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Lithium intercalation into the copper, nickel or manganese vanadates $\text{Me}(\text{VO}_3)_2 \cdot y\text{H}_2\text{O}$

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Abstract

Divalent transition metal vanadates, containing cobalt, nickel or manganese, were found to reversibly intercalate lithium. By a precipitation method, a hydrated divalent metal vanadate was formed, with stoichiometry $\text{Me}(\text{VO}_3)_2 \cdot y\text{H}_2\text{O}$, where $\text{Me} = \text{Co}, \text{Ni}$ or Mn . Composite electrodes of Co and Ni vanadates dried in the 100–300 °C range had initial energy densities in the range of 1.1 to 1.5 Wh/g of active cathode material, at average voltages from 1.3 to 1.8 V (versus Li). The specific capacity faded quickly for $\text{Co}(\text{VO}_3)_2$ (15 to 30%) over the first 10 cycles because of partial amorphization of the structure and then stabilized to fade < 1%/cycle. Capacity of the divalent transition metal vanadates was related to the transition metal ion present, with Co and Ni vanadates yielding the highest specific capacities for a transition metal vanadate electrode. © 1997 Elsevier Science S.A.

Keywords: Lithium; Intercalation; Metal oxides; Vanadate; Vanadium

1. Introduction

Rechargeable lithium-based batteries require suitable cathodes, such as transition metal oxides, for optimum performance. These metal oxides must have a relatively low molecular weight and a layered crystal structure that can easily accommodate the Li ion. Transition metal vanadates show promise for use in Li batteries for this reason [1–3]. However, the transition metal vanadates $\text{Me}^{\text{II}}\text{V}_2\text{O}_6$ ($\text{Me} = \text{Mg}, \text{Ca}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) with a monoclinic-brannerite structure had very poor electrochemical properties despite their favourable structure.

By the use of a precipitation technique, novel transition metal vanadates have been synthesized. This paper examines intercalation of Li for the transition metal vanadates $\text{Me}_x(\text{VO}_3)_2$, $\text{Me} = \text{Co}, \text{Ni}, \text{Mn}$. High-temperature synthesis of metal vanadates has yielded materials with poor electrochemical properties in the past [2,3]. The use of low-temperature annealing improved the electrochemical properties of these transition metal vanadates. They offer the highest specific capacity for a vanadate based material to date, with an average discharge voltage of about 1.5 V.

2. Experimental

The divalent transition metal vanadates were prepared by a method similar to that described for the formation of BiVO_4

[4,5]. The precipitate was washed and dried at 60 °C for several days. The vanadate was fabricated into electrodes using a 85–10–5 wt.% mixture of vanadate, Ketjen black carbon and polytetrafluoroethylene (PTFE) binder, respectively. Composites with a 0.5–2.0 cm² surface area were pressed onto a 150 grid nickel mesh. The electrodes were heated for 40 h at 200 °C under vacuum. 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/cm². A cell with an Li anode and reference electrode in 1 M LiClO_4 -propylene carbonate/ethylene carbonate (50:50) was used in a glove box.

3. Results and discussion

From XRD, ICP and chemical analysis, the air-dried transition metal vanadates had the stoichiometry, $\text{Me}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$, where $\text{Me} = \text{Mn}, \text{Co}$ or Ni . The XRD pattern for the three air-dried vanadate hydrates have been shown previously [5]. Analysis of the vanadate confirmed the presence of the transition metals and vanadium with a 1:2 Me/V stoichiometry. It was also possible to produce mixtures of various

transition metals within the vanadate by using two different transition metal salts in the precipitation process. In this way several $M_xMe_y(VO_3)_2 \cdot 2H_2O$ (where $Me = Ni, Co$ or Mn , $x + y = 1$) were formed. The amounts of the various transition metals present were determined by ICP spectroscopy.

Heating the hydrated vanadates over $300^\circ C$ was found to remove all of the hydrate from the vanadate to form a $Me(VO_3)_2$ monoclinic structure. The removal of water from the vanadate was dependent on the temperature and the length of time of the drying process. However, from XRD spectroscopy, it is above this temperature that the XRD peaks begin to broaden significantly indicating a decrease in crystallinity. Therefore, the pressed composite vanadates were heated no higher than $200^\circ C$ under vacuum for over 24 h. This removed the water added during the process of fabricating the composite electrodes and the bulk of the hydrated water while still retaining a more crystalline structure.

