



Study of $\text{Me}_x(\text{VO}_3)_2$ vanadates, (Me = Co, Ni, Mn, $1 < x < 2$) for lithium rechargeable cells

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Abstract

Transition metal vanadates, $\text{Me}_x(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$, where Me = Co, Ni, and Mn and $1.0 < x < 2.0$, were found to reversibly insert lithium. The efficiency of reversible insertion depended on both the transition metal present and the stoichiometric ratio of Me:V in the vanadate structure. The Ni and Co vanadates gave the highest specific capacities using lithium metal coin cells, with initial specific capacities above 0.7 A h/g (1.0 W h/g) when x is near 1.0. The operating voltage of these materials was in the range of 1.0 to 2.0 V. Lithium ion coin cells using LiCoO_2 coupled with the vanadates, were also examined. These were found to deliver about 200 mA h/g, with average voltages of 2.5 to 2.0 V for values of x from 1.1 to 1.2. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium insertion; Transition metal oxides; Vanadate; Vanadium oxide

1. Introduction

Transition metal vanadates have been studied in the past for use as cathode materials for lithium batteries [1–4]. Despite a favourable structure, such as the monoclinic-brannerite structure of $\text{Me}^{\text{II}}\text{V}_2\text{O}_6$ (Me = Mg, Ca, Mn, Co, Ni, Zn, or Cd), these materials had poor electrochemical properties. The $\text{Me}(\text{VO}_3)_2$ materials, prepared using low-temperature synthesis techniques, were found to have good initial specific capacity average operating voltages in the range of 1.4 to 2.3 V [4]. They worked well for a lithium primary cell application, yielding over 1.5 W h/g, which is one of largest specific capacities for a vanadate material however, for a rechargeable application, they displayed significant capacity fading over the first few cycles. This limited their practical use in rechargeable lithium cells, since a higher specific capacity is needed to offset the low operating voltage of around 1.5 V. Recent work on high specific capacity MeVO_4 [5] anode materials which has prompted examination of the $\text{Me}_x(\text{VO}_3)_2$ type of materials for rechargeable application. A range of materials with different Me:V ratios was produced by using either precipitation or electrodeposition techniques. By discharging

these hydrated $\text{Me}_x(\text{VO}_3)_2$ vanadates to lower voltages than is normal, between 1.0 V and 0.4 V, usable reversible capacity of up to 400 mA h/g was obtained for some materials. Electrochemical performance was evaluated for different transition metals and various ratios of x from $1.0 < x < 2.0$. The most promising electrode was a cobalt based vanadate with a value of x in the range of 1.05 to 1.20.

2. Experimental

2.1. Precipitation method

Stock solutions used for materials preparation were 0.05 M and 0.1 M NH_4VO_3 and 0.5 M solutions of the transition metal nitrates, $\text{Me}(\text{NO}_3)_2$ where Me = Co, Ni, or Mn. The preparation of transition metal vanadates using the precipitation method has been described elsewhere [6]. The $\text{Me}(\text{NO}_3)_2$ was added to NH_4VO_3 to produce Me:V molar ratios in the range of 1:2 to 1:1. The mixtures were heated at 80°C for several hours and the precipitated material was collected and washed with distilled water, then allowed to dry in an oven overnight at 70°C. Some variations on the original method included a more stringent control of the temperature of the hot plate and the use of 0.05 M and

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0.1 M solutions of NH_4VO_3 , which was found to optimise the yield while limiting the formation of impurities such as V_2O_5 in the precipitate.

2.2. Electrodeposition method

The electrochemical preparation was similar to the method used for the formation of alkali metal vanadates by cyclic voltammetry, described elsewhere [7]. However, in the present work the transition metal nitrate was not added to the 50°C NH_4VO_3 solution until the cell had been cycled for at least 1 h (a colour change was observed in the solution). The electrodeposited materials were collected, washed in distilled water and allowed to dry overnight in an oven at 70°C . The materials were analyzed by Atomic Absorption (A.A.), powder X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC) methods.

2.3. Electrochemical measurements

The preparation of electrodes involved first mixing the active material with 10 wt.% carbon and 5 wt.% polyvinylidene fluoride (PVDF) binder in 1-methyl-2-pyrrolidione (n-mp), using a mortar and pestle to make a slurry. The n-mp was added as needed during mixing. The slurry was spread on an aluminium sheet using a doctor blade (set between 50 to 350 μm). The wet cast was left in a convection oven at 60°C until it appeared dry, then transferred to a vacuum oven at 120°C for 1 h. A disc of 1.3 cm diameter was cut from the cast and then pressed at 3500 kPa. The pressed disk can range from approximately 50 to 150 μm in thickness, including the aluminium current collector. Coin cells were then assembled using an electrolyte composed of 1 M LiPF_6 dissolved in 1:1 of ethylene carbonate and dimethyl carbonate (EC:DMC) and a counter electrode of either Li metal or LiCoO_2 . The cells were cycled continuously at a rate of about 20 mA/g for discharging and 10 mA/g for charging to approximate a C/20 and C/40 discharge/charge rate.

