

OPTIMIZATION OF THE VANADIUM OXIDE (V_6O_{13}) ELECTRODE IN A NONAQUEOUS SECONDARY LITHIUM CELL

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Summary

The V_6O_{13} electrode was tested in a nonaqueous lithium cell using 1M $LiAsF_6$ in propylene carbonate-acetonitrile mixture as the electrolyte. It was shown that incorporation of acetylene black in the V_6O_{13} electrodes improved cell performance in terms of active material utilisation. Also, cells using hydrophilic microporous polypropylene separators, e.g., Celgard 5511 and 3501, displayed less resistive losses enabling larger charge/discharge rates to be used. Voltage changes in the cell were shown to be controlled almost entirely by the V_6O_{13} electrode. Analysis of the exhausted V_6O_{13} electrodes showed that they contained at least 4 moles of lithium per mole of V_6O_{13} .

1. Introduction

Earlier studies [1, 2] of several vanadium oxides, particularly V_6O_{13} , have indicated that they were potentially attractive materials as high energy density cathodes for Li cells. Interest in these cells has led to tests being carried out in various electrolytes such as 1.5M $LiAsF_6$ in 2-methyltetrahydrofuran [3] and 1.0M $LiAsF_6$ in propylene carbonate [4]. The performance characteristics of various vanadium oxide compositions ranging from $VO_{1.88}$ to $VO_{2.19}$ have also been reported [3, 4].

Recent investigations [5, 6] have demonstrated that an electrolyte of 1M $LiAsF_6$ in propylene carbonate-acetonitrile mixture possesses properties which lead to the efficient performance of lithium batteries. These include high discharge rates and a high conductivity which minimises ohmic losses. It has been shown [7] that Li- V_6O_{13} cells applying this electrolyte display

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promising characteristics. In this paper we report further investigations designed to optimise the performance of the cell and to identify the problems limiting its capacity and rechargeability. The cell performance has been related to the type of separators used, the cathode composition, and the electrochemical behaviour of the electrodes.

2. Experimental

Vanadium oxide (V_6O_{13}) was prepared using the method described by Murphy *et al.* [2]. Ammonium metavanadate (Cerac Inc., USA, 99.99% pure) was thermally decomposed by heating in a flowing argon atmosphere at 150 °C for ~12 h and then at 400 °C for two days. An X-ray diffraction analysis confirmed that the product was V_6O_{13} with traces of V_2O_5 . The range of particle size of the V_6O_{13} as determined by SEM was 1 - 20 μm .

Lithium hexafluoroarsenate (LiAsF_6) was of electrochemical grade (U.S. Steel Agri-Chemicals) and was vacuum dried at ~200 °C and then used without further purification.

Propylene carbonate (Aldrich Chemical Company, Inc., USA, 99% pure) was first dried with 4A molecular sieves and then vacuum distilled using a spinning band distillation system (Perkin-Elmer Model 251, USA). Acetonitrile (Ajax Chemicals, Australia, HPLC-grade) was dried for ~2 weeks with CaH_2 and then twice distilled over CaH_2 . The electrolyte was 1M LiAsF_6 in a 50 - 50% by volume mixture of propylene carbonate and acetonitrile. The moisture content as determined from Karl Fischer titrations indicated that the acetonitrile and the electrolyte contained ~70 ppm and ~80 ppm of water, respectively.

The graphite powder (May & Baker, UK, native) was purified by high-frequency dispersion in 1M HCl and then left to soak for several days. It was then washed continuously with doubly distilled water until the final washings gave a specific conductance of $1.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The acetylene black (Electronic Industries, Australia) was similarly treated and both were vacuum dried before use. According to Croft *et al.* [8], the manufacturing process for the acetylene black used here was the same or similar to that for the Shawinigan acetylene black.

The separators were microporous polypropylene films (Celgard, Celanese Corporation, USA). These films were already treated with wetting agents by the manufacturer to make them hydrophilic. Table 1 shows the types used in this work and the physico-chemical properties reported by the manufacturer.