3.1. Lithium intercalation in the divalent metal vanadates

The discharge voltage (versus Li) was plotted versus the specific capacity (Ah/g) for the Mn, Co and Ni vanadates in Fig. 1. During discharge, intercalation of Li^+ was found to occur into the metal vanadates. This was confirmed by chemical analysis similar to that performed for Li intercalation of alkali metal vanadates [6]. The vanadates show an initial rapid drop from 3 to below 2 V over the first five to ten percent of its total capacity, followed by a relatively stable operating voltage to about 1.0 V. As shown in Fig. 2, when the specific energy (Wh/kg) or operating voltage (versus Li) was plotted versus the specific capacity (Ah/kg), Co and Ni vanadates have the highest initial specific capacities compared with other Li intercalation metal oxide materials used in Li cells. The initial energy densities of Ni and Co vanadates were found to be in the 1.0–1.7 Wh/g (to 0.8 V) range. The average discharge voltage was in the range of 1.4 to 1.6 V and above 1.2 V, the capacities for Co and Ni vanadates was >0.65 Ah/g (Table 1). This was better than the primary CuO cathode used commercially, which has a similar operating voltage (1.4 V versus Li) and delivers a theoretical specific energy of about 0.8 Wh/g [1].

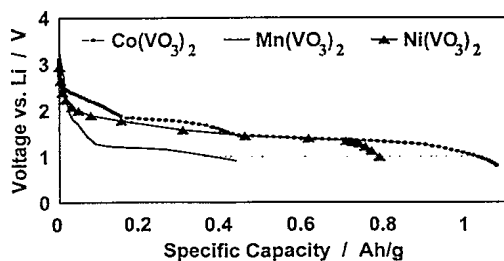


Fig. 1. Single discharge curves for the transition metal vanadates, $Me^{II}(VO_3)_2$ ($Me = Mn, Co$, or Ni), using constant current at current densities between 0.5 and 2.0 mA/cm². The discharge voltage (vs. Li reference electrode) was plotted vs. the specific capacity from a known mass of active material, in a composite electrode, in 1 M $LiClO_4$ -organic solvent and an Li counter electrode.

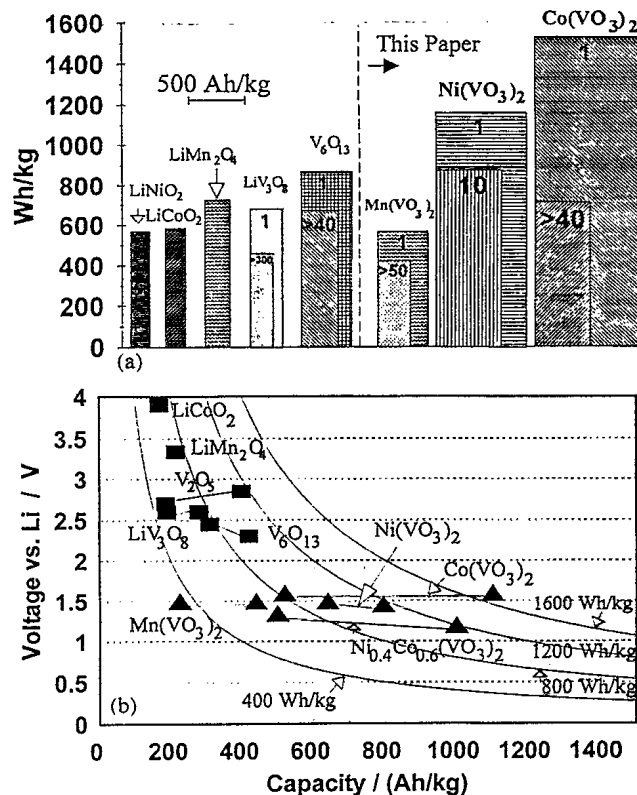


Fig. 2. (a) Specific energy vs. specific capacity of several Li intercalation oxides and $Me^{II}(VO_3)_2$ ($Me = Mn, Co$, or Ni) (500 Ah/kg scale shown). The number of cycles for the $Me^{II}(VO_3)_2$ vanadates is shown within each box. (b) Discharge capacity plotted against the voltage for several Li intercalation transition metal oxides (\square) and $Me^{II}(VO_3)_2$ ($Me = Mn, Co$, and/or Ni) (\blacktriangle).

