

## SMALL PARTICLE-SIZE LITHIUM-VANADIUM OXIDE: AN IMPROVED CATHODE MATERIAL FOR HIGH RATE RECHARGEABLE LITHIUM BATTERIES

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### Summary

A Li rechargeable battery with a cathode based on small particle-size  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  has a high cathode utilization and a long cycle life at high discharge rates. It is shown that decreasing the particle diameter from 10 to 1  $\mu\text{m}$  decreases 10 times the current density really applied to the cathode. This is particularly beneficial by limiting the cathodic capacity losses and thereby increasing the life to several hundreds of cycles. The high rate capability afforded by the use of small particles results in good power-energy characteristics.

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### Introduction

One of the most unfavourable features of the insertion cathodes used in secondary Li cells is the capacity loss observed upon cycling, especially during the first few cycles. A steady state, if any, is only reached when the capacity is too low to be useful.

Theoretical calculations have shown that the cathode efficiency in the 1st cycle is closely related to that in the  $n$ th cycle [1]. Further, a satisfactory 1st discharge has been shown to be strongly dependent upon the particle size of the cathode material, all other conditions being equal.

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For a  $\text{MoO}_2$  cathode discharged at the 1 h rate in a polymeric electrolyte cell, the utilization has been calculated to drop from 85% to 20% when the grain size of the powder rises from 10 to 50  $\mu\text{m}$  [1]. Similar calculations for a model insertion cathode indicated that the efficiency at the  $C/3$  rate fell from 100 to 50% when the particle size increased from 2 to 20  $\mu\text{m}$  [2].

The importance of using cathodes with reduced particle size has been shown by Atlung and coworkers [2 - 4]. In the theory developed by this group, the discharge rate is described by a dimensionless parameter such as the load factor,  $L$ , which decreases when the particle size is reduced [2]. This is to say that, when the particles are small, the cathode can virtually be discharged at a rate sufficiently low to compensate for the limiting factor represented by the slow  $\text{Li}^+$  diffusion into the cathode.

In practice, this means that only an electrode formed by small grains, *i.e.* a porous electrode, can be expected to provide a high utilization and, also, a satisfactory cycle life. Indeed, they both depend critically on the electrode availability in the pores of the cathode. At relatively high rates electrolyte depletion occurs in the inner part of the electrode [2, 3].

Previously, we showed how the capacity provided by the bronze  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  increased by decreasing the particle size [5]. This compound, however, could not, until now, be obtained with particles small enough to avoid a high capacity loss in the first cycles at relatively high discharge rates. This agrees with theoretical calculation discussed above [1].

In the present work, we report an improved cathode based on  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  obtained with particles of about 1  $\mu\text{m}$ . Both its 1st discharge capacity and its capacity retention upon cycling are superior to those shown by the material so far used.