The V_6O_{13} electrodes were made by hot-pressing (~150 °C, ~5000 psi) a mixture of V_6O_{13} , carbon, and polyethylene onto a 2 cm square nickel grid (24 mesh). All mixtures were tumble-mixed in an argon atmosphere for at least a week to achieve uniform blending. The anode was constructed by pressing Li-Al (90 - 10 at.%) foil (Foote Mineral Company, USA) onto a nickel grid of similar dimensions. The V_6O_{13} electrode was sandwiched

TABLE 1

Some physical properties of the hydrophilic Celgard separators used in this work (manufacturer's data)

Properties	Celgard 3400	Celgard 3500	Celgard 3501	Celgard* 5511
Thickness (mm)	0.03	0.03	0.03	0.13
Weight (mg cm ⁻²)	1.4	1.2	1.2	3.4
Electrical resistance (40% KOH) (mΩ cm ²)	45	16	16	64
Electrolyte absorption (40% KOH) (%)	65	90	90	190
Flowrate, water at 1 atm/cm ³ (cm ⁻² min ⁻¹)	0.07	0.7	0.7	0.5

*This separator has a heat-embossed, nonwoven, polypropylene web as electrolyte absorber.

between two lithium electrodes and held firmly in parallel plate configuration inside a Teflon cell filled with electrolyte. There was only one layer of Celgard separator between electrodes. The cells were cycled between the preset voltages of 1.5 and 2.9 V at room temperature (~23 °C) using the instrumental technique described previously [7]. V₆O₁₃ electrodes of the following compositions (by weight) were prepared and tested:

(a) 70% V₆O₁₃ + 20% graphite + 10% polyethylene;

(b) 80% V₆O₁₃ + 10% acetylene black + 10% polyethylene;

(c) 75% V₆O₁₃ + 10% graphite + 5% acetylene black + 10% polyethylene;

(d) 70% V₆O₁₃ + 10% TiS₂ + 10% acetylene black + 10% polyethylene.

3. Results and discussion

Cell separators

A hydrophobic separator, Celgard 2400, was used in all our previous work on lithium organic batteries. This material has had wide applications in research on lithium organic batteries. However, we found that, on a number of occasions, large resistive losses were experienced in cells with a Celgard 2400 separator, rendering the cells inoperative. This could arise from non-uniform wetting of the separator with the organic solvent. With hydrophilic separators negligible resistive losses were encountered and therefore tests were carried out to select the most suitable separator for use in the cell. The results and sequence of the tests are presented in Table 2. In this work initial tests were performed on electrodes of composition 70% V₆O₁₃ + 20% graphite + 10% polyethylene. They were cycled at the charge/discharge rates of 1.25/5.0, 2.5/10.0 and 0.63/2.5 mA cm⁻². In this work, 'active material utilisation' (denoted by a.m.u.) is the utilisation of V₆O₁₃ based on 8 electrons/mole, *i.e.*, according to the equation,



TABLE 2

Influence of separator on cell performance

Electrode composition: 70% V_6O_{13} + 20% graphite + 10% polyethylene.

Cell performance	Celgard type				
	2400*	3400	3500	3501	5511
Charge/discharge 2.5/10.0 mA cm ⁻²					
Primary discharge capacity (% a.m.u.)	18	18	18	19	22
Cycle-life (No. to 5% a.m.u.)	9	10	5	17	13
Charge/discharge 1.25/5.0 mA cm ⁻²					
Primary discharge capacity (% a.m.u.)	32	39	43	47	45
Cycle-life (No. to 5% a.m.u.)	15	21	14	21	20
Charge/discharge 0.63/2.5 mA cm ⁻²					
Primary discharge capacity (% a.m.u.)	54	—	—	53	55
Cycle-life (No. to 5% a.m.u.)	20	—	—	> 12**	50

*Data from previous work [7].

**Terminated after 12th cycle because of long duration at this cycle rate.

The number of cycles obtained before the a.m.u. falls to 5% is slightly higher with Celgard 3501 and 5511 than with 2400. Celgard 5511 also gives rise to slightly better primary capacities at the higher discharge rates than Celgard 2400. Most importantly, the difficulties experienced with cells containing Celgard 2400, discussed above, were not observed. It should be noted that the number of charge/discharge cycles passed before the a.m.u. falls to 5% has been chosen as a measure of cycle life because it is a convenient parameter for making comparisons. This value should not be considered as the practical operational cycle life.

Figure 1 shows the discharge characteristics of the Li(Al)- V_6O_{13} cell using hydrophilic separators (Celgard 3501 and 5511) compared with that using a hydrophobic separator (Celgard 2400) reported previously [7].

