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Comparison of LiV_3O_8 Cathode Materials Prepared by Different Methods

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ABSTRACT

Lithium trivanadate, LiV_3O_8 , can be prepared in a finely dispersed form by dehydration of aqueous lithium vanadate gels. Two methods of dehydration, both easily adaptable to large-scale production, are described in this work: freeze drying and spray drying. After heat-treatment of the dried gels (xerogels) to remove loosely bound water they show a high capacity for lithium insertion, approaching four additional lithium per formula unit, and good reversibility as electrode materials for high energy density lithium cells. How the heat-treatment temperature influences the crystal structure is demonstrated as well as the electrochemical properties of the vanadium oxide.

Introduction

The layered trivanadate, LiV_3O_8 ,¹ is an interesting alternative to V_6O_{13} for use as the positive electrode in secondary lithium cells. The intercalation chemistry of this material was pioneered by Besenhard and Schöllhorn, who found it possible to insert lithium ions from a non-aqueous electrolyte² as well as a number of hydrated cations from aqueous electrolytes.³ Early in the development Nassau and Murphy⁴ realized that the methods used to prepare the oxide strongly influenced its electrochemical properties. They demonstrated that LiV_3O_8 prepared in an amorphous, glassy state by rapid quenching from the melt had a higher initial capacity than the crystalline analogue. These findings were, however, not pursued further in the next decade, where several research groups reported on the use of crystalline LiV_3O_8 as host material for lithium intercalation.⁵⁻¹⁷

High initial capacities were reported for low-rate discharges, the maximum lithium uptake corresponding to more than three additional Li per formula unit, giving a stoichiometric energy density in excess of 650 Wh/kg. There has been a rather large variation between the values for the maximal lithium uptake from different research groups, but in a structural characterization of lithium inserted $\text{Li}_{1+x}\text{V}_3\text{O}_8$, Thackeray *et al.*¹⁸ found that the multiplicity of the sites occupied by lithium in the fully intercalated trivanadate suggests the limiting composition $\text{Li}_5\text{V}_3\text{O}_8$. Recently, Manev *et al.* have shown how this value can be approached using a specially conditioned LiV_3O_8 material.¹⁹

The reported rate capability and cycling properties have, in general, not been satisfactory. Several preparation procedures have been devised to improve the performance of LiV_3O_8 , including control of stoichiometry by rapid cooling,¹⁶ more efficient grinding,²⁰ and addition of inert nucleation centers like silica or alumina to the melt.²¹ The main problem seems to be that on slow cooling, LiV_3O_8 crystallizes as a very hard and tough material, which is difficult to process into proper electrode structures that can maintain their integrity during deep cycling.

In 1990 Pistoia *et al.*²² reported that fully amorphous LiV_3O_8 obtained from a precipitation technique showed significantly higher capacity, better rate capability, and longer cycle life than conventionally made crystalline LiV_3O_8 . In the present paper we describe how an adaption of this sol-gel technique, combined with proper dehydration methods and heat-treatments, can lead to materials with a controlled degree of crystallinity and a particle morphology well suited to the processing steps involved in electrode fabrication. Our method is based on the dehydration of stable gels prepared from LiOH and V_2O_5 . These

gels are dehydrated to xerogels by spray drying or by freeze drying, and can be further dehydrated in a heat-treatment step.

The electrochemical characteristics of these materials are described, and compared with those of LiV_3O_8 made by the conventional high-temperature synthesis.

Experimental

An aqueous LiV_3O_8 gel was prepared following the procedure described by Pistoia *et al.*²² V_2O_5 (Werk Nürnberg, Analytical Grade) was slowly added to a stirred LiOH solution, the resulting concentrations of the two compounds being 0.75 and 0.5 M, respectively. The mixture was then heated to 50°C and stirred overnight. A dark red gel gradually formed. This gel is stable and does not convert to a sol or precipitate even when left for more than two years. In the present work the gel was dehydrated either by freeze drying²³ or by spray drying.²⁴

Freeze-dried material was made in quantities of up to 0.5 kg using a HETOSIC laboratory freeze dryer. Batches of 100 to 250 ml gel were frozen as 1 to 1.5 cm layers on the inside of cylindrical glass containers under rotation in a cold bath maintained at about -40°C. These containers were then attached to the freeze dryer and evacuated to 0.1 mbar. Sublimation of water kept the temperature of the gel well below its freezing point until all free water was removed and the gel converted to a highly porous, solid crust that could easily be reduced to a finely dispersed powder. The heat consumed during water sublimation was provided by convection of air; active heating was not applied. The as-prepared material contained up to about 20% water by weight.