## Experimental

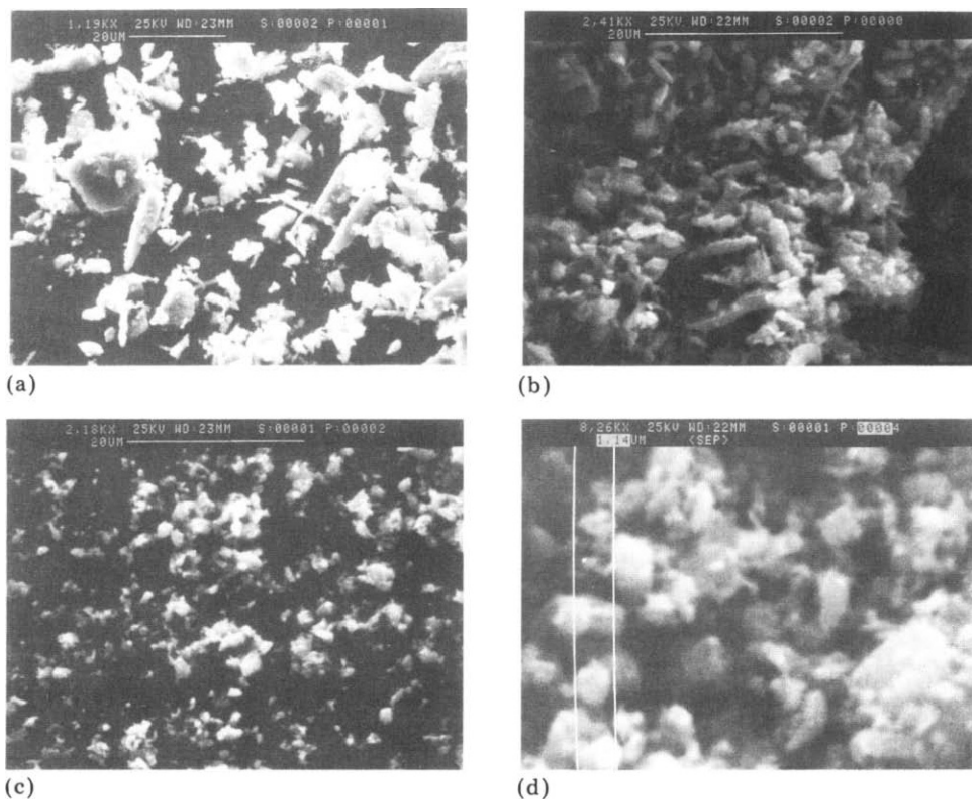
$\text{Li}_{1+x}\text{V}_3\text{O}_8$  crystals were obtained by heating  $\text{Li}_2\text{CO}_3$  and  $\text{V}_2\text{O}_5$  (the latter obtained by decomposing  $\text{NH}_4\text{VO}_3$  at 500  $^\circ\text{C}$ ) at 630  $^\circ\text{C}$  in a muffle furnace for 24 h. At this temperature, the bronze melts, so that a hard lump is recovered upon cooling to room temperature. Previously, after an initial crushing, the material was finely ground without solvent in an agate jar with a vibrating agate ball. This was followed by sieving the powder through a 400-mesh sieve, so that particles having diameters  $<38 \mu\text{m}$  were recovered. An alternative was to vibrate the raw material in a plastic jar containing several small corundum rolls. In this case, methanol was added to obtain finer particles [6].

In an effort to further reduce the particle size, in this study the powder obtained with the dry-mixing technique was submitted to a high pressure ( $>15 \text{ tons/cm}^2$ ) when placed between two thick stainless steel plates. In Fig. 1, scanning electron micrographic (SEM) pictures of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  samples obtained with the three different techniques are shown.

When the fine powder obtained by the pressing technique was dry-mixed (in a device similar to a coffee grinder) with 30% teflonized acetylene black (TAB), the formation of a non-homogeneous mixture was observed. To obtain a more homogeneous mixture, the cathode components had to be put into a beaker with methanol and stirred vigorously for several minutes. After heating at 100 °C to remove the methanol and moisture, the composite shown in Fig. 2 was obtained.

This powder was initially compacted on a 0.87 cm<sup>2</sup> Ni exmet at several tons/cm<sup>2</sup> and then sintered for a few minutes at 320 °C under a slight pressure. Sintering improves particle adhesion and, especially at high rates, the cycling life of the electrode is enhanced.

Cells were assembled by surrounding the capacity-limiting cathode with a Ni-supported Li anode doubly wrapped in a glass wool separator.



**Fig. 1.** SEM pictures of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  samples ground with different techniques: (a) dry-grinding with a vibrating ball in a jar (X1190); (b) wet-grinding (in  $\text{CH}_3\text{OH}$ ) with vibrating small cylinders in a plastic jar (X2410); (c) and (d) pressing the powder at several tons/cm<sup>2</sup> (X2180 and 8260, respectively).

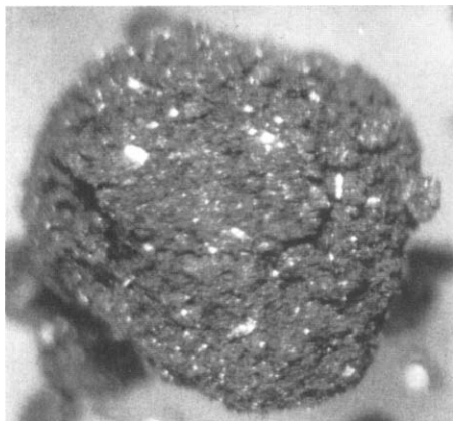


Fig. 2. Micrograph of a cathode composite obtained with the wet-mixing technique ( $\times 100$ ).

The electrode couple, lightly clamped, was housed in a prismatic glass container and about  $4 \text{ cm}^3$  of solution (usually  $\text{LiClO}_4$  in PC-DME) was added. The solutions were prepared according to standard purification procedures [7].

