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Lithium intercalation in the divalent metal vanadates MeV_2O_6 ($\text{Me} = \text{Cu}, \text{Co}, \text{Ni}, \text{Mn}$ or Zn)

E. Andrukaitis^{a,*}, Judy P. Cooper^a, John H. Smit^b^a Directorate Research and Development Air, Department of National Defence, 101 Colonel By Drive, Ottawa, Ont., K1A 0K2, Canada^b Electrochemical Science and Technology Centre, University of Ottawa, 33 Mann Avenue, Ottawa, Ont., K1N 6N5, Canada

Abstract

Divalent metal vanadates, $\text{Me}_x\text{V}_2\text{O}_6$, where $\text{Me} = \text{Cu}, \text{Co}, \text{Zn}, \text{Mn}$ or Ni , were found to reversibly intercalate lithium. These transition metal vanadates were made by a precipitation method which formed a hydrated divalent metal vanadate ($\text{Me}_x\text{V}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$). The hydrated water was removed by heating the vanadate above 300 °C and composite electrodes were prepared with carbon and polytetrafluoroethylene. The cell voltage and energy density were dependent on both the divalent metal present and the temperature to which the vanadate was annealed. The Zn, Mn, Co and Ni vanadates were reversible to lithium intercalation at average voltages from 1.3 to 1.9 V (versus Li) and their specific capacities were dependent on the annealing temperature. The copper vanadate yielded the best cell voltage and energy density.

Keywords: Lithium intercalation; Vanadium; Transition metals

1. Introduction

Rechargeable batteries with lithium anodes require a suitable cathode for optimum performance. Transition metal oxides make good cathodes because of their relatively low mol. wt. and layered crystal structure. Research has shown that transition metal vanadates, such as copper vanadates, may be promising cathode materials for lithium batteries [1,2]. Copper vanadates and other transition metal vanadates may have structural advantages that result in an increased reversible intercalation of Li^+ . The $\text{Cu}_2\text{V}_2\text{O}_7$ copper vanadate has charge densities similar to or exceeding V_2O_5 and is reversible for Li/Cu ratios less than two, with over 100 cycles between 2 and 3.5 V [2]. The transition metal vanadates having a brannerite-type structure $\text{Me}^{\text{II}}\text{V}_2\text{O}_6$ ($\text{Me} = \text{Mg}, \text{Ca}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ and Cd) were found to have very poor electrochemical properties when compared with CuV_2O_6 [3]. This may be a result of the high-temperature synthesis methods used and the preparation of these materials by a low-temperature method may improve their electrochemical properties.

This paper presents the electrochemical insertion of lithium for five transition metal vanadates $\text{Me}_x\text{V}_2\text{O}_6$

($\text{Me} = \text{Co}, \text{Ni}, \text{Mn}, \text{Cu}$ and Zn), prepared for the first time by a precipitation method. These divalent metal vanadates are of interest because of their structural relationship to $\gamma\text{-MnO}_2$, the non-stoichiometric form of manganese dioxide used in the battery industry.

2. Experimental

Transition metal vanadates were prepared in aqueous NH_4VO_3 with transition metal salts by a method similar to the procedure described by Roth and Waring [4] for the formation of BiVO_3 . After filtration, the air-dried precipitate was heated in a tube furnace at temperatures from 300 to 600 °C for up to 24 h. Electrodes were fabricated from an 85:10:5 wt.% mixture of vanadate, Ketjen black carbon and polytetrafluoroethylene (PTFE) binder (60% suspension in water). Composites with a surface area from 0.8 to 2.0 cm^2 were pressed on to a 150 grid nickel or stainless-steel mesh which provided conductive support. Water introduced during the preparation process was removed by heating the electrodes for 24 h at 200 °C under vacuum (about 1 mmHg). The vanadates were examined by X-ray powder diffraction (XRD) (Scintag Inc., XDS 2000), inductively coupled plasma (ICP) spectroscopy and chemical analyses. Capacity and reversibility to

* Corresponding author.

lithium insertion of these composite electrodes were determined using galvanostatic or cyclic voltammetry methods at current densities from 0.5 to 2.0 mA/cm² (1 to 4.5 V). Lithium foil anodes and 0.5 M LiClO₄ in propylene carbonate (PC) electrolyte were used in flooded cells and button cells in a glove box, under argon.