In Fig. 2 the a.m.u. has been plotted *vs.* the number of cycles performed on the cells. These were the same cells as those shown in Fig. 1. The graphs show that the decrease in a.m.u. on the second discharge can be as much as 27% but the decrease for each cycle is much less after the 5th cycle. It is difficult to relate this behaviour to the separators. This behavior is probably due to the poor rechargeability of one or both of the electrodes. Based on these initial findings and because of its superior physical qualities, Celgard 5511 was selected as a suitable cell separator for testing other cells. Although it was ~4 times thicker than Celgard 3501 (see Table 1), it did not give rise to large resistive losses in the cells. Also, its physical strength and thickness would reduce the possibility of cell short-circuit from dendritic growth and at the same time provide more electrolyte retention (see Table 1).

The results presented here indicate that the major *iR* losses occur through transport in the electrolyte within the pores of the positive elec-

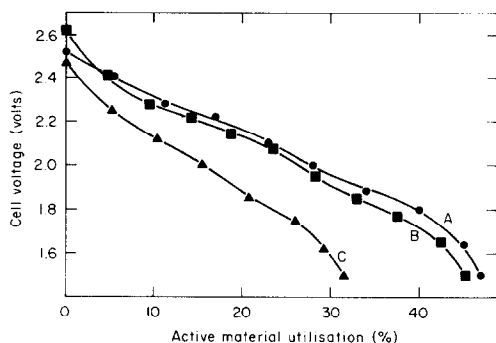


Fig. 1. Comparison of primary discharge characteristics of the Li(Al)- V_6O_{13} cell in 1M LiAsF₆/PC-AN using different types of separators. $i_D = 5.0 \text{ mA cm}^{-2}$. A = Celgard 3501 (213 mg V_6O_{13} , hydrophilic); B = Celgard 5511 (204 mg V_6O_{13} , hydrophilic); C = Celgard 2400 (148 mg V_6O_{13} , hydrophobic). Cathode composition: 70% V_6O_{13} + 20% graphite + 10% polyethylene.

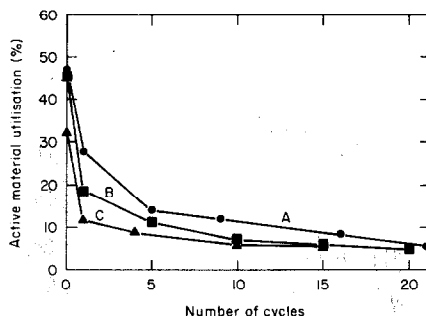


Fig. 2. Cycling behaviour of Li(Al)- V_6O_{13} cells in 1M LiAsF₆/PC-AN. $i_D = 5.0 \text{ mA cm}^{-2}$, $i_C = 1.25 \text{ mA cm}^{-2}$. A = Celgard 3501; B = Celgard 5511; C = Celgard 2400. (The electrodes were the same as in Fig. 1.)

trode material rather than across the separator. Thus, the use of thin-layer positive electrodes is more important than the use of thin separators.

Electrodes using acetylene black

It has been recognised for many years that cathodes fabricated using carbon blacks, like acetylene black, differed in electrochemical properties from those using graphite [8, 9]. Cells using acetylene black showed improved capacity on high drain continuous discharge as well as longer shelf-life [9, 10]. Some workers have tried to improve their cell performance by using a mixture of graphite and acetylene black [11]. Although various qualitative reasons have been given, the chemical behaviour of the conductive carbon blacks in batteries continues to be a subject of research [12, 13]. However, most of these investigations were related to aqueous cells. There seems to be insufficient information on carbon blacks in nonaqueous cells since graphite has been normally used. It is known that to obtain maximum capacity from V_6O_{13} cells an electronically conductive material must be added to the cathode because highly lithiated V_6O_{13} is a poor electronic conductor [1].

The performance of electrodes fabricated using only acetylene black is presented in Table 3. Because the apparent density of acetylene black is much lower than that of graphite, it was necessary to use a weight of acetylene black only half that of graphite. When the results in Table 3 are compared with those in Table 2, it can be seen that electrodes using only acetylene black gave improved a.m.u. values. Thus, at the discharge rates of 10.0, 5.0 and 2.5 mA cm^{-2} the a.m.u. values improved by $\sim 11\%$, $\sim 8\%$ and $\sim 9\%$, respectively. Another advantage in using acetylene black is the

TABLE 3

Results of tests on V_6O_{13} electrode fabricated using acetylene black
 Electrode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene. Separator type: Celgard 5511.