Cycling was carried out galvanostatically within preset voltage limits. The rate and the cathode efficiency were calculated relative to the capacity achievable at low to medium rates to a 1.8 V cut-off, *i.e.*  $0.235 \text{ A h/g}$  ( $2.5 \text{ Li}^+/\text{mol}$ ).

## Results and discussion

Cells containing about  $8 \text{ mA h}$  of active cathode material were assembled with the samples shown in Fig. 1a and 1c, respectively, and cycled at a relatively high rate. The advantage brought about by the use of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  with smaller particles was immediately apparent, as shown in Fig. 3. The gain in capacity and enhancement of the average voltage is obvious, *i.e.* the energy content of the cathode was more fully exploited.

This can be rationalized in terms of differences in the current density really applied to the cathode.

The effective working surface,  $S$ , of a cathode can be written as

$$S = kmA \quad (1)$$

where  $m$  is the weight,  $A$  is the BET surface area and  $k$  is an efficiency coefficient.  $A$  is inversely proportional to the material density,  $d$ , and grain size,  $r$

$$A = \frac{3}{rd} \quad (2)$$

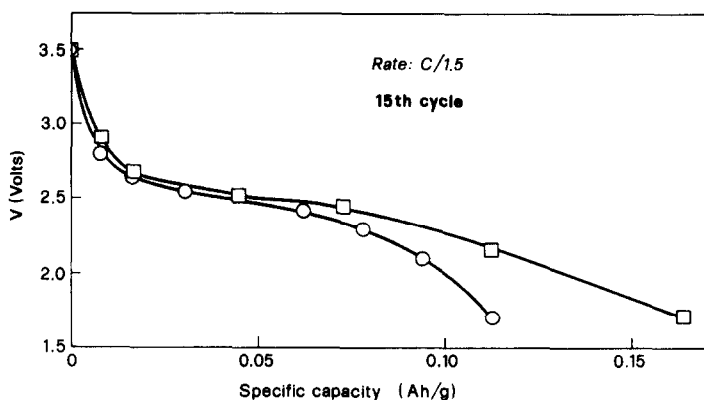


Fig. 3. Influence of the particle size of  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  on the discharge capacity:  $\square$ , material obtained with the pressing technique;  $\circ$ , material obtained with the dry-grinding technique. Discharge rate,  $C/1.5$ , charge rate,  $C/2.3$ .

By introducing (2) into (1), one obtains, for a given material

$$S = k' \frac{m}{r} \quad (3)$$

The current density then becomes

$$I_0 = \frac{I}{S} = \frac{Ir}{k'm} \quad (4)$$

For two cathodes having the same weight, but grains of different sizes, one obtains from eqn. (4)

$$\frac{I_{01}}{I_{02}} = \frac{r_1}{r_2} \quad (5)$$

So, if we assume an average diameter of  $1 \mu\text{m}$  for the highly pressed bronze, and of  $10 \mu\text{m}$  for the dry-ground form (Fig. 1) the current density ratio will also be  $1/10$ .

This is a significant result, although, in practice, such factors as porosity, mechanical stability and inadequate mixing of the cathode components may reduce the differences.

As described above, we experienced difficulties in dry-mixing small-particle  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  with TAB and obtained better results with the wet-mixing technique, as shown in Fig. 2. The composite looks fairly homogeneous with reduced segregation of different particles (the white spots may belong to both  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  and teflon grains).

The advantage provided by the use of  $1 \mu\text{m}$  particles is even more evident when long cycling tests under relatively severe regimes are compared. As shown in Fig. 4, a remarkable improvement in cycle life could be obtained with a more porous electrode. As expected, the performance (not

reported here) of the material shown in Fig. 1b was also inferior to that corresponding to curve 1. All cathodes were formed with the wet-mixing technique to improve homogeneity and sintered to improve particle adhesion. The capacity loss in the first 20 cycles is still significant even for the small-particle bronze and this calls for a further reduction of the particles. As mechanical techniques cannot produce a material with a large fraction of sub-micron grains, the only way to reach this goal would be a modification of the synthesis procedure. In other words, one should try and obtain a very fine grade powder when the bronze is formed. So far, attempts to synthesize  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  by a solid state reaction below  $500^\circ\text{C}$  have not produced a completely homogeneous material.

