

## AN IMPROVED LITHIUM-VANADIUM PENTOXIDE CELL AND COMPARISON WITH A LITHIUM-THIONYL CHLORIDE CELL

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### Summary

This paper describes a programme of experiments conducted to assess the effects of: (a) diluting the electrolyte in lithium-vanadium pentoxide cells; (b) optimizing the volume of electrolyte per unit cathode mass.

This programme led to the development of an improved cell, the performance of which is compared with that of a lithium-thionyl chloride cell of similar configuration.

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### Introduction

Philips Usfa's product range includes reserve batteries which are manufactured under licence from Honeywell USA.

These batteries are based on the lithium-vanadium pentoxide technology recently reviewed by Walk [1]. They operate at temperatures from  $-40^{\circ}\text{C}$  to  $+63^{\circ}\text{C}$ , have a wide storage-temperature range (with a guaranteed shelf-life of ten years at room temperature) and comply fully with the environmental requirements of MIL-STD-331A.

Our recent re-evaluation of the  $\text{Li/V}_2\text{O}_5$  system, reported in this paper, has led to the development of an improved cell containing a smaller volume of less concentrated electrolyte, together with a number of design and production improvements.

The paper also reports on comparative tests carried out with the improved cell and an  $\text{Li/SOCl}_2$  cell of similar configuration.

### Experimental

Electrolyte concentrations of 1M and 0.5M were made by adding methyl formate to the normal 2M electrolyte (2M  $\text{LiAsF}_6$  and 0.4M  $\text{LiBF}_4$  in methyl formate). The specific conductivity of all three solutions was then measured, using a Philips PW9504 Conductivity Meter and PW9512/01 Measuring Cell.

Ampoules containing 0.5M and 1M solutions were built into cells which were otherwise identical with standard production units (Fig. 1(a)). The

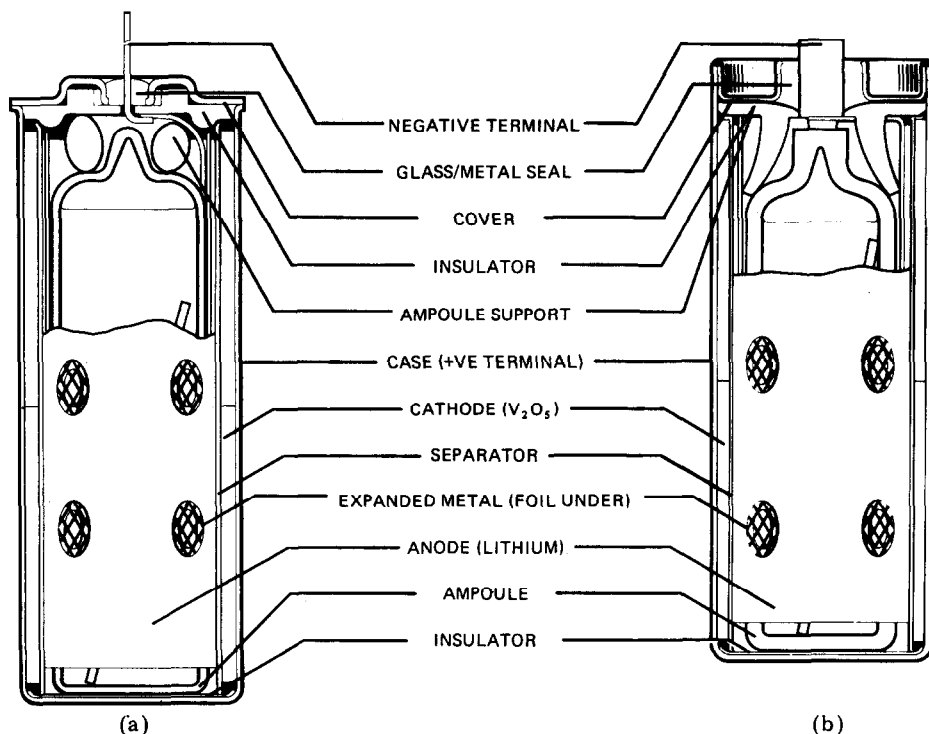


Fig. 1. (a) Original and (b) improved  $Li/V_2O_5$  reserve cells.

performance of all three types was then tested at  $-40^\circ\text{C}$ , room temperature, and  $+63^\circ\text{C}$ .

After analysing the data we made a further batch of sample cells containing various amounts of 1M electrolyte, representing electrolyte volume/cathode mass ratios from 0.37 to  $0.66\text{ ml g}^{-1}$ . The results obtained during tests on these cells prompted our decision to produce a cell containing a reduced volume of 1M electrolyte.