3. Results and discussion

The XRD patterns of the five transition metal vanadates before and after heating in air at 550 °C are shown in Fig. 1. The XRD pattern for the air-dried

copper vanadate material was the least crystalline and only three broad major peaks of CuV₂O₆·2H₂O were observed [5] (Fig. 1(a)). The zinc vanadate did not have a stoichiometric Me/V ratio of 1:2 and appeared to be a mixture of the zinc vanadate dihydrate and another product of the precipitation procedure which contained detectable amounts of ammonium (Table 1).

The XRD pattern of the air-dried cobalt vanadate is similar to that of CoV₂O₆·2H₂O [5] (Fig. 1(b)). ICP and XPS spectroscopy of the vanadate confirmed the presence of cobalt with a 1:2 Co/V stoichiometry (Table 1). A matching XRD pattern for the air-dried nickel vanadate was not found in the XRD files but it was very similar to the XRD pattern of CoV₂O₆·2H₂O [5].

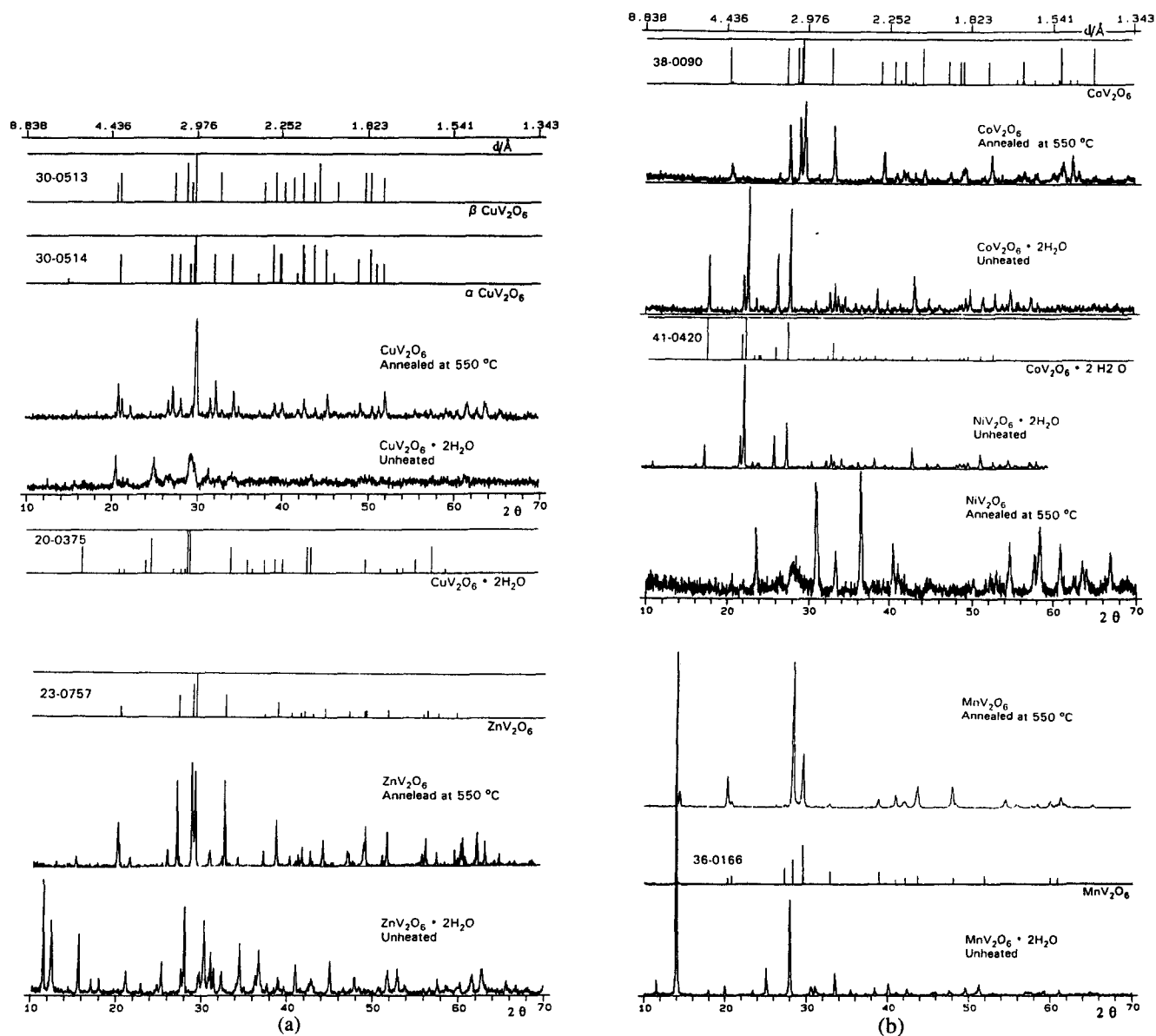


Fig. 1. X-ray powder diffraction patterns of the five transition metal vanadates MeV₂O₆: (a) Me=Cu and Zn and (b) Me=Co, Ni and Mn. Both the air-dried precipitate (40 °C for 24 h) and the vanadates annealed at 550 °C for 20 h are shown with X-ray patterns from the X-ray powder diffraction file [5].

Table 1