For spray drying, a total amount of 14 liter gel prepared as described above, was used as the starting material. A centrifugal atomizer from Pasilac Anhydro A/S rotating at 50,000 rpm was used. The inlet temperature was set to 280°C, and the liquid feed rate was adjusted to give an outlet temperature of 120°C. The temperature of the material never exceeded the outlet temperature. The as-made product contained approximately 2% by weight of loosely bound water, determined from the weight loss observed on infrared heating to 150 to 200°C. The material reabsorbed water from humid air on standing.

Crystalline LiV_3O_8 was also prepared by the classical high-temperature route from a melt containing Li_2CO_3 and V_2O_5 . The mixture, in the appropriate molar ratio, was heated to 700°C and quench cooled to room temperature. Chemical analysis of all three products showed only traces of vanadium in oxidation states below five, and a ratio between Li and V close to 1:3.

Thermogravimetric analysis was carried out using a Perkin Elmer TGA7 with 5 to 10 mg samples and a scanning rate 10°C/min. The structure of the materials was

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probed by powder x-ray diffraction using a Siemens D5000 diffractometer ($\text{CuK}\alpha$ radiation).

Electrochemical characterization of the vanadates was performed in cells with metallic lithium as the negative electrode and either a liquid organic electrolyte (LiPF_6 in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), absorbed in porous polypropylene separators, Cellgard 2500] or a solid polymer electrolyte (LiCF_3SO_3 in polyethylene oxide, PEO). The positive electrode composites were made by solvent casting of suspensions of trivanadate and carbon onto nickel foils with PEO added as binder.

The cells were cycled galvanostatically between preset voltage limits. At the end of being charged, the cells were kept potentiostatically at the upper voltage limit until the current had decreased by 50 or 75%. This was done to ensure that the electrodes were in well-defined states at the start of each discharge. By numerical differentiation the corresponding "differential capacity," dx/dE , curves were obtained. For convenience the differential capacity during charge (lithium extraction) is plotted as positive values. In this way curves comparable with cyclic voltammograms are obtained.

In order to ascertain the amount of lithium inserted per formula unit of vanadate, the vanadium content of the cells was determined both by weighing the electrodes prior to cell assembly and by spectrophotometrical vanadium determination after completion of the cycling experiments.

Results and Discussion

Thermogravimetric analysis.—The freeze-dried xerogels typically contained 15 to 20% water by weight, and the product prepared by spray drying reabsorbed water from the atmosphere, eventually reaching a similar water content. Before using these materials as electrodes in lithium batteries, loosely bound water must be removed by the proper heat-treatment procedure in order to obtain reversible cell operation.

Figure 1 shows thermogravimetric (TG) curves for both types of lithium trivanadate xerogels. It is seen that water is lost in two distinct steps: the major part at temperatures

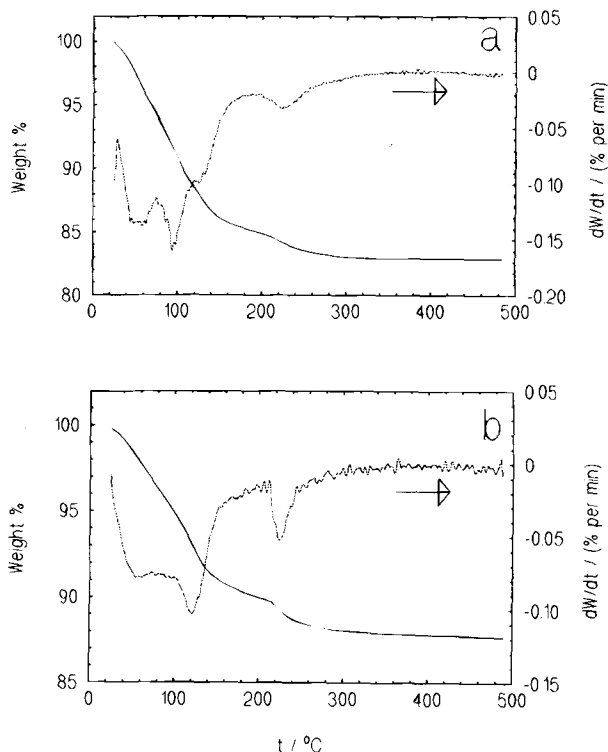


Fig. 1. Thermogravimetric curves for dehydration of lithium trivanadate xerogels made (a) by freeze drying and (b) by spray drying. Heating rate: $10^\circ\text{C}/\text{min}$.

