were prepared by a precipitation method, using metavanadate and a transition metal salt. The XRD pattern for the $\text{Cu}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ was semi-crystalline and has been shown in Ref. [5]. The air-dried Fe and Cr vanadates were both amorphous hydrated materials. ICP and chemical

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analysis confirmed the presence of Cu, Fe or Cr in the vanadate structure with a 1:2 Me/V stoichiometry. A precipitate with a mixture of the transition metals Fe and Cr in the vanadate was produced by using the two transition metal salts in the precipitation process. Results for one such electrode using a mixture of Fe and Cr in the ratio of 0.77:0.23 will be discussed below.

Cu, Fe or Cr vanadates have a $\text{Me}^{\text{IV}}\text{V}_2\text{O}_{5+\lambda/2}$ stoichiometry when the air-dried precipitate was thermally decomposed above 550 °C. The $\text{Me}^{\text{IV}}\text{V}_2\text{O}_{5+\lambda/2}$ formulation was used because, unlike brannerites such as CuV_2O_6 which have Me in the (+II) oxidation state, Fe and Cr have (+III) as their most stable oxidation state. Annealing the Fe and Cr vanadates above 550 °C will form an oxygen-rich material with a monoclinic-type structure and a $\text{FeV}_2\text{O}_{6.5}$ and $\text{CrV}_2\text{O}_{6.5}$ stoichiometry. The possibility of forming Fe and Cr materials which are less oxygen rich is presently being pursued. The XRD patterns were similar to those reported in the XRD database for CuV_2O_6 , $\text{CrV}_2\text{O}_{6.5}$ and $\text{FeV}_2\text{O}_{6.5}$. These annealed materials were of a less crystalline nature than the metal vanadates prepared by high-temperature synthesis.

3.1. Lithium intercalation in the transition metal vanadates $\text{Me}^{\text{IV}}\text{V}_2\text{O}_{5+\lambda/2}$

The discharge voltage plotted versus the specific capacity for Cu, Fe or Cr vanadates had average voltages from 1.7 to 2.3 V (versus Li) and initial specific capacities in the 0.4–0.7 Ah/g range for the active cathode material (Table 1). The transition metal vanadates $\text{Me}^{\text{IV}}\text{V}_2\text{O}_{5+\lambda/2}$ (Me = Cu, Fe or Cr) had a two tiered discharge voltage between 2.5 and 1.0 V with Cu vanadate having the highest specific capacity (Fig. 1). Fe and Cr vanadates had similar capacity to Li intercalation with less defined voltage plateaus than CuV_2O_6 . This was largely due to the less crystalline nature of Fe and Cr vanadates compared with Cu vanadate.

When the specific energy (Wh/kg) was plotted versus the specific capacity (Ah/kg), Cu and Fe vanadates had a higher initial specific capacity compared with other lithium intercalation metal oxide materials, see Fig. 2(a). The initial specific energy of $\text{Me}^{\text{IV}}\text{V}_2\text{O}_{5+\lambda/2}$ vanadates varied from 0.7 to 1.3 Wh/g. This was similar or higher than CuO (0.84 Wh/

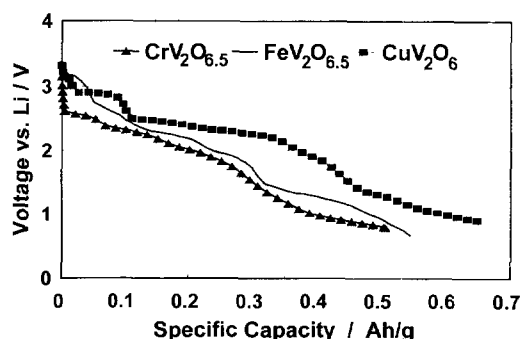


Fig. 1 Single discharge curves for the transition metal vanadates, $\text{Me}^{\text{IV}}\text{V}_2\text{O}_{5+\lambda/2}$ (Me = Cu, Fe or Cr), using constant current at current densities of about 1.0 mA/cm². Discharge voltage (vs. an Li reference electrode) plotted against the specific capacity from a known mass of active material, in the composite electrode, in 1 M LiClO_4 -organic solvent and a lithium counter electrode

g), $\text{Cu}_2\text{V}_2\text{O}_7$ (0.93 Wh/g) and the V_6O_{13} benchmarks for operation as a primary lithium cell.