Mn vanadate had a much lower initial specific capacity (0.33 Ah/g) and a slightly lower operating voltage of about 1.35 V. The reason for this much lower specific energy compared with the other two vanadates has not yet been determined. By heating only to $200^\circ C$, the specific capacity improved by several times compared to Mn, Co and Ni vanadates studied previously that were either annealed or synthesized above $550^\circ C$ [2.5]. This can be shown for the initial Li intercalation into the $Me^{II}(VO_3)_2$ and the MeV_2O_6 ($Me = Mn, Co$ and/or Ni) formed when annealing the vanadates above $550^\circ C$ in Fig. 3. The cyclic voltammograms of the various vanadates were taken at a very slow scan rate (25 $\mu V/s$) and the voltage (versus Li) was plotted versus the current per unit mass of active material (mA/g). The $Me^{II}V_2O_6$ electrodes have much poorer Li insertion capability compared with these monoclinic based $Me^{II}(VO_3)_2$ vanadates. These vanadates, with their large initial specific capacity and flat discharge profile, may be suitable for Li primary cathodes in the 1.5 V range, such as microelectronics that require a steady potential or relatively low current pulse applications.

Table 1
Summary of the specific capacity, specific energy and number of cycles to one half capacity for transition metal vanadates $\text{Me}^{\text{II}}(\text{VO}_3)_2$ ($\text{Me} = \text{Mn, Co, or Ni}$) discharged at current densities of about 1 mA/cm^2

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)
$\text{Co}(\text{VO}_3)_2$	1.2	0.0198	0.940	1.62	1.52	20 (50%)
	0.8	0.0198	1.10	1.60	1.76	15 (47%)
$\text{Ni}(\text{VO}_3)_2$	1.2	0.0295	0.725	1.50	1.09	20 (79%)
	0.8	0.0295	0.795	1.46	1.16	10 (81%)
$\text{Mn}(\text{VO}_3)_2$	1.0	0.0150	0.334	1.35	0.45	30 (67%)
$\text{Co}_x\text{Ni}_y(\text{VO}_3)_2$ $x=0.6, y=0.4$	1.0	0.03699	1.00	1.5	1.50	34 (50%)