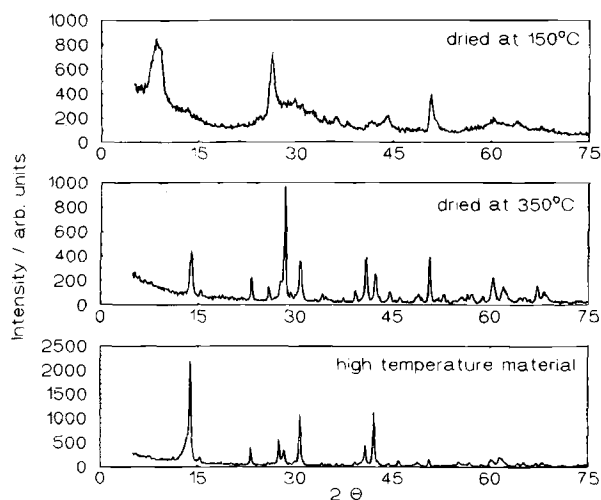


Fig. 2. X-ray diffractograms of heat-treated lithium trivanadate xerogels made by spray drying compared with the diffractogram of the material prepared at high temperature.

below 150 to 175°C , whereas a smaller part of the water, roughly corresponding to $0.5 \text{ H}_2\text{O}$ per LiV_3O_8 unit, is more strongly bound to the oxide and only released at temperatures above 200°C . The similarity between the TG traces for the two materials indicates that the water loss up to at least 120°C (the outlet temperature of the spray dryer) is fully reversible.

Based on these results, two sets of drying conditions were chosen for the further characterization of trivanadate xerogels: overnight heating in air to 150 and 350°C , respectively. Freeze-dried material heat-treated at 150°C contained 4.0% water by weight determined as the residual not accounted for by chemical analysis for lithium, vanadium, and the oxidation state of vanadium. Heat-treatment at this temperature for prolonged periods did not lead to further weight loss. A typical analysis of freeze-dried material heat-treated at 350°C showed it to be 99.7% pure $\text{Li}_{0.96}\text{V}_3\text{O}_{7.98}$, i.e., containing less than 0.3% water.

X-ray diffraction.—Figure 2 shows x-ray diffractograms of the spray-dried material heat-treated at 150 and 350°C , compared with a diffractogram of LiV_3O_8 prepared by the high-temperature route. The peak positions of the 350°C material coincides with the peak positions observed for the conventional high-temperature material, although the

