LITHIUM/LITHIUM VANADIUM OXIDE SECONDARY BATTERIES IV. EVALUATION OF FACTORS AFFECTING THE PERFORMANCE OF TEST CELLS

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Summary

With the aim of optimizing the performance of $Li/Li_{1+x}V_3O_8$ cells, several aspects of cathode preparation have been examined. The influence of synthesis technique, nature and amount of conductive additives, compacting pressure, cathode loading, and particle size, has been investigated. Furthermore, the role played by the solutions on cathode efficiency has been outlined. The formulations which perform best are based on small-sized particles blended with about 20% acetylene black and compacted at very high pressures to improve the contact between particles. Such cathodes can provide high capacities at high rates and good cycling efficiencies. The kinetic loss of capacity, observed during the first few cycles, may be alleviated by choosing solutions with high fluidity and conductivity.

Introduction

In previous papers [1 - 3], $Li_{1+x}V_3O_8$ has been shown to possess a number of features which make it one of the most promising cathode materials for secondary cells.

The relevant thermodynamic and kinetic aspects of the mechanism of Li^+ uptake by this compound have been elucidated. In particular, such characteristics as:

(i) high capacity (stemming from the possibility of accepting up to 3 Li^+/mol);

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(ii) high rate capability (connected to a high $\tilde{D}_{Li^+}$);

(iii) long cycle life (due to an outstanding structure stability), were highlighted.

A more technological approach to the investigation of this material now seemed to be necessary. This would include an evaluation of the performance of relatively small test cells and a subsequent scaling up to cells of practical dimensions.

In the present work we have tried to accomplish the first task, hoping that the results might constitute a good basis for the second one. To this end, relatively thick electrodes, reduced electrolyte volumes, and high rates have often been used. These conditions are not too far from those in large size cells.

Experimental

Lithium vanadium oxide ($Li_{1+x}V_3O_8$) preparation

This was synthesized using different techniques (see Table 1) [4]. When prepared in air, Li_2CO_3 and V_2O_5 (obtained by decomposing NH_4VO_3 at 500 °C) were used. When using evacuated quartz ampoules, V_2O_5 was mixed with $LiVO_3$. After standing for 24 h at the temperatures given in Table 1, the melt was slowly cooled to room temperature; the possible influence of fast cooling was also evaluated. The samples were then ground and sieved and, unless otherwise stated, only that fraction passing through a 400 mesh sieve (grain size < 38 μm) was used. $Li_{1+x}V_3O_8$ is insensitive to moisture (even when lithiated) and can be handled in air. Its formula has been shown to be close to $Li_{1.2}V_3O_8$ [3], which agrees with the results of other authors [4 - 6]. The BET surface area of the sample prepared at 680 °C in air was found to be 3.2 m^2/g.

TABLE 1

Influence of the synthesis technique on the initial capacity
Current density: 1 mA/cm^2. 1.9 V cut-off

Temperature (°C)	Atmosphere	Specific capacity (A h/g)
680	air	0.21
680	evacuated quartz ampoules	0.20
545	air	0.19
560	O$_2$ stream	0.15

Salt and solvent purification

"Anhydrous" $LiClO_4$ was melted at 300 °C under vacuum to remove H_2O; the $LiAsF_6$ (U.S. Steel Agri-Chemicals) was used without further purification.

Propylene carbonate (PC) and ethylene carbonate (EC) were distilled under vacuum without additives, while dimethoxyethane (DME) was distilled under argon after standing some days over LiAlH$_4$. Dioxolane (DOL) and methyl formate (MF) were distilled on molecular sieves under argon.

All the solvents were stored in a dry box on molecular sieves after purification. Karl Fischer titrations indicated an H$_2$O content below 100 ppm for all solutions. Where not otherwise indicated, a 1M LiClO$_4$–PC/DME (1/1) solution was used.

Cathode preparation

Li$_{1.2}$V$_3$O$_8$, Teflon and conductive diluent were ball milled to obtain an homogeneous mix for pressing on a nickel exmet. Shawinigan acetylene black (high density) was mostly used for the diluent, but battery grade carbon (supplied by Ensagri, Willebroek, Belgium), and graphite (supplied by Lonza, Basle, Switzerland) were also tested. Unless otherwise indicated, a typical mixture was obtained by blending 70% Li$_{1.2}$V$_3$O$_8$ with 30% of a 2:1 acetylene black/Teflon composite and, except for a few experiments, the mixture was pressed at 0.8 - 1.0 ton/cm^2.