3.2. Reversible Li intercalation of vanadates

Lithium insertion into these vanadates was expected to yield a reaction in which Cu, Fe or Cr was reduced, along with V, to give higher capacities compared with vanadium oxides studied in the past [5]. The $\text{Me}^{\text{IV}}\text{V}_2\text{O}_6$ vanadates (Me = Mg, Ca, Mn, Co, Ni, Zn, Cd), having a brannerite-type structure were found to have very poor electrochemical properties [3]. The good insertion capacity of CuV_2O_6 was because the Cu^{2+} ion can be reduced to Cu^{+} during Li insertion. The larger ionic radii of Cu ions in their reduced state may increase the interlayer spacing of the vanadate leading to improved Li intercalation [3]. Because Fe and Cr have (+III) as their most stable oxidation state and can be reduced to (+II) during Li insertion, it was expected that these metal vanadates would have better specific capacities and reversibility than the other $\text{Me}^{\text{IV}}\text{V}_2\text{O}_6$ metal vanadates, examined previously [3].

Specific energies were better than 1.0 Wh/g during the first ten cycles for CuV_2O_6 electrodes, Fig. 2(a). They were better than V_6O_{13} or $\text{Cu}_2\text{V}_2\text{O}_7$ [1], although at a slightly lower operating voltage of about 2.2 V, as shown in

Table 1

Summary of the specific capacity, specific energy and number of cycles to one half of initial capacity for the transition metal vanadates MeV_2O_x , (Me = Cu, Cr, or Fe) discharged at current densities of about 1.0 mA/cm²

Cathode material	Cutoff voltage (V)	Electrode mass (g)	Initial specific capacity (Ah/g)	Average discharge voltage (V)	Initial specific energy (Wh/g)	No. cycles (% of initial capacity)
CuV_2O_6	1.2	0.0228	0.560	2.20	1.23	10 (85%)
	0.9	0.0220	0.650	2.00	1.30	>6
$\text{FeV}_2\text{O}_{6.5}$	1.5	0.0288	0.316	2.25	0.71	8 (81%)
	0.8	0.0385	0.525	1.90	1.00	10 (50%)
$\text{CrV}_2\text{O}_{6.5}$	0.8	0.0200	0.433	1.80	0.78	15 (75%)
$\text{Fe,Cr,V}_2\text{O}_{6.5}$	1.0	0.0325	0.350	1.85	0.65	10 (71%)