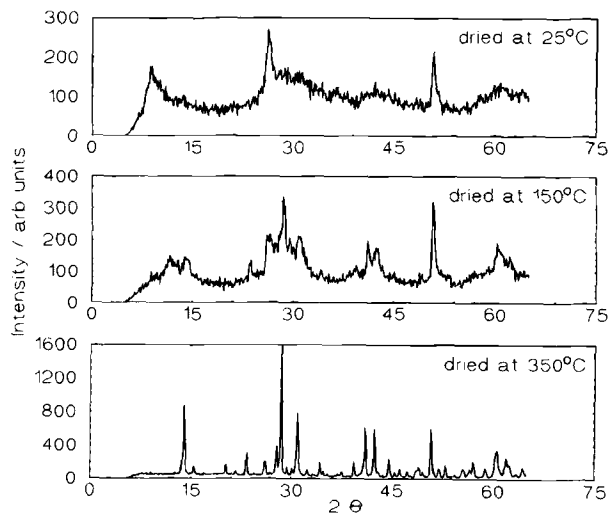


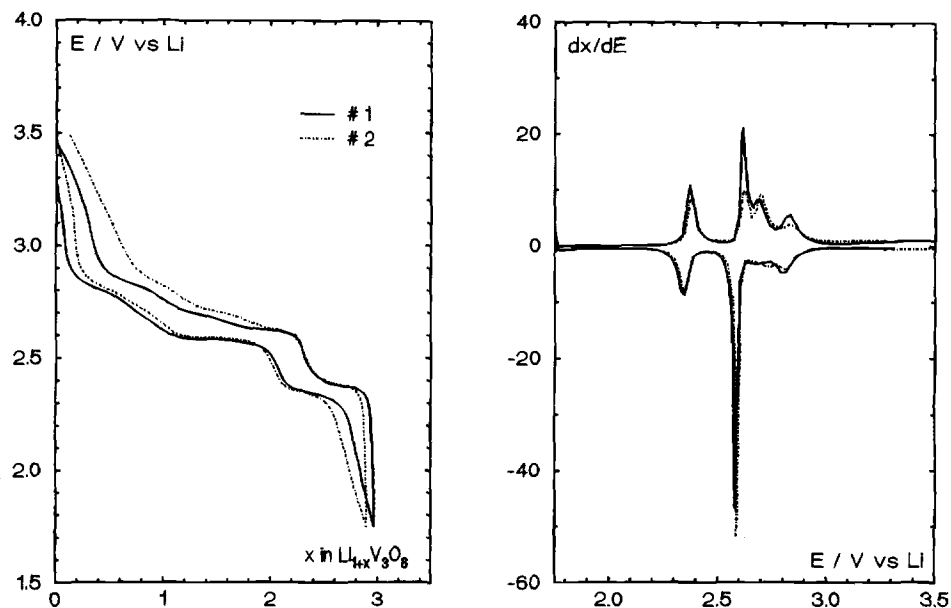
Fig. 3. X-ray diffractograms of lithium trivanadate xerogels made by freeze drying. The as-prepared material is compared with materials heat-treated at 150 and at 350°C .

Fig. 4. First two cycles of a cell with lithium trivanadate prepared at high temperature

Li | LiCF₃SO₃ - PEO (100°C) |

Li_{1+x}V₃O₈

The discharge and charge currents: 25.5 μ A/cm² corresponds to the load 4 h/x.



intensity distributions are quite different. The observed intensities for the high-temperature material are in good agreement with those reported by Wickham,²⁵ while the observed intensities for the 350°C material are better in accordance with calculated intensities based on Wadsley's¹ structure data, showing that the latter material is a well-crystallized material with isotropic, strain-free crystallites.

It is noteworthy that the (100) peak at $2\theta = 14^\circ$ is stronger than predicted in the material prepared at high temperature but is too weak in the 350°C material. This indicates a difference in the aspect ratio of the crystallites of these two materials. The high-temperature material is prepared by the crushing of larger crystallites, preferentially cleaved along the {100} planes corresponding to layers of VO_n polyhedra. Consequently the dimension of the crystallites in directions in the {100} plane will be considerably larger than in the out-of-plane directions, leading to relatively long diffusion paths for the lithium ions inserted between these planes. Preferential ordering of crystal platelets will lead to an enhancement of the measured intensities of (*n*00) peaks. In contrast, the 350°C material is prepared in a microcrystalline state that need

not be further reduced by grinding. The low intensity of the (100) peak indicates, that the dimensions of these crystallites in the {100} plane are relatively small.

The 150°C material is much less crystalline, showing rather few broad peaks at positions that do not correspond to the high-temperature crystalline modification of LiV₃O₈. The peak positions are consistent with the increase in interlayer spacing, from 6.36 to 9.82 Å, reported by Schöllhorn *et al.*³ as the result of the uptake of water in the interlayer spacing between neighboring V₃O₈ sheets. The number of peaks is, however, too small to allow a positive identification of the structure.

Figure 3 shows that the freeze-dried material undergoes the same structural transition upon dehydration, and that even the as-prepared material, containing nearly 20% water by weight, has some degree of long-range order.