Some cathodes were also prepared by rolling, *i.e.*, a nickel net containing a hand pressed mixture was passed between properly spaced rollers.

Cell preparation

Prismatic glass cells, shaped so as to accommodate the electrodes and the separators without needing an excess of electrolyte, were used. Typical volume to cathode ratios were 0.3 - 0.4 cm^3/mA h. Lithium (supported on Ni) was in large excess compared with the cathode capacity to limit the effect of the Li cycling efficiency on the cell performance. A double layer of glass wool separator was wrapped round the Li anode which was "U" shaped around the cathode. The latter, typically, had an area of 2.5 cm^2 (both faces) and contained 50 - 100 mg of active material (10 - 20 mA h). The cells were galvanostatically cycled between preset voltage limits.

Details of the chemical lithiation, the $\tilde{D}_{Li^+}$ measurements and the X-ray diffractometry experiments have been reported previously [2].

Results and discussion

For almost all the experiments carried out in this work, the cell behaviour was evaluated for several charge–discharge cycles. The performance during the 1st cycle matched that of subsequent cycles, with one partial exception, which will be mentioned later, in connection with an LiAsF$_6$–MF solution. Therefore, for brevity, only 1st cycle results will be reported. The capacity data always refer to the cathode active material only.

Influence of the Li$_{1+x}$V$_3$O$_8$ synthesis technique

As shown in Table 1, the highest capacity was obtained by heating stoichiometric amounts of Li$_2$CO$_3$ and V$_2$O$_5$ to a temperature somewhat

higher than that which corresponds to the solid state reaction of the formation of $Li_{1.2}V_3O_8$ (so called γ phase), *i.e.*, 500 - 600 °C [4]. This is in agreement with the observation that the crystals obtained from the melt have compositions closer to stoichiometry, *i.e.*, Li^+ excess is limited so that the V oxidation state approaches 5 [4]. The sample obtained in O_2 at 560 °C (to limit possible Li_2O losses, and therefore to reduce departures from stoichiometry) has a surprisingly low capacity: no explanation for this is yet available. All of the samples showed very similar X-ray powder patterns.

No difference in the electrochemical behaviour was found between samples obtained from melts rapidly cooled in air and those slowly cooled. Their X-ray diffractograms also showed no appreciable dissimilarities, even in terms of their degree of crystallinity.

In an attempt to remove excess Li^+ ($\sim$0.2 Li^+/mol), thus increasing the V^{5+} content in comparison with V^{4+}, some samples were treated with a solution of dichlorodicyanobenzoquinone (DDQ) in acetonitrile. No improvement in performance was found. This matches analogously attempted electrochemical oxidation and suggests that these Li^+ ions are too strongly bound to the lattice to be removed at ordinary potential levels.

Influence of additives

$Li_{1+x}V_3O_8$ is a semiconductor whose resistivity is of the order of 10^3 ohm cm, which increases linearly with lithiation (as shown in Fig. 1), to 10^7 ohm cm. The addition of conductive diluents is therefore essential, and the influence of their nature and amount was evaluated. In Table 2 some results are given which show the superiority of acetylene black over battery grade carbon and graphite. We believe it is likely that this results from the different surface areas (BET area: $\sim$70, $\sim$40, and $\sim$15 m^2/g for acetylene black, carbon and graphite, respectively). A higher porosity is forecast for cathodes containing acetylene black, thus resulting in the advantages known to accrue.
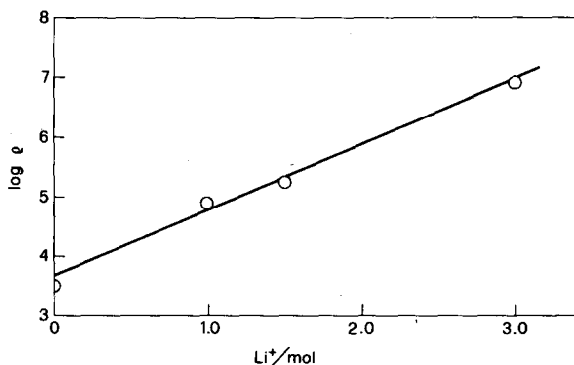

Fig. 1. Specific resistivity of $Li_{1.2+x}V_3O_8$ as a function of the degree of lithiation. Pellets pressed at 1.3 tons/cm^2.