Summary of chemical and inductively coupled plasma (ICP) analysis of various transition metal vanadates prepared from a transition metal salt with ammonium meta-vanadate

Component added to vanadate (M/V)	ICP analysis ratio Me/V		NH ₄ ⁺ present (%)	Stoichiometry from XRD and chemical analysis	
	Mass	Molar		Air dried	Heated 550 °C
Co(NO ₃) ₂ ·6H ₂ O	0.571	0.494	<1.0	Co(VO ₃) ₂ ·2H ₂ O	CoV ₂ O ₆
NiCl ₂ ·6H ₂ O	0.580	0.504	<1.0	Ni(VO ₃) ₂ ·2H ₂ O	NiV ₂ O ₆
CuSO ₄ ·5H ₂ O	0.642	0.514	<1.0	Cu(VO ₃) ₂ ·2H ₂ O	CuV ₂ O ₆
MnSO ₄ ·H ₂ O	0.548	0.508	<1.0	Mn(VO ₃) ₂ ·2H ₂ O	Mn(VO ₃) ₂
ZnCl ₂	0.553	0.431	≈ 4	Zn _{0.9} (VO ₃) ₂ ·2H ₂ O	Zn _{0.9} V ₂ O ₆

The air-dried manganese vanadate was thought to be a hydrated form of Mn(VO₃)₂.

By annealing the metal vanadates at 550 °C crystalline MeV₂O₆ where Me = Co, Ni, Cu, Mn or Zn were formed. The XRD patterns were similar to those reported previously [2,5–7] on metal vanadates prepared by high-temperature synthesis. The XRD pattern for the manganese vanadate resembled that of Mn(VO₃)₂ [5]. The ZnV₂O₆ contained V₂O₅ as a significant impurity (> 10%) since other vanadate species precipitated out of solution with the zinc vanadate and decomposed to V₂O₅ when heated [8]. Attempts to reduce the amount of the V₂O₅ in the zinc vanadate were unsuccessful.