Further cycling experiments with fine grain  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  at the same rate ( $C/1.5$ ) were performed in different solutions. As shown in Fig. 5, the best cycling performance was obtained in  $\text{LiClO}_4/\text{PC-DME}$ . No special attempt was made in this work to rationalize the different efficiencies of the various solutions. In particular, as no reference electrodes were enclosed in the cells, it was impossible to distinguish the anodic and the cathodic contributions to the overall polarizations. Therefore, we confine ourselves to a few qualitative remarks. The use of methyl formate (MF) in these experiments tends to produce, in the long run, a very thick brown film on Li. The use of ethylene carbonate (EC) instead of PC is disappointing. This solvent is now receiving a great deal of attention because it gives high Li cycling efficiencies in  $\text{LiAsF}_6/\text{EC-2MeTHF}$  (2-methyltetrahydrofuran) [9]. The high viscosity of the sulfolane (S)-based solution may have been responsible for electrolyte depletion in the inner pores of the cathode.

Further experiments were aimed at ascertaining the ability of small particle-size  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  to sustain high current drains while cycling. The discharge rate was increased either by reducing the weight (at constant  $I$ ) or by increasing  $I$  (at constant weight). As shown in Fig. 6, no substantial difference between the two methods was observed. The cathode utilization, at the 15th cycle, decreased to acceptable levels with increasing rates: at the  $3C$  rate, 55% of the theoretical capacity ( $0.235\text{ A h/g}$ ) was still obtained. The high utilizations observed point to the fact that, even at rates near  $3C$ ,

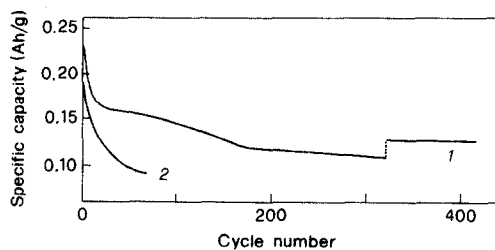


Fig. 4. Capacity vs. cycle number for: 1, material obtained with the pressing technique; 2, material obtained with the dry-grinding technique (particles  $< 38\ \mu\text{m}$ ). Discharge rate,  $C/1.5$ ; charge rate,  $C/2.3$  ( $C/4.6$  for the final part of curve 1).

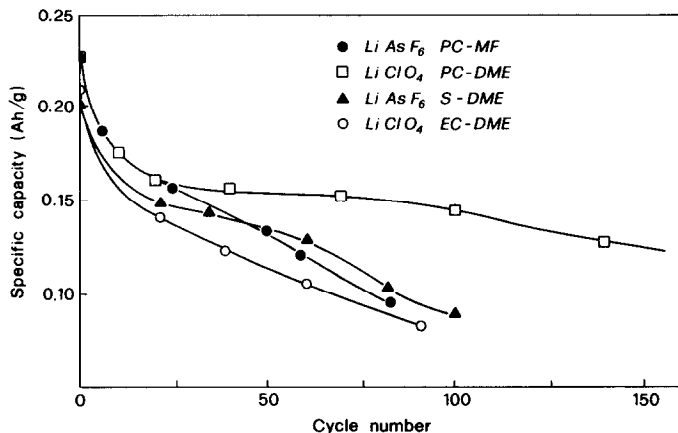


Fig. 5. Cycling tests in different solutions. Discharge rate,  $C/1.5$ ; charge rate,  $C/2.3$ . Weight of the cathode composite, 50 mg.

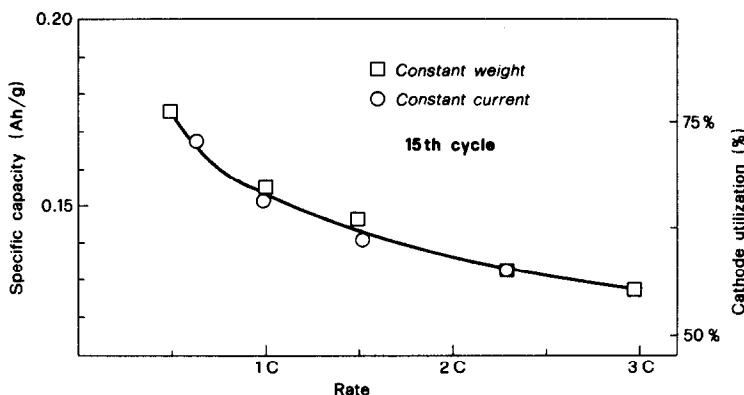


Fig. 6. Cathodic specific capacity and efficiency as a function of the discharge rate (15th cycle). The rate was varied by changing either the weight (○) or the current (□). Charge rate,  $C/1.5$  for □, and in the range  $C/1.5 - C/2.3$  for ○.

the two mechanisms limiting the capacity, *i.e.*  $\text{Li}^+$  saturation at the cathode surface and electrolyte depletion in the inner layers [2], are not yet operative.