TABLE 2

Influence of the types of additives (30% of total cathode weight) on the initial capacity
Current density: 3 mA/cm^2. 1.6 V cut-off

Additives	Specific capacity (A h/g)
Acetylene black*/Teflon(1/1)	0.18
Acetylene black/Teflon(2/1)	0.18
Acetylene black/Teflon(3/1)	0.19
Carbon black**/Teflon(3/1)	0.16
Graphite***/Teflon(3/1)	0.13

*Shawinigan high density.
**Ensagri type "Super S".
***Lonza KS 15.

TABLE 3

Influence of the active material/additives ratio on the initial capacity
1.6 V cut-off

Amount of acetylene black/Teflon(2/1) (%)		Specific capacity (A h/g)
3 mA/cm^2*	20	0.095
	30	0.18
	40	0.18
10 mA/cm^2 **		
x% in (Li$_{1.2}$V$_3$O$_8$ + x% acetylene black)***		
	20	0.11
	30	0.12
	40	0.13

*In LiClO–PC/DME.
**Rolled cathodes in LiClO$_4$–EC/DME.
***Plus 10% Teflon in all formulations.

It may be noted that the performance is only slightly increased on vary-
ing the acetylene black/Teflon ratio between 1:1 and 3:1. The results given
in Tables 2 and 3 indicate that an Li$_{1.2}$V$_3$O$_8$:C ratio of 5:1 is sufficient for a
good performance, even at high rates. On the other hand, lower values did
not give useful cathode efficiencies. With 10% acetylene black/Teflon
(Li$_{1.2}$V$_3$O$_8$:C = 13:1) no appreciable capacity could be drawn at 3 mA/cm^2,
whereas with 20% of this mixture the capacity was still rather low (see Table
3). In cycling experiments at relatively high rates (> 2 mA/cm^2) it was ob-
served that mixtures containing 30% teflonized acetylene black (Li$_{1.2}$V$_3$O$_8$:C
= 3.5:1) gave higher efficiencies. Therefore, for most of the experiments, the
cathode mix containing 70% Li$_{1.2}$V$_3$O$_8$ was chosen.

TABLE 4

Influence of particle size on the initial capacity
Current density: 1 mA/cm^2. 1.9 V cut-off

Size interval	Specific capacity (A h/g)
$\mu < 38$	0.21
$38 < \mu < 74$	0.17
$74 < \mu < 150$	0.15

Influence of particle size

To investigate the effect of cathode porosity on cell performance further, Li$_{1.2}$V$_3$O$_8$ of different particle sizes were used. The results are shown in Table 4, and the improvement obtained when using particles passing through a 400 mesh sieve is noticeable. As demonstrated by Atlung [7], a material simultaneously endowed with high $\tilde{D}_{Li^+}$ and small average particle radius may give high utilization efficiencies.

It was shown previously [2] that about 3 eq Li$^+$/mol could be accepted by Li$_{1.2}$V$_3$O$_8$ both chemically (BuLi) and in a low rate discharge. However, at rates above 1 mA/cm^2, utilizations greater than 70 - 80% of this capacity could not be achieved. This is probably a consequence of the nucleation of a new phase for Li$^+$ uptakes greater than about 1.8 Li$^+$/mol [3]. Such a process at ambient temperature is necessarily slow and it is likely to bring about a further overvoltage due to a crystallization polarization.

Influence of cathode density

The model recently developed by Atlung to account for the behaviour of porous electrodes [8] assigns the role of capacity limiting factor to electrolyte depletion in the pores. Especially at high current density, the inner parts of the cathodes may become starved of electrolyte, thus explaining the higher efficiencies given by thin electrodes.