It proved difficult to form adherent electrodeposits of the transition metal vanadates using the same electrodeposition method which had been used to make alkali metal vanadates [7]. The advantage of an electrodeposition technique is that no binders or carbon are necessary, because the material is directly deposited on a conducting substrate. The Mn-containing vanadates formed the most adherent and uniform deposits, while the Ni and Co vanadates were not adherent to any of the substrates used. However, a precipitate would gradually form in the bottom of the electrochemical cell during continuous cycling for 24 h. These precipitates were washed and analysed in the same way as the precipitates made using the heated solution method. These materials tended to have much higher transition metal content (Table 1) and were amorphous in nature. Because adherent materials could not be made by this method (as was done with $\text{K}_x\text{V}_6\text{O}_{13+y}$ [7]), coin cells were prepared in the same manner as for the precipitation method.

3. Results and conclusions

3.1. Physical and chemical analyses

Analysis of the transition metal (TM) vanadates made using both the precipitation and electrochemical methods confirmed the materials to have stoichiometries of $\text{Me}_x(\text{VO}_3)_2 \cdot y\text{H}_2\text{O}$ where $1.0 < x < 2.0$. The results of the A.A. analysis for vanadates used in electrochemical studies are given in Table 1. X-ray diffraction spectroscopy indicated most of the samples were either semi-crystalline or crystalline. From X-ray diffraction, the Co, Ni and Mn vanadates in the range of $1.0 < x < 1.2$ had a structure similar to orthorhombic $\text{CoV}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ [8,9]. For example, $\text{Co}_{1.1}\text{V}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ had a small shift in d-spacing and a small change in unit cell dimensions as shown in Table 2. As the value of x became larger, the XRD pattern became

Table 1

Summary of analysis of various vanadates with stoichiometry of $\text{Me}_x(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$. Electrode mass, initial specific capacity and capacity after several cycles at a rate of about 20 mA/g discharge and 10 mA/g charge are also given

Vanadate formula	Mass of active material/mg	Initial specific capacity to 0.5 V/(A h/g)	Specific energy/(W h/g)	% capacity loss from 2nd to (x) cycles
$\text{Co}_{1.11(0.04)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	13.1	0.79	0.95	95(10)
$\text{Co}_{1.20(0.04)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	13.5	0.70	0.65	97(15)
$\text{Co}_{1.52(5(0.06))}\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	8.4	0.44	0.41	88(5)
$\text{Ni}_{0.95(0.1)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	9.3	0.95	1.20	66(10)
$\text{Ni}_{1.18(0.02)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	6.8	0.93	1.12	70(8)
$\text{Ni}_{1.52(0.05)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	7.5	0.42	0.45	82(15)
$\text{Mn}_{0.83(0.03)}\text{Ni}_{0.15(0.03)}(\text{VO}_3)_2$	11.3	0.38	0.55	93(15)
$\text{Mn}_{1.1(0.02)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	15.1	0.42	0.40	91(20)
$\text{Mn}_{1.21(0.03)}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	10.6	0.37	0.35	89(25)

Table 2

Summary of cell parameters for transition metal vanadates prepared by low temperature precipitation. The $\text{CoV}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ single crystal data was also given for comparison [7,8]

TM vanadate	Symmetry	Source	Unit cell dimensions			
			<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
$\text{CoV}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$	Orthorhombic	Single crystal	5.572(2)	10.709(1)	11.860(2)	707.7(5)
$\text{Co}_{1.1}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	Orthorhombic	Low temperature precipitation	5.545(5)	10.67(1)	11.80(1)	698(2)
$\text{Co}_{1.2}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	Orthorhombic	Low temperature precipitation	5.545(5)	10.70(1)	11.81(1)	701(2)
$\text{Ni}_{1.01}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	Orthorhombic	Low temperature precipitation	5.46(2)	10.58(2)	11.63(5)	674(8)
$\text{Ni}_{1.18}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	Orthorhombic	Low temperature precipitation	5.524(5)	10.616(9)	11.74(1)	688(2)
$\text{Mn}_{1.1}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$	Orthorhombic	Low temperature precipitation	5.56(1)	10.85(2)	11.97(2)	722(4)

less crystalline and only three or four very broad bands were observed.