Finally, we made a batch of  $Li/SOCl_2$  cells of similar configuration to the improved  $Li/V_2O_5$  cell except for a Shawinigan black/Teflon 30 depolarizer (in place of the  $V_2O_5$  cell's cathode) and 1M lithium aluminium chloride in thionyl chloride as liquid cathode/electrolyte. In comparative tests, both types of cell were activated and discharged at  $-40^\circ\text{C}$ , at current densities ranging from  $12\text{ mA cm}^{-2}$  to  $0.06\text{ mA cm}^{-2}$ .

## Results and discussion

### (a) Electrolyte dilution

Conductivity measurements on the three electrolyte solutions showed that below  $-10^\circ\text{C}$  the specific conductivity of 1M electrolyte is higher than that of the other solutions (Fig. 2).

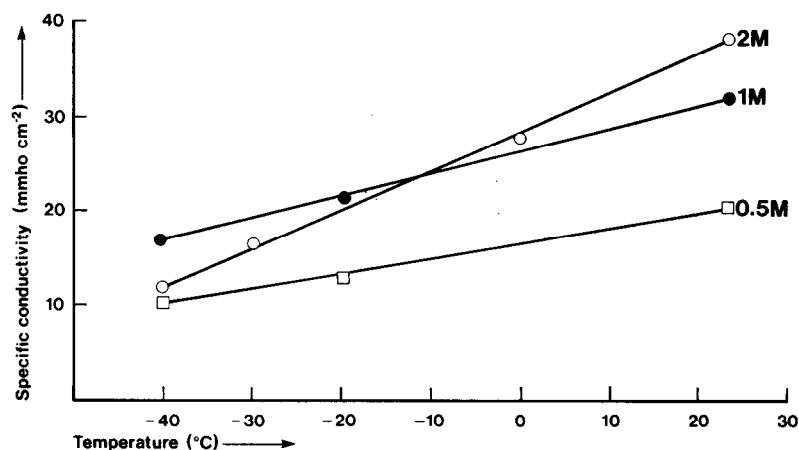


Fig. 2. Specific conductivity of 2M, 1M and 0.5M electrolyte from  $-40^{\circ}\text{C}$  to  $+30^{\circ}\text{C}$ .

TABLE 1

Influence of electrolyte concentration on rise times

Temp. (°C)	Electrolyte concentration (M)	Current density (mA cm <sup>-2</sup> )					
		12	6	3	1.5	0.6	0.3
		Rise time to 3 V (ms)					
−40	0.5	2.2 V*	2.4 V*	2.5 V*	4000	400	280
	1.0	2.2 V*	2.6 V*	2.7 V*	600	400	280
	2.0	2.1 V*	2.6 V*	2.6 V*	2200	600	360
+20	0.5	4000	600	540	180	150	60
	1.0	420	360	280	140	80	60
	2.0	1250	530	300	140	80	60
+63	0.5	1200	500	380	180	50	50
	1.0	240	160	80	50	50	50
	2.0	290	200	50	50	50	50

\* = Voltage after one second (3 V not reached).

The cells containing 1M electrolyte also exhibited the shortest rise times to 3 V (Table 1). In those cases where 3 V was not reached, the voltage measured one second after activation was highest in the 1M cells.

Table 2 shows that at  $-40^{\circ}\text{C}$  and high discharge rates the 1M concentration is also superior in terms of capacity efficiency up to 2.5 V. Its excellent low-temperature performance at discharge rates below  $1.5 \text{ mA cm}^{-2}$  is also evident and, despite a sharp decrease in efficiency at higher discharge rates, it remains capable of producing high current pulses on top of a continuous current drain without serious voltage drop.

TABLE 2

Influence of electrolyte concentration on efficiency of capacity

Temp. (°C)	Electrolyte concentration (M)	Current density (mA cm <sup>-2</sup> )					
		12	6	3	1.5	0.6	0.3
		Efficiency of capacity (%)					
-40	0.5	0	5	19	49	66	86
	1.0	10	30	58	79	84	86
	2.0	0	13	64	79	86	87
+20	0.5	14	29	70	74	97	98
	1.0	22	74	86	95	100	100
	2.0	65	83	91	94	99	100
+63	0.5	21	54	87	92	96	99
	1.0	81	91	95	96	96	100
	2.0	81	98	100	100	100	100

The 0.5M concentration is clearly too low for efficient operation at high current densities. At lower densities, however, it gives virtually the same rise time and efficiency as the 1M and 2M solutions.

#### (b) Electrolyte optimization

The results obtained with diluted electrolyte at low current densities encouraged us to investigate the feasibility of optimizing the volume of electrolyte per gram of cathode. We therefore conducted a series of performance measurements on cells containing different amounts of 1M electrolyte; all measurements were made at -40 °C, with loads below 1.5 mA cm<sup>-2</sup> and electrolyte volumes ranging from 0.37 to 0.66 ml/g of V<sub>2</sub>O<sub>5</sub>.