Our experiments with electrodes of different thickness and, as will be shown later, with different electrolytes confirm the need for a proper Li$^+$ supply throughout the channels formed by the pores. For the present electrodes, however, we noticed a limited capacity decrease with cathode loading. In Fig. 2 this is shown for a current density of 10 mA/cm^2. In the range 20 - 100 mg/cm^2, a decrease of 7% only was observed. This points to the satisfactory availability of Li$^+$ ions, even for the innermost layers, in connection with a good porosity ($\sim$ 32% at 0.8 tons/cm^2).

The capability to sustain high current drains was confirmed with the experiments reported in Fig. 3. With cathodes of 40 mg/cm^2 of active material acceptable capacities were still obtained at up to 20 mA/cm^2. This would not be possible unless both the macroscopic (in the electrode pores) and the microscopic (in the lattice sites) Li$^+$ transport were fast. It was
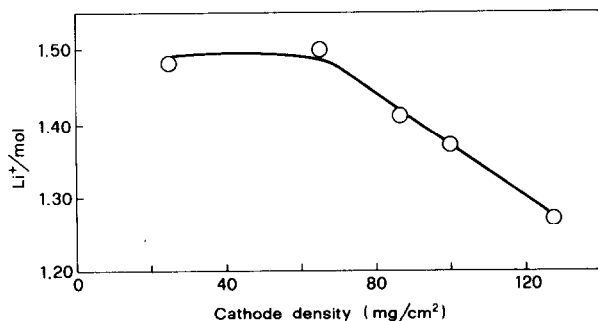
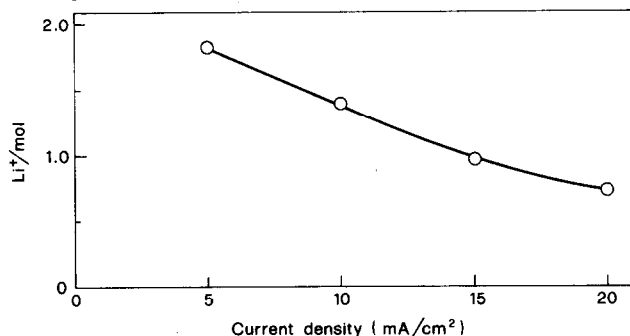Fig. 2. Dependence of cell capacity on cathode density (active material only). Current density: 10 mA/cm^2.

Fig. 3. Cell capacity at high discharge rates. Electrolyte: 1M LiClO$_4$–EC/DME (1/1). Cathode density: 40 mg/cm^2, rolled electrodes.

previously shown that $\tilde{D}_{Li^+}$ is 10^{-8} - 10^{-9} cm^2 s^{-1} in the range $0 < Li^+/mol < 1.5$ [2], thus allowing fast jumping of Li$^+$ between the tetrahedral sites available in the structure.

Influence of the electrolyte

The possibility that the internal grains of the cathode are being supplied with Li$^+$ ions correlates with the transport properties of the solution. Atlung demonstrated that the performance of a porous electrode is optimized by choosing electrolytes with a transport number for the cation as close to unity as possible [8]. We may add that these electrolytes must possess such prerequisites as high fluidity and high conductivity. The first prerequisite is given by low-viscosity solvents, and the second by solvents of high dielectric constant. They can obviously be present at the same time in a solution. In this case the solution would easily flow through the capillaries formed by the porous mat, so reaching the innermost layers. If the conductivity is also high, Li$^+$ would be made more readily available, the more so with a high Li$^+$ transport number.

We have obtained confirmation of this reasoning from results in various electrolytes (Table 5). The most fluid and conductive solutions give good capacities, even at -14 °C. At room temperature, the highly fluid and con-

TABLE 5

Influence of solution type on the initial discharge capacity
1.6 V cut-off

Solution	Specific conductivity* (ohm^{-1} cm^{-1})	Specific capacity (A h/g)
−14 °C; 1 mA/cm^2		
0.5m LiClO$_4$–PC	1.6	0.052
0.9m LiClO$_4$–PC/DME(28/72)	7.4	0.13
1.0M LiClO$_4$–EC/DME/DOL(1/1/1)	8.7	0.13
25 °C; 3 mA/cm^2		
1.0M LiClO$_4$–PC	5.6	0.15
1.0M LiClO$_4$–PC/DME(1/1)	12.0	0.18
2.0M LiAsF$_6$–MF	42.4	0.19