DSC results confirmed that the hydrated water could only be removed by heating above 300°C. However, the electrochemical performance of these materials was affected by high temperature drying [6]. In this paper, materials were not dried above 120°C. Pressing the electrode material after casting was found to be important in improving electrical contact to the Al foil.

3.2. Electrochemical results

Only materials with Me:V ratios listed in Table 1 were electrochemically tested. Use of coin cells rather than flooded cells improved the reproducibility of the electrochemical performance of the various materials and eliminated problems such as flaking (loss of adherence to substrate) and the common problem of vanadium ions slowly dissolving into the electrolyte [10]. However, in casting the electrode materials, it was found that thinner electrodes (50–100 μm before pressing) were giving poorer results when compared with thicker casts of the same material. Loss of electrical contact between localised regions of the active material and the substrate was thought to be the cause. The impedance analysis of a fresh and cycled coin cell had only small changes occurring in the

charge transfer resistance during cycling. The charge transfer resistance increased slightly from about 45 to 50 Ω to about 60 to 65 Ω after ten cycles. With a two-electrode geometry, the impedance analysis reflects only the bulk cell properties and the change in shape to a flatter shaped semi-circle is largely due to passivation effects on the lithium metal anode. The conclusion from impedance analysis was that no unexpected bulk surface effects or interactions were occurring on the electrodes during cycling.

The cycling of transition metal vanadates of the type $\text{Me}(\text{VO}_3)_2 \cdot y\text{H}_2\text{O}$ (where Me = Co, Ni or Mn and Me:V = 1:2) has been discussed previously [4]. They were found to operate in both lithium primary and rechargeable systems, with a voltage of 1.5 V. In the present work, cells containing lithium metal electrodes were cycled using $\text{Me}_x(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ with *x* in the range of 1.0 to 2.0. The discharge trends for the different vanadates are shown in Fig. 1. Both the value of *x* and the nature of the transition metal present influenced the specific capacity. For operation as a 1.5 V lithium primary cell materials with a Me:V value of 1:2 provided the best specific capacity. Values of *x* higher than 1.3 led to a degradation of performance (Table 1). This degradation could have been due to several factors because the vanadates were amorphous and there was the possibility of producing a mixture of materials or other impurities.

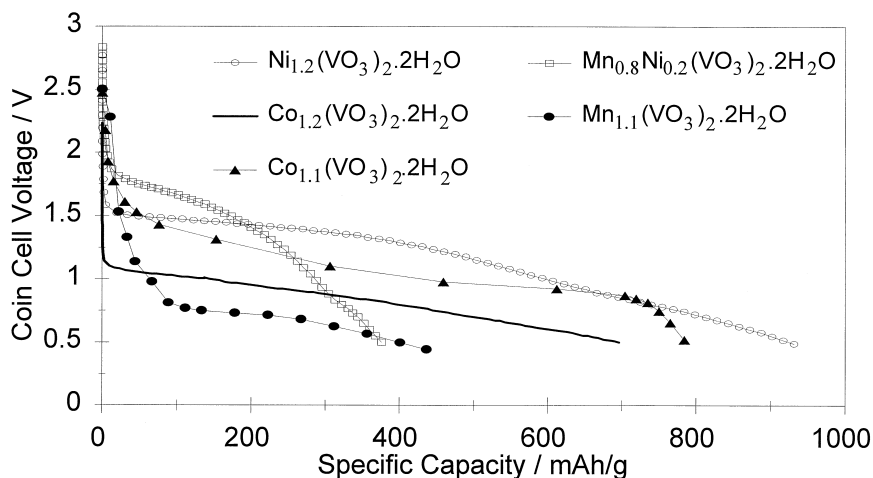


Fig. 1. Plot of the voltage versus the specific capacity for the initial discharge of a coin cell with a various $\text{Me}_x(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ electrodes, Li metal anode and 1 M LiPF_6 in 1:1 EC:DMC electrolyte.