Charge/discharge (mA cm ⁻²)	Primary discharge capacity (mA h)	a.m.u., primary discharge (%)	No. of cycles up to 5% a.m.u.
2.5/10.0	26	33	13
-/5.0	43	53	—
1.25/5.0	49	50	> 20
0.63/2.5	62	64	35
0.25/1.25	66	67	50
-/0.50	79	74	—

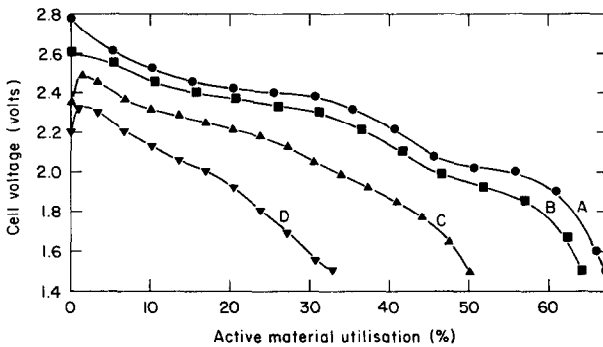


Fig. 3. Primary discharge characteristics of the Li(Al)- V_6O_{13} cell in 1M LiAsF₆/PC-AN with cathodes fabricated using acetylene black. A, $i_D = 1.25$ mA cm⁻² (236 mg); B, $i_D = 2.5$ mA cm⁻² (231 mg); C, $i_D = 5.0$ mA cm⁻² (234 mg); D, $i_D = 10.0$ mA cm⁻² (188 mg). Values in brackets indicate amounts of V_6O_{13} in cathodes of composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene.

increased loading of active material in the electrode because of the low apparent density of acetylene black. The primary discharge curves of these electrodes are shown in Fig. 3. At the higher discharge rates of 5.0 and 10.0 mA cm⁻², the so-called 'voltage delay' effect [14, 15] was observed. This effect was, however, negligible for the electrodes fabricated with graphite alone. It is worth noting here that in all the cells tested, the equilibrium OCV was 2.9 V and this value was also observed previously [7]. The discharge characteristics of a cell at a very low discharge rate (0.5 mA cm⁻²) are shown in Fig. 4. The three plateaus obtained indicate the presence of at least three, two-phase regions and this is consistent with the OCV observations of Murphy *et al.* [4] and the galvanostatic discharge profiles of VO_{2.19} reported by Abraham *et al.* [3]. This observation tends to confirm that our V_6O_{13} sample does not behave substantially differently from that of other workers. The use of acetylene black, however, did not extend cycle-life. The

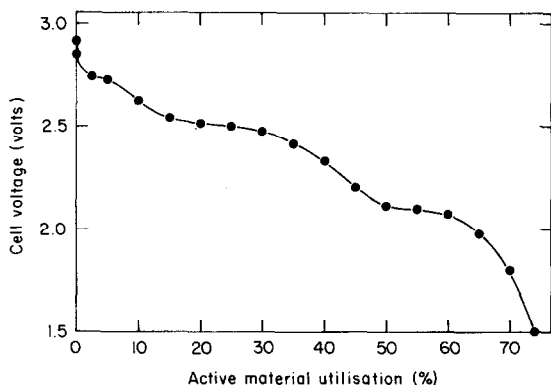


Fig. 4. Discharge curve for Li(Al)- V_6O_{13} cell in 1M LiAsF₆/PC-AN. Presence of at least three two-phase regions. $i_D = 0.5 \text{ mA cm}^{-2}$ (254 mg V_6O_{13}). Cathode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene. Separator: Celgard 5511.

TABLE 4

Results of tests on V_6O_{13} electrode fabricated using a mixture of graphite and acetylene black

Electrode composition: 75% V_6O_{13} + 10% graphite + 5% acetylene black + 10% polyethylene. Separator type: Celgard 5511.

Charge/discharge (mA cm ⁻²)	Primary discharge capacity (mA h)	a.m.u., primary discharge (%)	No. of cycles up to 5% a.m.u.
2.5/10.0	22	26	15
1.25/5.0	41	42	18
0.63/2.5	55	58	30
0.25/1.25	64	64	> 30

number of cycles obtainable remained about the same as that using graphite alone.