*Literature data at the specified temperature.

ductive LiAsF$_6$–MF electrolyte shows little improvement over the standard LiClO$_4$–PC/DME solution. On cycling, however, this difference is enhanced, thus forming the above-mentioned exception to the rule that the 1st discharge is typical of later cycle behaviour. As shown in Fig. 4, Li$^+$ uptake is still above 1.5 Li$^+$/mol by the 35th cycle in LiAsF$_6$–MF, while it has dropped to 1.0 Li$^+$/mol in LiClO$_4$–PC/DME. We noticed that the former solution allows better recharge efficiencies to the 3.5 V cut-off. Unfortunately, its tendency to turn yellow with cycling does not encourage its use in a secondary cell. Its performance testifies, however, to the fact that the main shortcoming presented by cathodes based on Li$_{1+x}$V$_3$O$_8$, i.e., loss of capacity during the first few cycles, due to an incomplete recharge, may be overcome by solutions of better fluidity and conductivity. As good results have often been reported for cycling experiments with fluid and moderately conducting solutions, such as LiAsF$_6$–2MeTHF [9], one is led to attribute greater importance to the first factor.
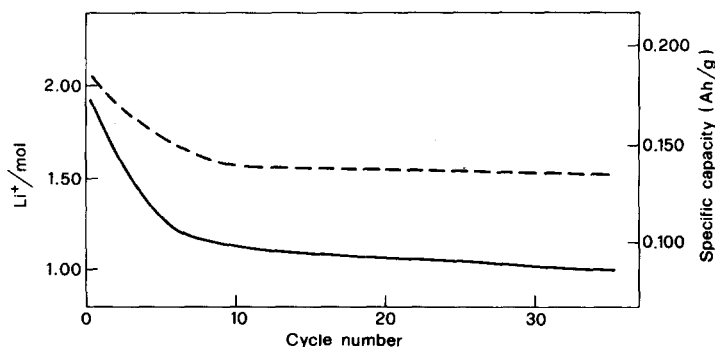

Fig. 4. Influence of the electrolyte on the initial cycling behaviour. ———, 1M LiClO$_4$–PC/DME; − − −, 2M LiAsF$_6$–MF. Current density: 3 mA/cm^2 during discharge, 2 mA/cm^2 during charge.

Influence of compacting pressure

As diffusion of the solution into the pores requires a suitable porosity, we attempted to improve it by decreasing the compacting pressure below the usual $0.8 \cdot 1.0$ tons/cm^2 but, higher capacities were not obtained, as shown in Fig. 5. To investigate this aspect further, the effect of higher pressures was also evaluated. The cell performance was improved even at pressures above 10 tons/cm^2. This was surprising: to our knowledge, there are no reports in the literature of such behaviour, which therefore appears to require more detailed investigation. In the meantime, we compared two pellets containing 30% acetylene black/Teflon and compacted at 0.8 and 11 tons/cm^2, respectively. Increasing the pressure showed that: (a) the resistivity increased slightly; (b) the porosity only decreased by 17% (from 32% to 15%). If a favourable effect of pressure on conductivity is discarded, a possible explanation accounting for the improved performance at 11 tons/cm^2 must be based on the assumption that at this pressure there is better particle-to-particle contact. The scanning electron microscope (SEM) pictures of Fig. 6 show that the grains, still distinguishable after low pressure compaction, are fractured and closely wedged when the higher pressure is used. Since the porosity still remained sufficiently high to allow solution penetration, the risk of particle isolation was greatly diminished, thus increasing the material utilization.
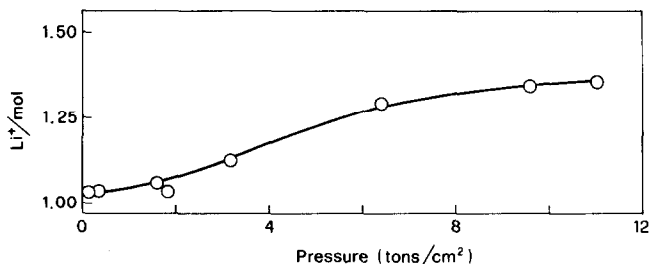

Fig. 5. Influence of cathode compacting pressure on the cell capacity at the 10th cycle. Current density: 3 mA/cm^2 during discharge, 2 mA/cm^2 during charge.