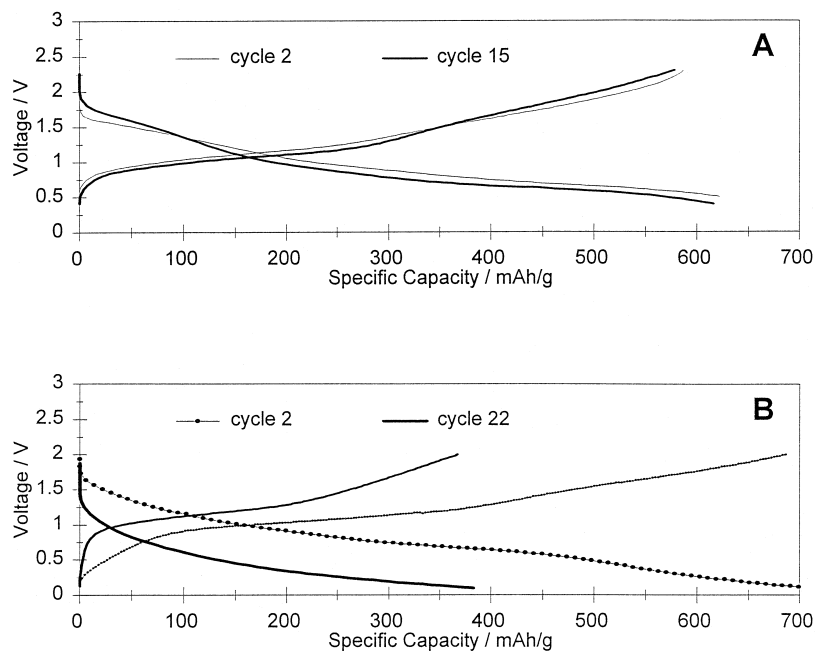


Fig. 2. Plot of the voltage versus the specific capacity for the discharge and charge of a coin cell with a $\text{Co}_{1.2}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ electrode, Li metal anode and 1 M LiPF_6 in 1:1 EC:DMC electrolyte. Discharge down to 0.5 V in **A** and to 0.1 V in **B**.

In order to explore the duality of these materials (either as cathode or anode) the materials with a value of x from 1.05 to 1.25 were examined. Although the average operating voltage of the coin cell decreased to about 1.0 V on discharge and 1.5 V on charge, a significant reversible capacity was possible as shown in Fig. 2 for $\text{Co}_{1.2}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ against a lithium metal anode. By discharging the vanadates to lower voltages, at or near 0.5 V, extra reversible capacity could be obtained in excess of 400 mA h/g below 1.0 V. The problem of high initial capacity fade was improved for these vanadates with a capacity loss on discharge of less than 1% in the first 15 cycles (Fig. 2a). The presence of hydrated water did not appear to

affect electrochemical performance of the material. Because of the formation of aluminum lithium alloys by cycling below 0.5 V, a copper current collector was used and found to be stable in the range of 3.0 to 0.0 V, as well as provide good adherence with the electrode material. However, as shown in Fig. 2b, although initial specific capacity improved up to 25% for cycling down to lower voltages, the penalty was a more substantial capacity fade after several cycles.

Only thicker casts (above 200 μm) were used for Li ion cells, but because of the higher capacity of the vanadate electrodes compared to the LiCoO_2 electrode (a factor of two to three), a cycling limitation was created. The spe-

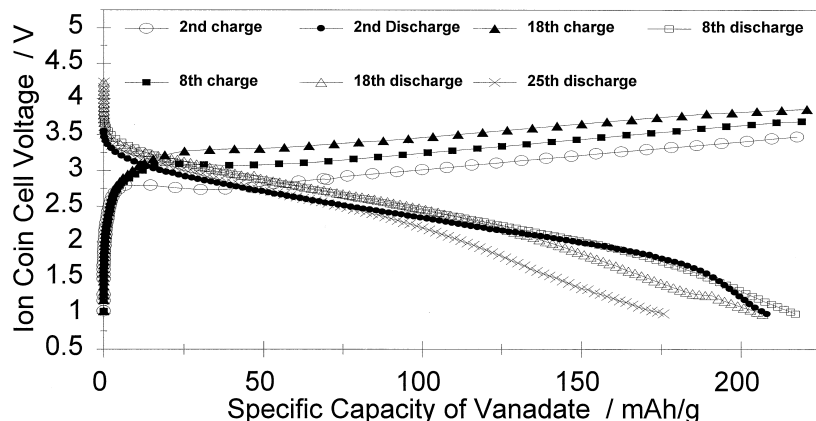


Fig. 3. Plot of the cell voltage versus the specific capacity of an Ion coin cell with $\text{Co}_{1.2}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ and LiCoO_2 electrodes and 1 M LiPF_6 in 1:1 EC:DMC electrolyte.

specific capacity of the Li ion coin cell was limited by the LiCoO_2 electrode, but the results still demonstrate that the vanadate material could be used in this type of cell. An example of such a cell is shown in Fig. 3 for a LiCoO_2 cathode and $\text{Co}_{1.2}\text{V}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$. The cell operated at an average voltage of 2.3 V with a capacity of 180 mA h/g for over 25 cycles. Because the matching of the two electrodes was not optimised the cell would fail after this point. Future studies will try to overcome this problem.

Acknowledgements

The National Research Council of Canada, Energy Materials Group, is thanked for use of resources, staff in this work.

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