Cathodes fabricated using a mixture of acetylene black and graphite were also tested. The results are shown in Table 4. It appears that such a mixture does not improve the discharge capacity and it is preferable to use only acetylene black. Thus, by comparing the results shown in Tables 3 and 4, the a.m.u. values are shown to decrease by $\sim 7\%$ (at 10 mA cm^{-2}), $\sim 11\%$ (at 5 mA cm^{-2}), $\sim 6\%$ (at 2.5 mA cm^{-2}) and $\sim 3\%$ (at 1.25 mA cm^{-2}). There is also no significant improvement in the cell cycle-life by using such a mixture. It is interesting to note that the 'voltage delay' effects observed earlier in Fig. 3 have decreased, probably through the presence of graphite.

Positive electrodes from mixed intercalation compounds

Mixed electrodes of V_6O_{13} and TiS_2 have been studied to determine if any synergistic effect occurs. It is possible to use these materials together because they intercalate lithium over the same potential range [1]. Other

desirable characteristics of TiS_2 included single phase behaviour with lithium intercalation [16] and low molecular weight. Furthermore, fresh samples of TiS_2 were freely available in our laboratory because of our earlier studies of the Li-TiS_2 cells [17].

Cycling was carried out at the charge/discharge rate of $0.63/2.5 \text{ mA cm}^{-2}$ using a cathode of composition; 70% V_6O_{13} + 10% acetylene black + 10% polyethylene binder + 10% TiS_2 . The primary discharge characteristics are shown in Fig. 5. As a comparison, the discharge characteristics of an electrode not blended with TiS_2 but subjected to the same cycling regime are also included. The curves suggest that the plateaux which characterised the pure V_6O_{13} electrodes have been slightly removed by the addition of TiS_2 . Although not shown here, the cycling characteristics (*i.e.*, specific capacity *vs.* cycle number) remained essentially the same as that of pure V_6O_{13} electrode. Thus no advantage is obtained by using a mixed electrode. More importantly for secondary applications, no improvement in cycle-life was observed for the cell compared with those utilizing V_6O_{13} or TiS_2 alone.

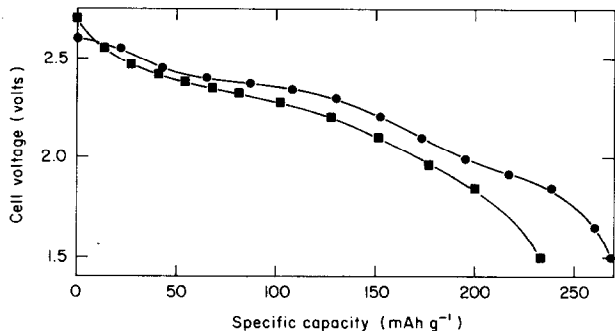


Fig. 5. Primary discharge characteristics of the $\text{Li(Al)-V}_6\text{O}_{13}$ cell in $1\text{M LiAsF}_6/\text{PC-AN}$ using cathode blended with TiS_2 . $i_D = 2.5 \text{ mA cm}^{-2}$. ■, Electrode composition: 70% V_6O_{13} + 10% acetylene black + 10% TiS_2 + 10% polyethylene ($\text{V}_6\text{O}_{13} + \text{TiS}_2 = 246 \text{ mg}$); ●, Electrode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene ($\text{V}_6\text{O}_{13} = 289 \text{ mg}$).

Relationship between cycle-life and depth of discharge

At this stage it would be interesting to analyse the a.m.u. values from the various discharge curves in terms of current densities and cycle-life. In Fig. 6 the a.m.u. from the primary discharge curves of two electrodes whose compositions were 70% V_6O_{13} + 20% graphite + 10% polyethylene and 80% V_6O_{13} + 10% acetylene black + 10% polyethylene have been plotted against their corresponding current densities. It can be seen that a linear relationship exists for each composition. Although not shown here, the values obtained from the cathodes of composition: 75% V_6O_{13} + 10% graphite + 5% acetylene black + 10% polyethylene follow the lower line. Hence, V_6O_{13} electrodes when fabricated with only acetylene black display larger discharge capacities than those using only graphite or a mixture of graphite and acetylene black.