3.1. Lithium intercalation in the divalent metal vanadates

The discharge voltage of composite electrodes made with the five transition metal vanadate materials plotted against the specific capacity (Ah/g) for the vanadates annealed at 550 and 300 °C are shown in Fig. 2(a) and (b), respectively. The lithium insertion and removal were done galvanostatically at current densities from 0.5 to 1 mA/cm². The copper vanadates had the highest energy densities at average voltages of 2.0 to 2.35 V. Above 2.0 V, the capacity was 3.8 Li/CuV₂O₆, with plateaus at 2.8 and 2.4 V. The CuV₂O₆ had a capacity greater than that reported by Sakurai et al. [2] because of a third plateau between 1.5 and 1.0 V (4 < x < 5 in Li_xCuV₂O₆). Annealing at 300 and 550 °C, maximum specific capacities of 0.66 to 0.56 Ah/g and energy densities of 1.26 to 1.34 Wh/g were respectively observed to a 1.2 V cutoff voltage (Fig. 2). This is higher than the energy density of CuO (840 Wh/kg to 1.2 V), used commercially in primary batteries [9]. The good insertion capacity of CuV₂O₆ was because the Cu²⁺ ion can be reduced to Cu⁺ during lithium insertion. The larger ionic radii of copper ions in their reduced state may increase the interlayer spacing of the vanadate leading to improved lithium intercalation [3].

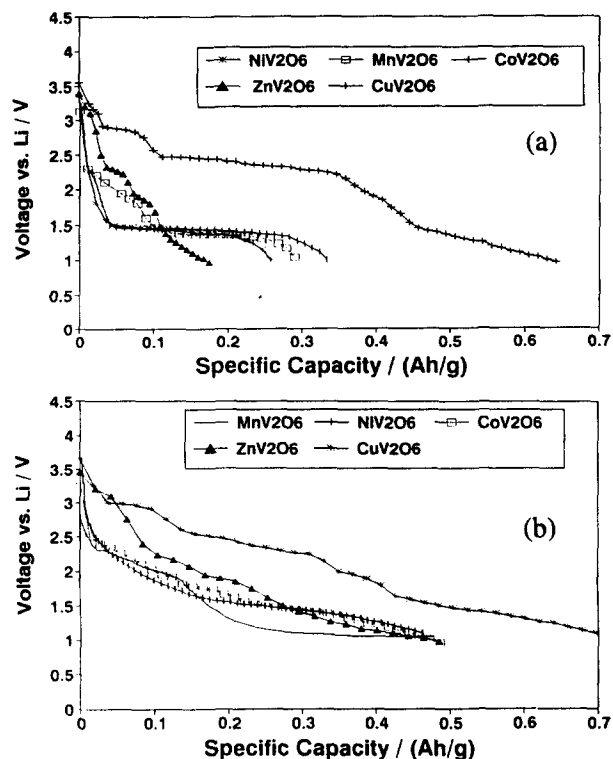


Fig. 2. Single discharge curves for the transition metal vanadates, MeV₂O₆, where Me = Cu, Mn, Ni, Co or Zn, using constant current at current densities between 0.5 to 1.0 mA/cm², for annealing temperatures of (a) 550 °C and (b) 300 °C.

The copper, nickel, manganese and zinc vanadates had capacities in the range 0.2 to 0.5 Ah/g with average voltages from 1.25 to 2.4 V. The lower voltages for these vanadates resulted in lower energy densities compared with CuV₂O₆ (Table 2). Because the zinc vanadate contained V₂O₅ as an impurity, ZnV₂O₆ annealed at 300 °C had a discharge profile which resembled that of V₂O₅, with phase changes at 0.5, 1.0 and 1.9 Li/ZnV₂O₆ and when annealed at 550 °C the phase changes were shifted to 0.3, 0.6 and 1.4 Li/ZnV₂O₆. Lithium insertion was reversible but ZnV₂O₆ had the lowest reversible energy densities (0.33 to 0.4 Wh/g). The

Table 2

Summary of the specific capacity, average discharge voltage, energy density and number of cycles for five transition metal vanadates MeV_2O_6 ($\text{Me} = \text{Zn}, \text{Cu}, \text{Co}, \text{or Ni}$) discharged to 1.0 V at a current density of about 1 mA/cm²

Cathode material (MeV_2O_6)	Annealing temperatures (°C)	Active electrode (mass/g)	Specific capacity (Ah/g)	Average discharge voltage (V)	Energy density (Wh/g)	Number of cycles to 1/2 capacity
MnV_2O_6	300	0.026	0.450	1.4	0.630	7
	550	0.029	0.300	1.46	0.438	> 80
CoV_2O_6	300	0.024	0.460	1.6	0.736	> 20
	550	0.033	0.327	1.55	0.500	> 100
NiV_2O_6	300	0.015	0.446	1.75	0.781	49
	550	0.019	0.260	1.5	0.390	125
CuV_2O_6^a	300	0.017	0.665	1.9	1.264	40
	550	0.027	0.596	2.25	1.341	23
ZnV_2O_6^b	300	0.016	0.442	1.9	0.840	20
	550	0.046	0.172	1.9	0.326	> 100

^a Reported to 1.2 V cutoff voltage for comparison to Sakurai et al. [2].