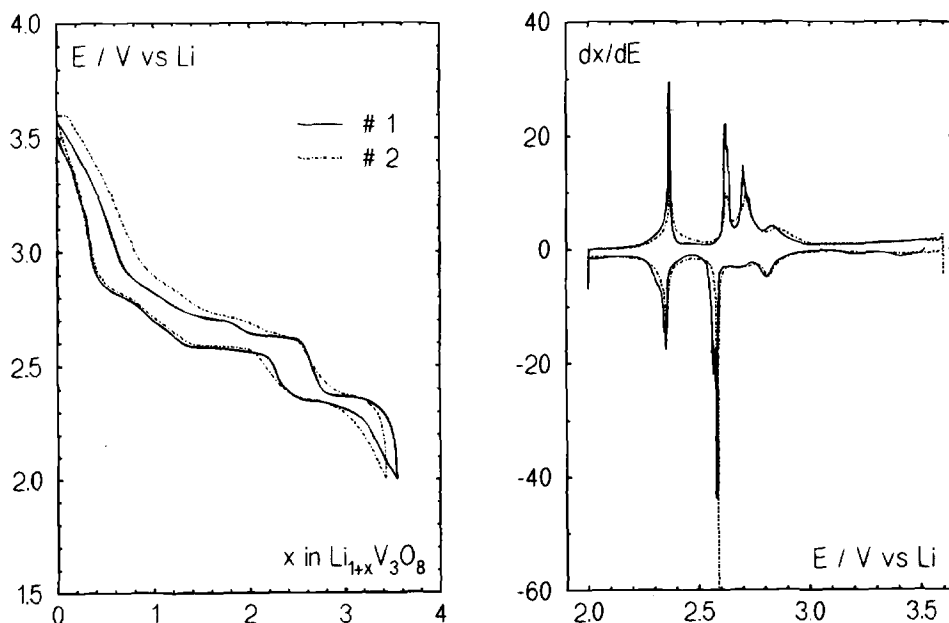
Electrochemical lithium insertion.—The characteristic voltage curve for cycling of crystalline Li_{1+x}V₃O₈ is illustrated in Fig. 4, showing the voltage (*E*) variation as a function of the overall lithium composition (*x* in Li_{1+x}V₃O₈). The "differential capacity" (*dx/dE*) calculated

Fig. 5. First two cycles of a cell with lithium trivanadate prepared from freeze-dried xerogel, heat-treated at 350°C

Li | LiCF₃SO₃ - PEO (100°C) |

Li_{1+x}V₃O₈

The discharge and charge currents: 6.4 μ A/cm² corresponds to the load 11 h/x.



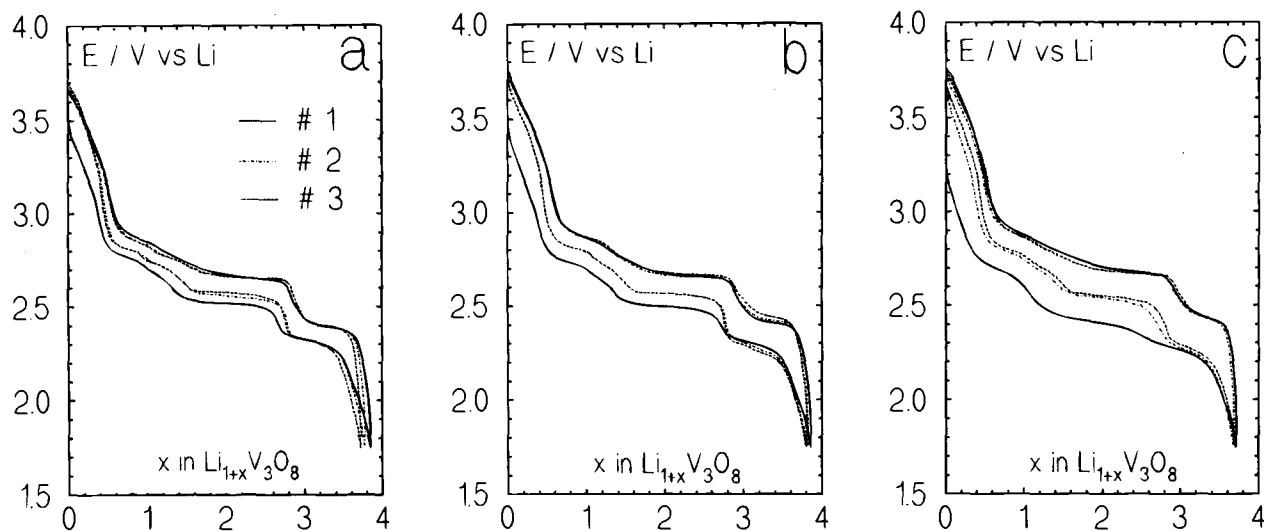


Fig. 6. Discharge/charge cycles of cells with lithium trivanadate prepared from spray-dried xerogel, heat-treated at 350°C

Li | LiPF₆ - EC-DEC (25°C) | Li_{1+x}V₃O₈

The discharge and charge currents: (a) 20 μA/cm² (corresponding to the load 23 h/x); (b) 80 μA/cm² (5 h/x); and (c) 200 μA/cm² (2 h/x).