$\lambda = 0.73$, $\lambda = 0.27$

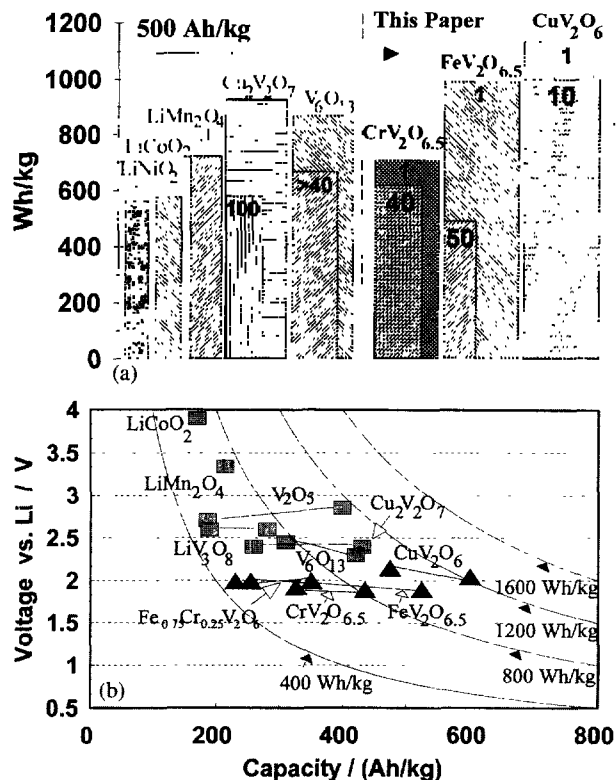


Fig. 2. (a) Specific energy plotted vs. the specific capacity of several Li intercalation oxides and $\text{Me}^{\text{V}}\text{V}_2\text{O}_{5+x/2}$, where $\text{Me} = \text{Cu}, \text{Fe}$ or Cr (500 Ah/kg scale shown). The number of cycles for the $\text{Me}^{\text{V}}\text{V}_2\text{O}_{5+x/2}$ vanadates is shown within each box. (b) Discharge capacity plotted vs. the average discharge voltage for (\square) several lithium intercalation transition metal oxides and (\blacktriangle) $\text{Me}^{\text{V}}\text{V}_2\text{O}_{5+x/2}$ ($\text{Me} = \text{Cu}, \text{Fe}$ and/or Cr).

Fig. 2(b), where the discharge capacity is plotted against the average operating voltage for a number of transition metal oxides. The $\text{FeV}_2\text{O}_{6.5}$ electrode, although initially about 1 Wh/g, faded rapidly to a lower capacity than the other transition metal oxides. $\text{CrV}_2\text{O}_{6.5}$ had the lowest initial specific energy of the three vanadates studied, but unlike its Fe analogue, did not lose its capacity as quickly and remained comparable, in specific energy, with the other metal oxides, see Fig. 2(a).

The $\text{Me}^{\text{V}}\text{V}_2\text{O}_{5+x/2}$ vanadate family has average discharge voltages in the 1.8–2.2 V range, with comparable performances with other metal oxides shown in Fig. 2(b). For CuV_2O_6 vanadate, slightly better specific energies were observed for the initial Li insertion and removal cycles. The specific capacity fade was largest over the first few cycles, and for $\text{FeV}_2\text{O}_{6.5}$ was as high as 50% in the first few cycles. The capacity fade was partly attributed to some loss of the pressed cathode material adhesiveness to the metal mesh substrate. But the major cause of capacity fade during initial cycling was the structural change taking place in the $\text{Me}^{\text{V}}\text{V}_2\text{O}_{5+x/2}$ electrode. The most dramatic changes occurred in Fe and Cr vanadates. Cyclic voltammograms of the three vanadates are shown in Fig. 3. Within the first two or three cycles, Fe or Cr vanadates became more amorphous and this was confirmed with XRD spectroscopy. Once the structural

change to an amorphous state was completed, the capacity fade dropped dramatically to about 0.6 to 0.8% per cycle. However, the discharge profile of Fe and Cr vanadates also changed due to the structural changes. An almost linear discharge curve developed in the 3–1 V range for these two materials, see Fig. 3.

In general, for the $\text{Me}^{\text{V}}\text{V}_2\text{O}_{5+x/2}$ vanadate family, the capacity and reversibility was related to the transition metal ion present. The structural stability for these vanadates was found to be $\text{Cu} > \text{Cr} > \text{Fe}$. These three vanadates showed