The high rate capability of small particle-size  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  is confirmed by the long cycling test of Fig. 7. At discharge/charge rates of  $2.3C$  and  $1.5C$ , respectively, the cathode could still be cycled 120 times before the capacity dropped to  $0.1 \text{ A h/g}$ . Again, the loss in capacity during the first 10 cycles, which would certainly be alleviated if sub-micron and more uniform particles could be used, was observed.

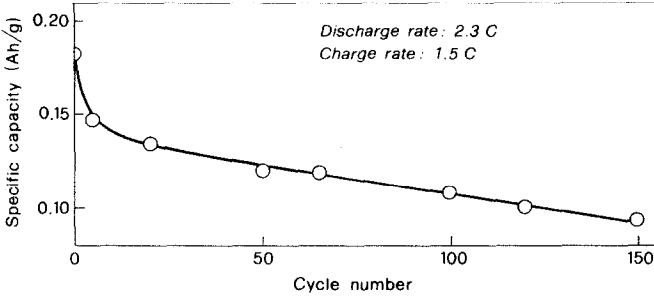


Fig. 7. Cycling at high rate of a cell with a thin cathode (9.7 mg active material, i.e. 2.2 mA h).

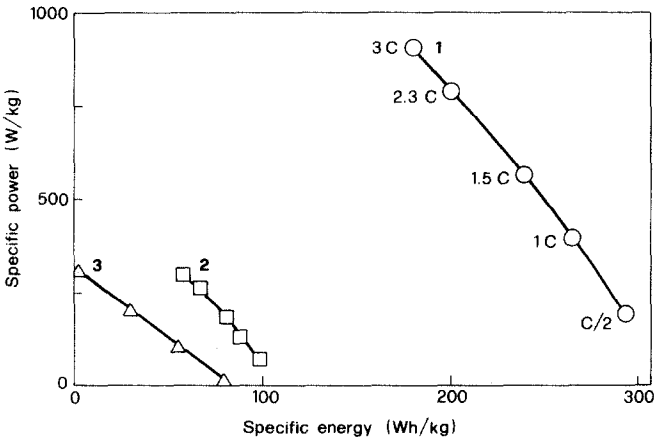


Fig. 8. Specific power vs. specific energy. Curve 1 is obtained at various rates from a cathode with a loading of 20 mg/cm<sup>2</sup> (the weight refers to all the cathodic mixture and the area to both faces); curve 2 is obtained from curve 1, after dividing by 3 both the energy and power values; curve 3 refers to a C-size Milicel<sup>TM</sup> (cathode loading, ~35 mg/cm<sup>2</sup>).

From the results with constant weight cathodes reported in Fig. 6 a power *versus* energy plot can be obtained (Fig. 8). If the values derived from the total cathode weight (curve 1) are divided by 3, curve 2 is obtained. This approximates to the power-energy characteristics of our prototype cells. A division of the theoretical energy density by a factor of 3 has been reported to represent the practical energy density of a cell [10]. Curve 2 can also be compared with the power-energy plot of a C-size Milicel<sup>TM</sup> [11] although we cannot attach too much significance to a non-homogeneous comparison. We believe, however, that the system investigated in the present work could, if optimized, provide specific energies >100 W h/kg at the power of 100 W/kg.



## Conclusion

The results obtained with cathodes based on small particle-size  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  confirm theoretical expectations of better material utilization in single discharges and reduced capacity losses upon cycling [1, 2]. Tests in progress with cells having the internal tight configuration typical of commercial cells, confirm the results reported here for cells with loosely packed electrodes in excess electrolyte.

An even better energy output and an enhanced capacity retention on cycling could be achieved if the morphology of the active material could be improved. If a synthesis route able to give homogeneous sub-micron particles could be found, the time- and energy-consuming steps such as grinding and sieving (or pressing) of the active material could be avoided.

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