Within this range we found that rise time does not vary as a result of altering the electrolyte volume to cathode mass ratio. We also found (Table 3) that, while 0.57 ml of electrolyte per gram of V<sub>2</sub>O<sub>5</sub> is needed at 1.5 mA cm<sup>-2</sup>, 100% efficiency can be obtained at 0.015 mA cm<sup>-2</sup> with a ratio of only 0.37 ml/g.

#### (c) Improved cell

As a result of these investigations we have been able to reduce the volume of electrolyte in the cell by 25%. This has enabled us to increase the wall thickness of the ampoule, thereby improving the cell's drop-test and shock-resistance properties. Furthermore, the use of 1M electrolyte has reduced the risk of thermal runaway under short-circuit conditions.

Several design and production improvements are also incorporated in the new cell (Fig. 1(b)). These include:

- a cover which fits into (instead of onto) the can
- the use of stainless steel 316L (DIN 17440, material no. 1.4435) for the can and the cover

TABLE 3

Influence of electrolyte/cathode ratio on efficiency of capacity (1M electrolyte cells tested at  $-40^{\circ}\text{C}$ )

Current density ( $\text{mA cm}^{-2}$ )	1M electrolyte/ $\text{V}_2\text{O}_5$ ( $\text{ml g}^{-1}$ )				
	0.37	0.43	0.49	0.57	0.66
	Efficiency of capacity (%)				
1.5	53	75	90	96	96
0.15	60	80	100	100	100
0.015	100	100	100	100	100

TABLE 4

Comparison of  $\text{Li}/\text{SOCl}_2$  and  $\text{Li}/\text{V}_2\text{O}_5$  cells at  $-40^{\circ}\text{C}$

Current density ( $\text{mA cm}^{-2}$ )	Rise time (ms)		$V_{\text{max}}$ (V)		Capacity (mA h)		Efficiency (%)	
	$\text{SOCl}_2$	$\text{V}_2\text{O}_5$	$\text{SOCl}_2$	$\text{V}_2\text{O}_5$	$\text{SOCl}_2$	$\text{V}_2\text{O}_5$	$\text{SOCl}_2$	$\text{V}_2\text{O}_5$
	(to 2.5 V)	(to 3 V)						
12	> 4000	> 4000	2.32	2.64	35	51	4	10
6	> 4000	> 4000	2.61	2.74	62	153	7	29
3	> 4000	> 4000	2.72	2.85	184	298	19	57
1.5	600	600	2.89	3.06	259	406	27	79
0.6	600	400	2.99	3.12	344	436	37	84
0.3	600	280	3.14	3.24	430	446	45	86
0.06	200	100	3.60	3.50	540	446	58	86

— new processes for melting-in the glass seal and feedthrough pin in the cover, and for annealing the can after deep-drawing, thereby eliminating subsequent pickling and passivation

— a new combined insulator and ampoule support.

#### (d) Performance comparison

Finally, the performance of the improved cell was compared with that of the  $\text{Li}/\text{SOCl}_2$  equivalent. Rise time to 2.5 V and capacity up to 2.5 V were measured at  $-40^{\circ}\text{C}$ , with current densities of  $0.06 - 12 \text{ mA cm}^{-2}$ . The results are shown in Table 4.

Between  $0.1$  and  $12 \text{ mA cm}^{-2}$ , the  $\text{Li}/\text{V}_2\text{O}_5$  cell has a shorter rise time, higher maximum voltage, and greater capacity. Below  $0.1 \text{ mA cm}^{-2}$  the  $\text{Li}/\text{SOCl}_2$  cell has the greater capacity, with a maximum of about 1.6 times that of the  $\text{V}_2\text{O}_5$  cell at very low current densities.

Whereas the capacity of  $\text{Li/SOCl}_2$  cells is strongly dependent on temperature and applied current density [2], that of  $\text{Li/V}_2\text{O}_5$  cells is less so. Hence at  $-40^\circ\text{C}$  the  $\text{V}_2\text{O}_5$  system is better suited for densities greater than  $0.1\text{ mA cm}^{-2}$  and the  $\text{Li/SOCl}_2$  system is the more suitable for lower densities.

## Conclusions

Re-evaluation of the lithium-vanadium pentoxide system has resulted in a more economical cell which is more simple to manufacture.

Optimization of the electrolyte concentration has yielded improvements in discharge-rate capability at low temperatures. The improved cell is better suited for higher loads and pulsed loads, and is safer.

At  $-40^\circ\text{C}$  and discharge rates above  $0.1\text{ mA cm}^{-2}$ , the capacity per cell volume of the lithium-vanadium pentoxide cell is higher than that of the lithium-thionyl chloride cell.

## References

- 1 C. R. Walk, in J. P. Galvano (ed.), *Lithium Batteries*, Academic Press, London, 1983, p. 256.
- 2 W. J. Eppley and R. J. Horning, *Proc. 28th Power Sources Symp., Atlantic City, NJ, 1978*, p. 257.