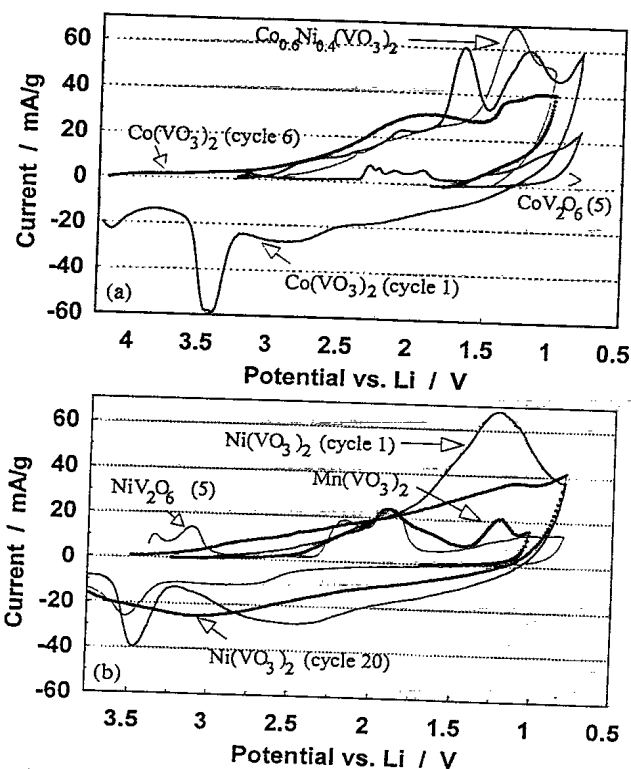


Fig. 3. (a) Cyclic voltammograms of the Li insertion into the transition metal vanadates, $\text{Co}(\text{VO}_3)_2$ (cycle nos. 1 and 6), $\text{Co}_{0.6}\text{Ni}_{0.4}(\text{VO}_3)_2$ and the CoV_2O_6 composite prepared above 600°C [5]. The discharge current (in mA/g active material) was plotted against the voltage vs. an Li reference electrode in 1 M LiClO_4 -organic solvent and an Li counter electrode in a glove box. The scan rate was $25 \mu\text{V/s}$. (b) Cyclic voltammograms of the Li insertion into the transition metal vanadate, $\text{Ni}(\text{VO}_3)_2$ (cycle nos. 1 and 20), $\text{Mn}(\text{VO}_3)_2$ and NiV_2O_6 composite prepared above 600°C [5]. The scan rate was $25 \mu\text{V/s}$ and under conditions similar to Fig. 3(a).

3.2. Reversible lithium intercalation of the $\text{Me}(\text{VO}_3)_2$ vanadates

Primary 1.5 V Li cells having BiVO_4 cathodes with a theoretical capacity of 0.25 Ah/g were found to be marginally reversible, but their capacity faded rapidly [7]. Unlike Li/ BiVO_4 cells which show a voltage delay, the $\text{Me}(\text{VO}_3)_2$ vanadates have a higher initial voltage than required. Ni and

Co vanadates are reversible to Li intercalation and initially delivered over three times the theoretical capacity of BiVO_4 cathodes. The reversible specific capacities and energies of $\text{Me}(\text{VO}_3)_2$, heated to only 200°C , were much higher than MeV_2O_6 formed when heating these vanadates above 550°C [5]. Over $0.5 \text{ Ah/(g of active material)}$ was delivered for the first several cycles (to 1.0 V) for Ni and Co vanadates.

The flat voltage plateau between 1.5 and 1.0 V during the initial discharge eventually becomes a smoother linear voltage drop between 2.5 to 1.0 V after a few cycles. This was a result of the increase in amorphous character of the metal vanadate during cycling. From cyclic voltammetry, by the sixth cycle, $\text{Co}(\text{VO}_3)_2$ has lost almost 30% of its initial capacity (Fig. 3(a)). $\text{Co}(\text{VO}_3)_2$ typically loses up to 50% of its initial capacity in the first ten cycles before it slows to a more steady capacity fade of $<1\%$ per cycle. $\text{Ni}(\text{VO}_3)_2$ had a lower initial capacity fade compared with Co vanadate and after ten cycles usually maintained a higher specific capacity and energy density. The initial rapid fade for these vanadates was partially attributed to the loss of adhesiveness of some of the cathode to the metal mesh substrate during cycling, but the largest influence was the structural changes that occurred as the amorphous nature of the metal vanadate increased during the first several charge/discharge cycles. Once these bulk structural changes had slowed, the capacity fade drops significantly to levels of $<0.8\%$ per cycle. Deep-discharge cycling ($<1.0 \text{ V}$) yielded higher specific capacities but the capacity faded more quickly.

4. Conclusions

The capacity and reversibility of $\text{Me}(\text{VO}_3)_2$ as an Li insertion electrode are related to the transition metal ion present. The initial specific capacities are in the sequence of $\text{Co} > \text{Ni} > \text{Mn}$, but as a reversible intercalation electrode $\text{Ni}(\text{VO}_3)_2$ has the advantage. Mixtures of Co and Ni vanadates also perform adequately during the initial cycles as well. These metal vanadates are reversible towards Li intercalation and may be practical cathode materials for primary or reversible 1.5 V Li systems that require high specific capacities at

low to moderate drain rates. The capacity fade is related to the depth-of-discharge and structural changes occurring in the electrode as crystallinity diminishes. Further investigation into optimizing cycle life of these vanadates is continuing.

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