^b V_2O_5 is present as major impurity.

capacity diminished about 40 to 45% during the first ten cycles to a capacity of only 0.1 to 0.15 Ah/g for over 100 cycles.

The three remaining vanadates, MeV_2O_6 ($\text{Me} = \text{Mn}, \text{Ni}$ or Co), when annealed above 500 °C, had very similar discharge profiles, with a long flat plateau from 1.5 to 1.4 V (Fig. 2(a)). The energy densities (0.4 to 0.5 Wh/g) were lower than those of CuV_2O_6 with a maximum capacity of about 3 Li/ MeV_2O_6 . However, when annealed at lower temperatures (≈ 300 °C), the energy density improved dramatically and doubled in the case of the NiV_2O_6 (Table 2). Discharge voltages of these vanadates had a larger slope from 2 to 1 V. Thus, annealing temperatures played an important role in the ability of these divalent metal vanadates to intercalate lithium.

3.2. Reversible lithium intercalation in copper, nickel, cobalt and manganese vanadates

The cycling behaviour of the four vanadates ($\text{Cu}, \text{Ni}, \text{Co}$ and Mn) are shown in Fig. 3(a) to (d), respectively. The copper vanadates annealed above 300 °C had a cycling behaviour similar to that of CuV_2O_6 studied by Sakurai et al. [2] at a moderate cycle depth of about 0.3 Ah/g to a 1.5 V cutoff voltage (Fig. 3(a)). A smooth linear voltage drop between 2.5 and 1.5 V was seen after only a few cycles. After the initial lithium insertion/removal cycle, the copper vanadate gained some capacity over the first few cycles and then lost capacity at a rate of about 1.2% per cycle with about 60% of the initial capacity retained on the 33rd cycle. Deeper discharge cycling (to 1.0 V) yielded higher specific capacities but the capacity faded more quickly.

The reversibility of copper vanadates may be limited by the mobility of copper in the crystal lattice. The copper ions are thought to permeate the separator and deposit on the lithium anode resulting in a loss of electrical contact due to the formation of a high impedance passive layer [2,10,11]. This was confirmed in our results by the failure of button cells to return to their open-circuit voltage during charging by their decreasing capacity with cycling. The capacity of the button cell improved significantly when the lithium anode was replaced by fresh lithium.

The nickel, copper and manganese vanadates performed best at the lower annealing temperatures. Although the energy density was lower at the higher annealing temperatures, the reversibility was better (capacity fade was lower), and over 100 cycles were obtained between 0.3 to 0.35 Wh/g. These vanadates appear to cycle reasonably well and are plausible in a 1.5 V rechargeable lithium system. Primary 1.5 V lithium cells having BiVO_3 cathodes with a theoretical capacity of 0.25 Ah/g were found to be marginally reversible but their capacity faded rapidly [12].

The specific capacity of the nickel vanadate, NiV_2O_6 , annealed at 300 °C was significantly higher than that of NiV_2O_6 , annealed at 550 °C (Fig. 3(b)). Capacity fade was initially about 0.6% per cycle. Over 100 cycles at energy densities of about 0.25 Wh/g (< 2 Li/ NiV_2O_6) were achieved. The cobalt vanadates (CoV_2O_6) annealed at 550 and 300 °C had a flat voltage plateau between 1.5 and 1.0 V over most of the discharge. Energy densities were better for the lower annealing temperature with about 0.45 Wh/g for the first 10 cycles. The capacity improved over the first several cycles and then faded at about 0.9% per cycle. The energy density after 50 cycles was about 0.25 Wh/g (< 2 Li/ CoV_2O_6). This