According to Voss and Huster [18] and Bode [19] the dependence of the cycle-life on the depth of discharge for the lead-acid batteries approximately followed the empirical equation,

$$\log x = A - By \quad (2)$$

where x and y represent the number of cycles and the percentage depth of discharge, respectively. A and B are constants in the equation.

As a preliminary test to relate cycle-life to a.m.u. for the $\text{Li(Al)-V}_6\text{O}_{13}$ cell, we have made use of eqn. (2) by substituting a.m.u. values for y . The result, which indicates the decay of cell capacity with respect to cycle number, is shown in Fig. 7. It appears that the linear relationship is more exact for data obtained at low charge/discharge rates. It is interesting to note that recently Chemelli *et al.* [11] and Kordesch *et al.* [20] have also utilised eqn. (2) to investigate the alkaline manganese dioxide cell.

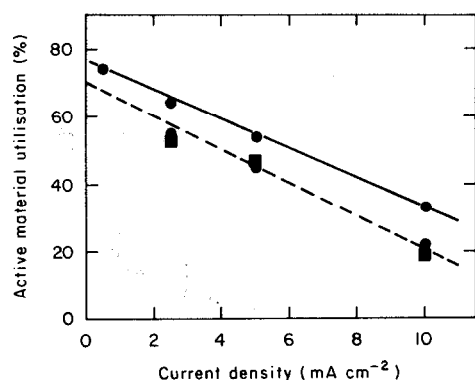


Fig. 6. Active material utilisation from primary discharge curves plotted against current density. - - - - Electrode composition: 70% V_6O_{13} + 20% graphite + 10% polyethylene. — Electrode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene. ●, Celgard 5511; ■, Celgard 3501.

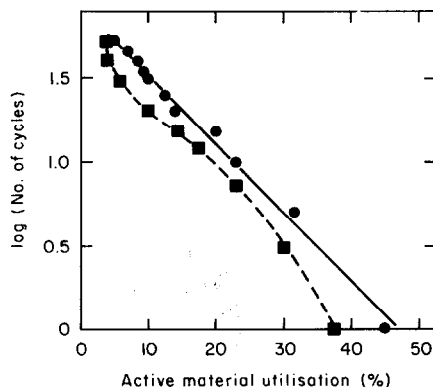


Fig. 7. Testing the relationship between the number of cycles and the depth of discharge (eqn. (2) in the text). Electrode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene. Cell cycled between voltage limits. ●, $i_D = 1.25 \text{ mA cm}^{-2}$, $i_C = 0.25 \text{ mA cm}^{-2}$. ■, $i_D = 2.5 \text{ mA cm}^{-2}$, $i_C = 0.63 \text{ mA cm}^{-2}$.

Reasons for cell failure

One of the reasons for cell failure in secondary nonaqueous lithium cells is the poor rechargeability of the lithium electrodes [14, 21]. In order to determine some of the reasons for the $\text{Li(Al)-V}_6\text{O}_{13}$ cell failure, we have monitored the potentials of each electrode (with respect to a reference lithium electrode) while the cell was being cycled. The reference electrode consisted of a piece of lithium wire immersed in the same electrolyte as that used in the cell. The Luggin capillary of the reference electrode was brought as close as possible to each electrode. All our cells can be considered as

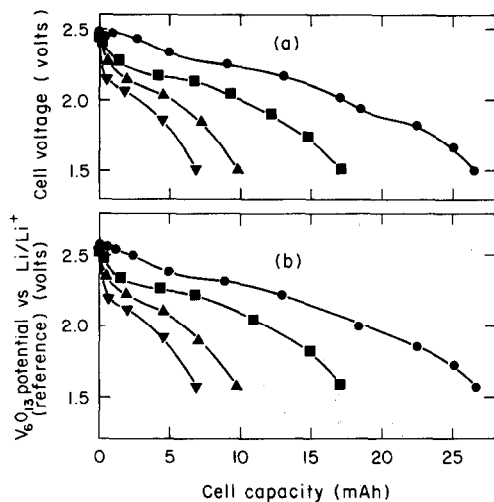


Fig. 8. Discharge characteristics of the V_6O_{13} electrode. (a) Actual cell voltage. (b) V_6O_{13} potential monitored against Li/Li^+ reference electrode. $i_D = 5 \text{ mA cm}^{-2}$, $i_C = 1.25 \text{ mA cm}^{-2}$. ●, Primary discharge; ■, 1st cycle; ▲, 10th cycle; ▼, 20th cycle. Electrode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene.