Cell failure mode upon cycling

To conclude this investigation on small test cells, we tried to determine some of the factors causing cell failure on cycling. A cell was cycled with 2 mA/cm^2 during discharge and 1 mA/cm^2 during charge (Fig. 7). The capacity levelled off to about 1 Li$^+$/mol after about 40 cycles and started to decrease rapidly after about 320 cycles. At this point the Li anode, solution, and separator were replaced without any improvement in the performance. A complete recharge at very low rate was accepted by the electrode but the subsequent discharge at 2 mA/cm^2 was again poor. In an attempt to discriminate macroscopic from microscopic factors, $\tilde{D}_{Li^+}$ was measured throughout the cycling experiment and an X-ray analysis of the cycled cathode was made. $\tilde{D}_{Li^+}$ matched the capacity trend very closely and, in particular, showed a sudden drop at cell failure. At first sight this would indicate
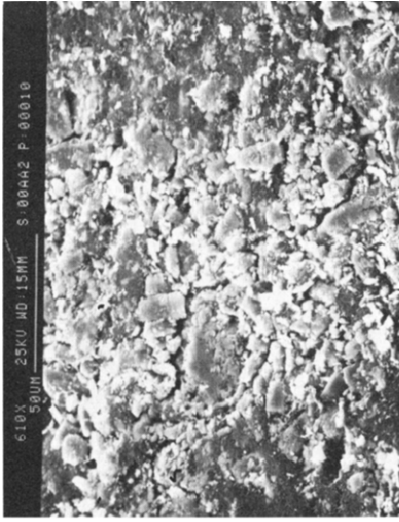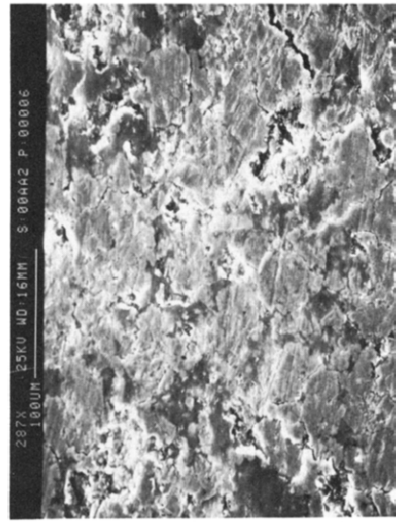
(a)
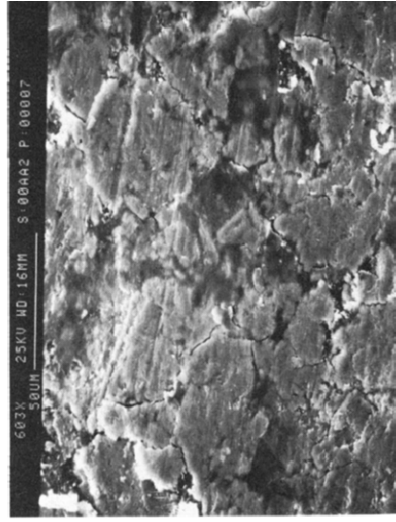
(b)

(c)

(d)

Fig. 6. Scanning electron microscope pictures of $Li_{1.2}V_3O_8$ + 30% acetylene black/Teflon (2/1) pressed at 0.8 tons/cm^2 (a) and (b) and at 11 tons/cm^2 (c) and (d). Magnifications indicated in each picture.
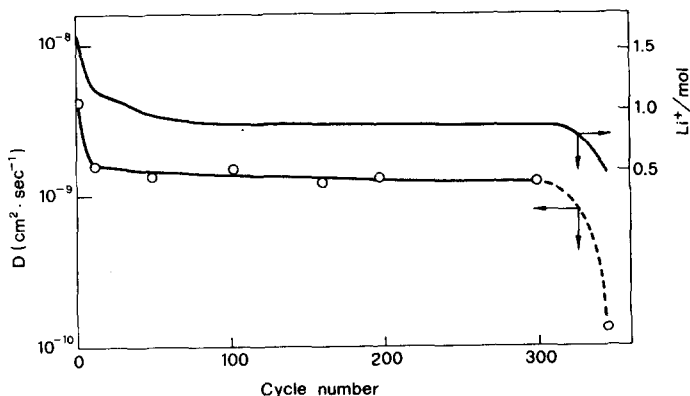
Fig. 7. Cell capacity and Li$^+$ diffusion coefficient in a long cycling experiment. Current density: 2 mA/cm^2 during discharge, 1 mA/cm^2 during charge.