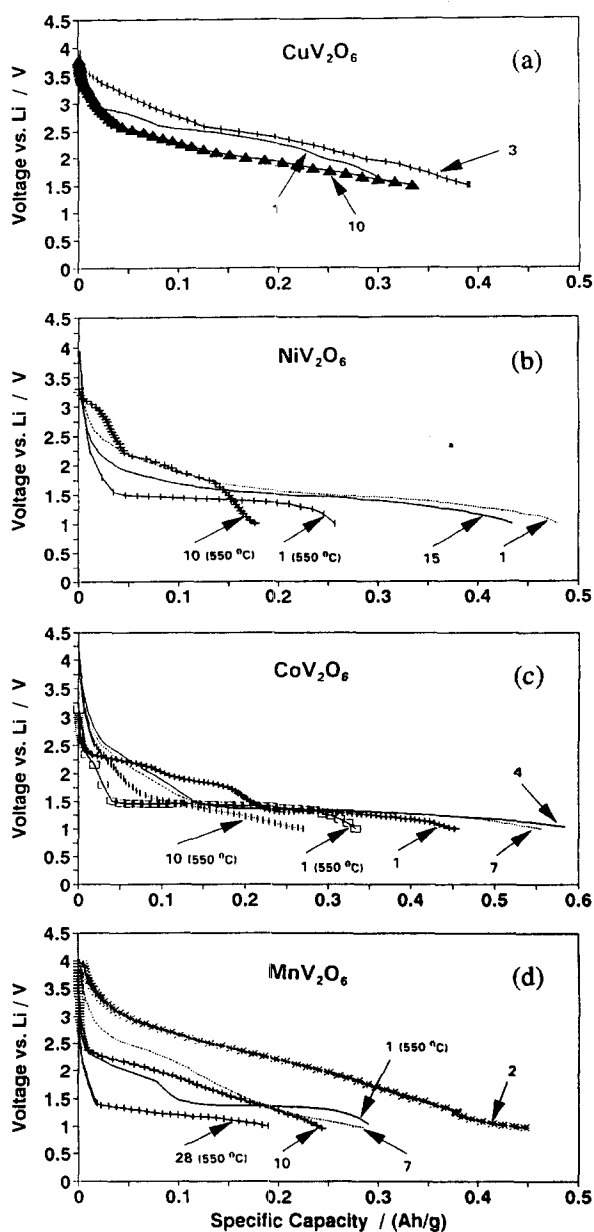


Fig. 3. Discharge curves during continuous constant-current cycling (current densities of 0.5 to 1.0 mA/cm²) of the transition metal vanadates, MeV₂O₆, where Me=Cu, Mn, Ni, Co, labelled as (a), (b), (c), and (d), respectively. Cycle numbers for annealing at temperatures of 550 °C are marked with a (550 °C) label and no label indicates a 300 °C annealing temperature.

capacity fade was partially attributed to the loss of adherence of some of the composite to the substrate which was observed when the electrode was examined after cycling.

The Mn(VO₃)₂ yielded poor energy densities after 10 cycles (Fig. 3(d)). However, of the four vanadates studied it had the best potential for long cycle life and reproducibly gave over 100 cycles. The specific capacity was in the range of 0.15 to 0.20 Ah/g (average of 1.3 V) which resulted in low energy densities of 0.2 to 0.26 Wh/g. The discharge had a voltage plateau at about 1.3 V which became flatter during the first 40 cycles and remained this way for over 100 cycles (Fig. 3(d)).

4. Conclusions

The capacity and reversibility of divalent transition metal vanadates are related to the transition metal ion present. The copper vanadate had the highest energy density of the vanadates studied (1.34 Wh/g to 1.2 V cutoff voltage). Although the presence of the copper ions made the higher capacity possible, but the migration of the copper ions from the cathode to the lithium anode has a detrimental effect. The nickel, copper and manganese vanadates show reasonable reversibility towards lithium intercalation, but at lower energy densities than Cu vanadate. However, they may be practical cathode materials for reversible 1.5 V lithium battery systems.

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