from the voltage variation is also shown on the figure, as this curve emphasizes the details of the voltage curve. The cell was cycled at 100°C with a polyethylene oxide (PEO) based electrolyte in order to exclude possible effects of solvent intercalation,^{15,17} and to accelerate the lithium insertion kinetics. In this material lithium insertion proceeds as a single-phase reaction up to $x = 1$, and then through a two-phase region and another single-phase region until the limit for reversible lithium uptake is reached. Two-phase reactions show up in voltage curves as regions where the potential is independent on the composition, and in capacity curves as high, narrow peaks without any overlap of the potentials covered by the peaks in the cathodic and the anodic scans. A close examination of the potential plateau occurring between $x = 2$ and $x = 3$ shows that this is not a genuine two-phase region, but it is a region with a strong guest-host interaction resulting in a very flat potential *vs.* composition relationship. At lower temperatures two-phase behavior is observed in this composition region as well.

Lithium vanadate xerogels heat-treated at 350°C behave very similar to the high-temperature crystalline

material as illustrated for the freeze-dried material on Fig. 5. At the low rate used here a good reversibility is obtained, and it is seen that despite the small loss of capacity from cycle one to cycle two, the changes in the shape of the voltage curves of these cycles are insignificant, illustrating the basic reversibility of the lithium insertion reaction. The differential capacity curve shows that lithium insertion proceeds as a two-phase reaction also at compositions above $x = 2$. Although the maximum lithium uptake varies from sample to sample, freeze-dried material heat-treated at 350°C generally shows higher lithium capacities than the material prepared by the high-temperature route. Cells cycled at 25°C with liquid organic electrolyte showed similar results to those reported here for cells cycled at 100°C with polymer electrolyte.

The highest lithium uptake, close to four additional Li per formula unit, was found with the spray-dried material, as illustrated on Fig. 6 for cells cycled at room temperature. The high capacity was maintained even under fairly high current loads, and was at room temperature associated with a kinetic effect not previously described