cathode limited because the amount of lithium in the anode was at least ~ 10 times the capacity ($\sim 1500 \text{ mA h}$) of the V_6O_{13} . The results of such an investigation are shown in Fig. 8. In Fig. 8(a) the discharge curves indicate the actual voltage of the $Li(Al)-V_6O_{13}$ cell whereas in Fig. 8(b) they indicate the potential of the V_6O_{13} electrode with respect to the reference Li/Li^+ electrode. A comparison of the curves in Fig. 8(a) and Fig. 8(b) shows that those in Fig. 8(b) are consistently $\sim 0.05 \text{ V}$ higher. This slight voltage difference may be attributed to ohmic potential drops and polarisation losses [22] of the lithium anode. Since this voltage difference is small and constant during cell cycling, the potential changes in the $Li(Al)-V_6O_{13}$ cell must be due almost entirely to the V_6O_{13} electrode. Hence, cell failure must be attributed to the V_6O_{13} electrode and not the lithium electrode.

The V_6O_{13} electrodes which had failed were analysed to determine the amount of lithium remaining in the V_6O_{13} interstices. The experimental method involved the delithiation of the V_6O_{13} electrode using a solution of iodine in acetonitrile [4]. The excess iodine was then back-titrated with a standard solution of $0.1 \text{ M Na}_2\text{S}_2\text{O}_3$. The titration was carried out potentiometrically using a saturated calomel electrode as reference and a piece of bright platinum as the indicator electrode [23]. The results are presented in Table 5. Assuming negligible losses in electrode material (*e.g.*, shedding) it can be concluded that at least 4 moles of Li per mole of V_6O_{13} are eventually left in the V_6O_{13} interstices. It is also interesting to note that this value is independent of the magnitude of the charge/discharge rates. These irreversibly intercalated lithium atoms have probably given rise to serious structural changes resulting in poor cycle-life for the cell. The large decrease in the

TABLE 5

The amount of lithium remaining in V_6O_{13} cathode at cell failure
 Electrode composition: 80% V_6O_{13} + 10% acetylene black + 10% polyethylene.

Charge/discharge (mA cm ⁻²)	Wt. of V_6O_{13} (mg)	x in $Li_x V_6O_{13}$
0.63/2.5	191	4.0 ± 0.2
1.25/5.0	199	4.0 ± 0.2
2.5/10.0	156	4.0 ± 0.2

a.m.u. values within the first few cycles (see Fig. 2) suggests that massive amounts of lithium must have been permanently left in the V_6O_{13} during the initial stages of cell cycling. Perhaps, the present cell cycling regime is too severe on the cell and should be modified to a lower depth of discharge, *e.g.*, using the preset voltages of 3.0 and 1.9 V as reported by Abraham *et al.* [3] or using a cell cycling technique as described by Chemelli *et al.* [11] for the alkaline MnO_2 cell. Further work in this direction should be beneficial.

4. Conclusions

It has been demonstrated that certain hydrophilic microporous polypropylene films, *e.g.*, Celgard 5511, can be successfully used as separators in the nonaqueous $Li(Al)/1M LiAsF_6$, PC-AN/ V_6O_{13} cell. These were preferred over the hydrophobic types, *e.g.*, Celgard 2400, because the cells experienced less electrical resistance and, hence, larger charge/discharge rates were possible without serious penalty on cell capacity. It was also demonstrated that cathodes fabricated using only acetylene black gave larger discharge capacities than those using only graphite or a mixture of graphite and acetylene black. Cycle-life of the cell was not, however, extended by the use of acetylene black. For secondary applications, there was no advantage in a mixed positive electrode (V_6O_{13} , 70 wt.% + TiS_2 , 10 wt.%) because there was no improvement in cycle-life over cells utilising V_6O_{13} and TiS_2 alone.

The cell voltage was shown to be controlled almost entirely by the V_6O_{13} electrode and cell failure was attributed to this electrode. The exhausted V_6O_{13} electrodes were found to contain irreversibly intercalated lithium and chemical analysis revealed that there were at least 4 moles of lithium per mole of V_6O_{13} . The results suggested that massive amounts of lithium may have been permanently left in the V_6O_{13} interstices during the initial stages of cell cycling and caused rapid cell failure.

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