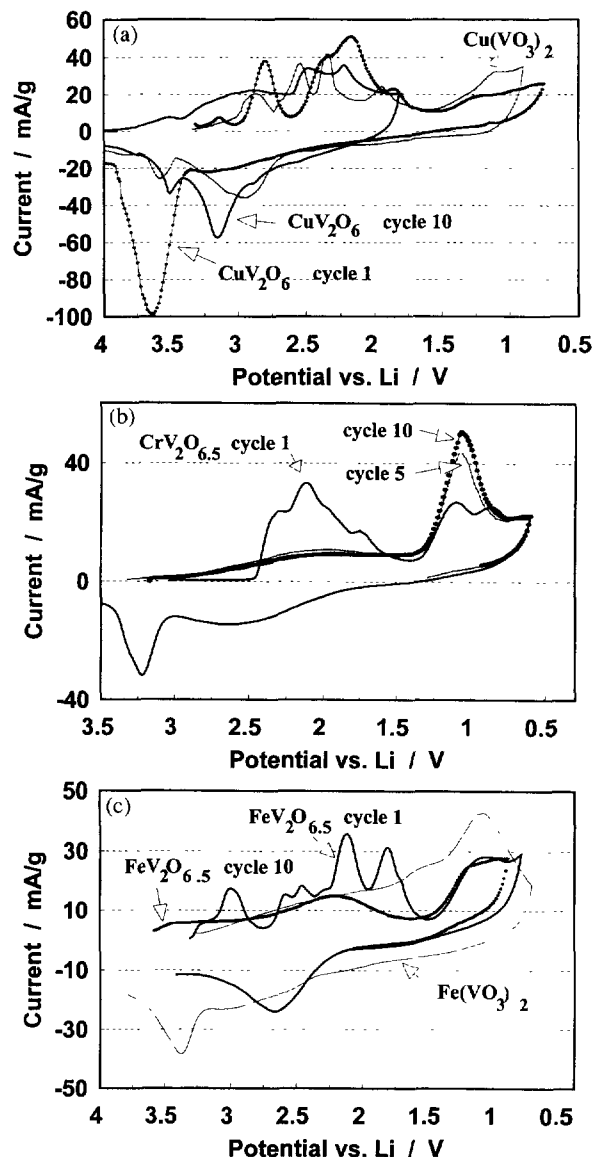


Fig. 3. (a) Cyclic voltammograms of Li insertion into the transition metal vanadates, CuV_2O_6 (cycle numbers 1 and 10), and the $\text{Cu}(\text{VO}_3)_2$ composite prepared below 200 °C. Discharge current (in mA/g active material) plotted vs. the voltage (vs. Li reference electrode) in 1 M LiClO_4 -organic solvent and an Li counter electrode in a glove box. The scan rate was 25 $\mu\text{V}/\text{s}$. (b) Cyclic voltammograms of the Li insertion into the transition metal vanadate, $\text{CrV}_2\text{O}_{6.5}$ (cycles numbers 1, 5 and 10) under conditions similar to Fig. 3(a). (c) Cyclic voltammograms of the Li insertion into the transition metal vanadate, $\text{FeV}_2\text{O}_{6.5}$ (cycles numbers 1 and 10) and the $\text{Fe}(\text{VO}_3)_2$ composite prepared below 200 °C under conditions similar to Fig. 3(a).

higher reversible capacity towards Li intercalation compared with the other $\text{Me}^{\text{II}}\text{V}_2\text{O}_6$ studied in the past [2,5]. The CuV_2O_6 transition metal vanadate gave higher capacities than other vanadium-based oxides, but the possibility of transition metal migration through the electrolyte to the Li anode, has been found to have a detrimental effect on cycle life [2,3].

4. Conclusions

The capacity and reversibility of transition metal vanadates are related to the transition metal ion present. The $\text{Me}^{\text{II}}\text{V}_2\text{O}_{5+x/2}$ electrodes where Me = Cu, Fe and Cr show reasonable reversibility towards Li intercalation, with specific energies comparable with other transition metal oxides proposed for Li rechargeable cells. The CuV_2O_6 electrodes

performed the best while the $\text{FeV}_2\text{O}_{6.5}$ and $\text{CrV}_2\text{O}_{6.5}$ electrodes underwent major structural changes in the first few cycles. As reversible materials for Li intercalation, it was unnecessary to anneal them above 500 °C as they readily convert back to their original amorphous form after several cycles.

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