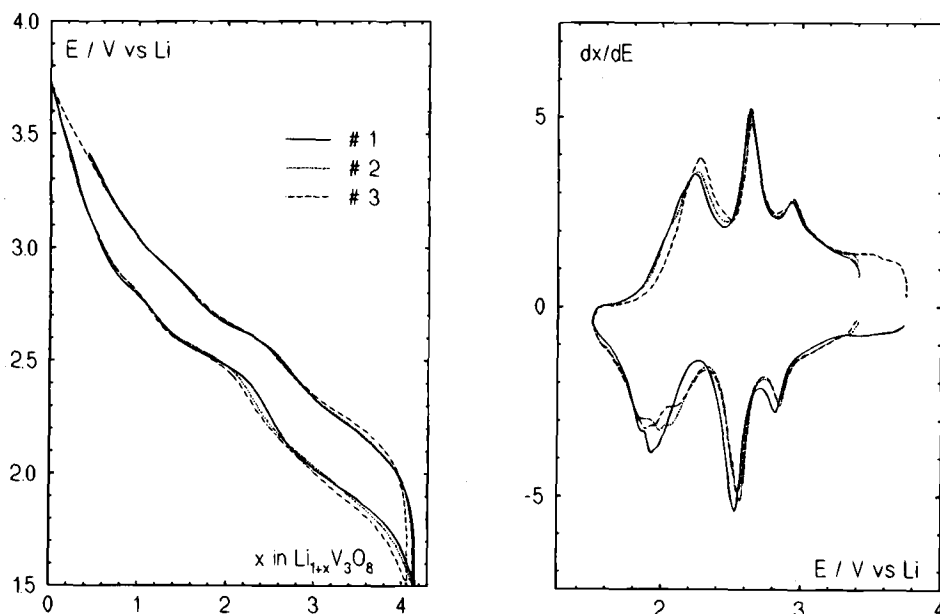


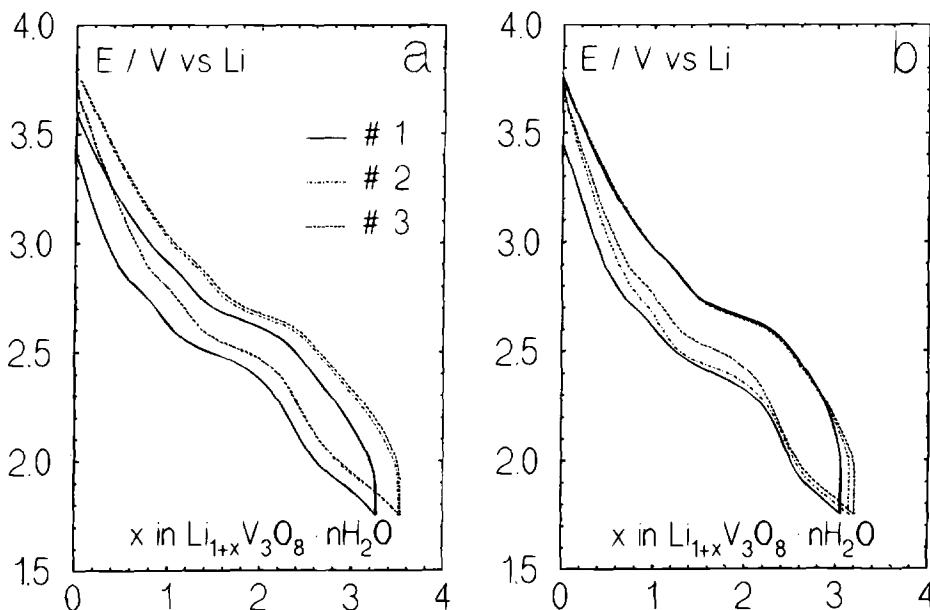
Fig. 7. First three cycles of a cell with lithium trivanadate prepared from spray-dried xerogel, heat-treated at 150°C

Li | LiPF₆ - EC-DEC (25°C) | Li_{1+x}V₃O₈

The discharge and charge currents: 32 μA/cm² corresponds to the load 19 h/x.

Fig. 8. Discharge/charge cycles of cells with lithium trivanadate prepared from spray-dried xerogel, heat-treated at 150°C

Li | LiPF₆ - EC-DEC (25°C) |
Li_{1+x}V₃O₈
The discharge and charge currents: (a) 80 μ A/cm² (5 h/x);
and (b) 200 μ A/cm² (1.5 h/x).



for lithium insertion into trivanadates. At high rates, the first discharge is associated with a rather high overvoltage, see Fig. 6b and c. At the composition corresponding to the onset of the last voltage plateau on the discharge curve, this overvoltage suddenly decreases, and the lower value is maintained throughout the rest of the cycle life of the cells. The nature of the transition leading to the decrease in overvoltage is not understood, but it is remarkable that it is not associated with a capacity decrease, as is often seen with similar effects in other oxides.

Lithium vanadate xerogels heat-treated at 150°C behave differently from what was described above, see Fig. 7. The voltage plateaus indicating two-phase transitions are absent, and the voltage range spanned is larger, discharge down to 1.5 V vs. Li is necessary in order to reach the saturation composition corresponding to the insertion of four additional Li per formula unit. Comparison of the differential capacity curves of the materials heat-treated at 350 and at 150°C (Fig. 5 and 7) shows that lithium insertion in these materials apparently proceeds through the same set of steps. A slight shift in peak positions show that lithium is inserted into sites that are similar but not identical, which is consistent with the increased interlayer spacing and the presence of bound water in the material heat-treated at 150°C. The capacity peaks are very broad, indicating that there is a distribution of site energies available for lithium insertion in this material, a common feature of highly defective or poorly crystalline materials. The rate capability of the 150°C material is fair, as a load corresponding to 1.5 h/x generates an overvoltage less than 200 mV, decreasing slightly when the cell is cycled, see Fig. 8. The overvoltage is largest at deep discharge and will severely limit the capacity at higher rates.

Both materials cycle well in laboratory cells, with capacity losses well below 0.5% per cycle in the first 50 cycles. It should be noted that these electrodes and cells are not optimized for cycling, and that more extensive cell tests would be required to resolve whether the presence of bound water in the low temperature material influences the cycle life of cells with this material.

Conclusion

This work describes the production of lithium trivanadate LiV₃O₈ in a semi-industrial scale from aqueous gels dehydrated to poorly crystalline xerogels by either freeze drying or spray drying. Both these drying methods are well suited for large scale industrial production, and the resulting xerogels can easily be reduced to finely dispersed powders with favorable electrochemical properties.