limited diffusion within the crystal lattice. It seems rather improbable, however, that this should occur so late in life and in a layered structure with no constrictions which could eventually become blocked. Furthermore, X-ray analysis (Fig. 8) confirmed the structure retention of the lithium vanadium oxide with the appearance of a new peak only (at $2\theta = {\sim}16.5°$). We believe that cell failure and $\tilde{D}_{Li^+}$ decrease are associated with alterations of the cathode at the macroscopic level such as:

(i) surface coating by insulating decomposition products from the electrolyte;

(ii) loss of contact (isolation) of some particles (the cathode was pressed at 0.8 tons/cm^2).

The first effect was mentioned by Shen *et al.* [10], who also found a similarity between cell capacity and $\tilde{D}_{Li^+}$ for TiS$_2$ electrodes cycled in LiAsF$_6$–3-methylsulfolane. The second effect was referred to as a major cause of the capacity loss of Li/Cr$_{0.5}$V$_{0.5}$S$_2$ cells [9].
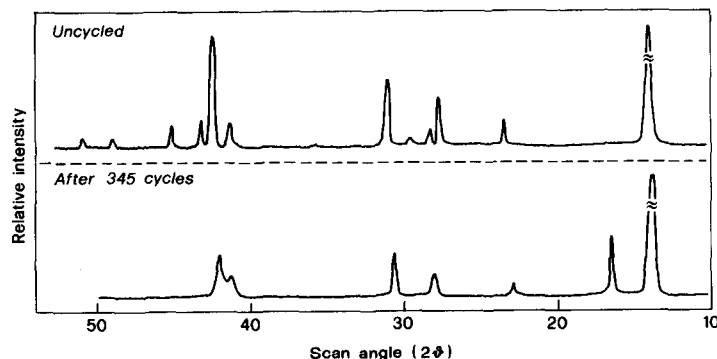

Fig. 8. X-ray powder patterns (Cu Kα) of Li$_{1.2}$V$_3$O$_8$ before and after prolonged cycling.

Conclusion

From the evidence collected in this work, it may be concluded that the performance of cathodes based on the compound $Li_{1+x}V_3O_8$ may be markedly altered by preparation conditions. We obviously refer to cells tested in relatively tough conditions, *i.e.*, high current density, low electrolyte volume, limited number of separator layers, and relatively thick electrodes. The latter three conditions would allow a high packing efficiency, defined as the ratio between active materials and total cell materials [7].

It now seems that an electrode made from $Li_{1+x}V_3O_8$ with low particle size, containing 30% of an acetylene black/Teflon mixture (2:1) and compacted at high pressure ($> \sim 6$ tons/cm^2) shows the best performance in a solution of sufficient fluidity and conductivity. The main limitation of this material seems to be connected with the loss of capacity during the 1st charge. It is remarkable that higher charge efficiencies were obtained at higher depths of discharge. For instance, with a 3 mA/cm^2 discharge and 2 mA/cm^2 charge, the 1st charge efficiencies (3.4 V cut-off) were 61, 67, and 75% for Li$^+$/mol values during discharge of 1.2, 1.6, and 2.0, respectively.

It has been pointed out already [2] that at lower current densities (*i.e.*, ~ 0.2 mA/cm^2) and/or at higher voltage cut-offs (3.8 - 3.9 V), the charge efficiency may approach 100%, thus pointing to the kinetic nature of this phenomenon. A major role is played by the solution, as was shown with $LiAsF_6$–MF. So, not only from the standpoint of Li cycling, but also from that of cathode cycling, the availability of satisfactory solutions seems to be of major concern. More tests will therefore be devoted to this aspect, while starting the planned scaling up to high capacity cells.

Acknowledgements

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