For the use as electrode materials in lithium batteries, the xerogels must first be subjected to a heat-treatment. It is shown here that the xerogel undergoes a structural transition when heat-treated above $\approx 225^\circ\text{C}$, leading to a material with the same crystal structure as Li_{1+x}V₃O₈ prepared by the conventional high-temperature synthesis. The material obtained by the xerogel route is, however, better suited as a lithium inserting electrode material, having higher capacity, better rate capability, and longer cycle life. This is thought to be a consequence of the difference in aspect ratio of the crystallites of these materials: on reduction of the particle size of the high-temperature material, it is preferentially cleaved along the (100) planes. This results in relatively long diffusion paths and an increased risk of excluding parts of the interior of the particles for lithium ions by crystal defects blocking the two-dimensional diffusion zone. The xerogel material, however, is directly prepared with a small particle size and short, unblocked diffusion paths, leading to capacities approaching the theoretical amount, four additional Li per formula unit. An analogous effect is known for V₆O₁₃, where the extensively defect nonstoichiometric material with short diffusion paths has a much higher capacity than the highly crystalline material with long, one-dimensional diffusion paths.²⁶ In practical electrodes, only 90% of the theoretical capacity of V₆O₁₃ can be cycled reversibly at reasonable rates.²⁷

The material heat-treated at lower temperatures is less crystalline, and has a crystal lattice with an increased interlayer spacing, possibly due to the presence of bound water in the interlayer space. The structure could not be refined from the poorly resolved x-ray diffractograms, but the differential capacity curves show, nevertheless, that lithium ions are still inserted at three distinct sets of lattice sites, apparently similar to the sites occupied in the material heat-treated at 350°C.

The similarity between results obtained from cells with and without a mobile electrolyte solvent indicate that solvent cointercalation does not occur readily in these materials (cf. Ref. 15 and 17). This is further substantiated by results obtained with a propylene carbonate plasticized polymer.^{28,29} The very high capacities (9 Li per 2LiV₃O₈) reported for the completely amorphous modification²⁰ were not observed in this work.

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An Investigation of Lithium Ion Insertion into Spinel Structure Li-Mn-O Compounds

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ABSTRACT

Two kinds of spinel structure lithium manganese oxides obtained by a melt-impregnation method were examined in a lithium nonaqueous cell. The first type shows a voltage profile of a typical spinel electrode with the characteristic two-step process, which delivers a larger capacity, but fading capacity on cycling (type I). The other type delivers a slightly lower capacity and has ideal rechargeability with a quasi-one-step process (type II). The mechanism of the lithium ion insertion into the spinel compound was studied by several physical and chemical methods (differential chronopotentiometric curves, cyclic voltammetry, and open-circuit voltage measurement). X-ray diffraction was also used to investigate the structural changes for both types of compounds at different oxidation depths at first charge. The results show that a two-phase reaction (cubic $a_0 = 8.154 \text{ \AA}$ and $a_0 = 8.072 \text{ \AA}$) occurred in the range of $0.1 < x < 0.45$, and a one-phase reaction [cubic $a_0 = 8.163$ to 8.247 \AA] occurred in the range of $0.45 < x < 1.0$ for the first charge for the type I spinel. A one-phase reaction (cubic $a_0 = 8.105$ to 8.223 \AA) was observed over the entire intercalated range of $0.25 < x < 1.04$ for the type II spinel compound. The capacity fading on cycling for the type I spinel occurs only in the range of $0.1 < x < 0.45$, where the shape of the charge and discharge curves in this range was gradually changed to an S-shape from and L-shape during cycling. This is attributed to the fact that the two-phase structure is transformed to more stable one-phase structure.

Introduction

It has been demonstrated that spinel structure lithium manganese oxides are most promising cathodes for "lithium ion" batteries because they are cheaper, less toxic, and more easily prepared than other candidates (nickel and cobalt oxides). An important problem prohibiting them from wider use as a cathode for lithium ion batteries is the unstable rechargeability. Despite this, the rechargeability has been greatly improved by several research groups.¹⁻⁵ These compounds deliver a rechargeable capacity of about 120 mAh/g. However, a gradual capacity loss was also

observed over cycling. This behavior was attributed to the fact that the $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode slowly dissolves into the electrolyte solution due to the disproportionation reaction $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$.^{5,6} Most research has been directed toward reducing the capacity fading by doping the spinel with another ion, such as Co, Ni, Fe, and Mg, to $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$. Great improvement in rechargeability on cycling was obtained for these compounds, but they deliver a slightly lower initial capacity.⁷⁻⁹ The goal of the modified cathode originally was to reduce the cathode solubility.^{6,7} In the course of extensively studying of the spinel structure compounds, we found that the capacity fading upon cycling of the cell occurred only during the second step (4.16 V plateau in charge curve) for stoichiometric

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