

HEAT DISSIPATION FROM LITHIUM/SILVER VANADIUM OXIDE CELLS DURING STORAGE AND LOW-RATE DISCHARGE

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Introduction

A lithium/silver vanadium oxide (SVO) battery, suitable for medical implantation, has been under development by this company since 1981 [1 - 3]. The voltage of the Li/SVO discharge curve slopes from 3.2 V at beginning-of-life to 2.0 V at end-of-life, allowing for convenient monitoring of the depth-of-discharge. For the study discussed here, hermetically sealed, case positive, cathode limited, rectangular prismatic cells have been used. From discharge, storage, and calorimetry tests [2], this battery has proved to be a high energy density, low internal impedance, low self-discharge power source for low to moderate rate applications.

As part of a continuing study on self-discharge, calorimetry data from storage and discharge test cells have been reviewed and integrated with results from a lithium digestion analysis on end-of-life test cells. Heat dissipation from cells under various constant resistive loads has been compared with heat dissipation under open circuit, and contributions to total heat dissipation have been investigated.

Experimental

Test batteries were manufactured using a rectangular prismatic cell design with nominal case dimensions of 45 mm × 23 mm × 8.6 mm and an external case volume of 7.9 cm³ (Fig. 1). To form the center anode (surface area: 12.5 cm²), lithium foil was pressed around a nickel current-collector and then wrapped in a heat-sealed polypropylene separator. Two solid cathode plates lined each side of the stainless steel case. These were formed from AgV₂O_x ($x \sim 5.5$) which was mixed with a conductor and a binder, and pressed around nichrome wire current-collectors. The electrolyte was 1 M lithium tetrafluoroborate in propylene carbonate.

Of all the batteries tested, thirteen have had microcalorimetry measurements recorded on a regular basis. Five of the cells have been on storage at room temperature for over two years, and eight have been discharged at

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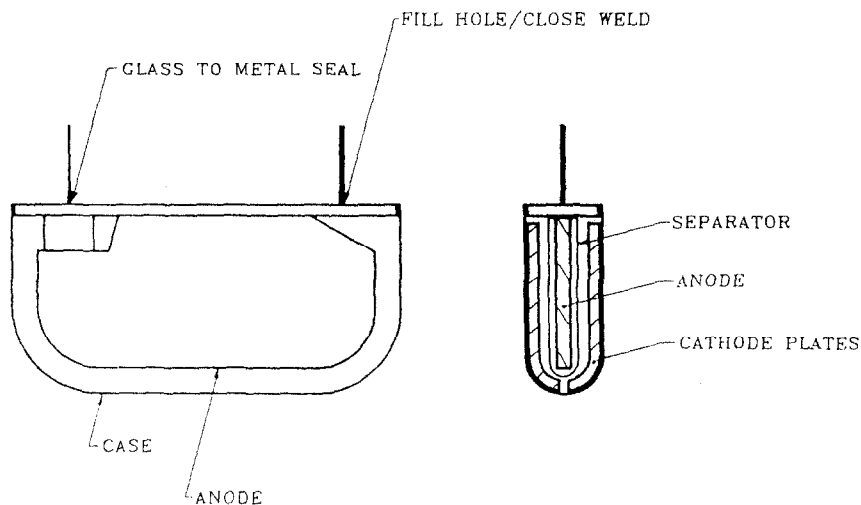


Fig. 1. Schematic diagram of Li/AgV₂O_x cell.

37 °C under constant resistive loads of 10.0 (20 $\mu\text{A cm}^{-2}$), 20.0 (10 $\mu\text{A cm}^{-2}$), 38.3 (5 $\mu\text{A cm}^{-2}$), and 80.6 (2 $\mu\text{A cm}^{-2}$) k Ω (Fig. 2). Open-circuit measurements have been taken periodically during discharge.

Microcalorimetry data were recorded using Tronac Model 350 microcalorimeters. Measurements were taken on room-temperature storage cells while under open circuit at 25 °C and on discharge cells while under both load and open circuit at 37 °C. The time allowed between the load and open-circuit measurement for the discharge cells was one to three days. It is estimated that the open-circuit voltage recovers to approximately 99% of its steady state within 24 h.

Open-circuit voltage as a function of temperature (dV_{oc}/dT) was also recorded for samples of cells at 0, 27, 53, and 88% depth-of-discharge (DOD). Voltages were measured at 4 °C intervals over the temperature range 20 - 40 °C in a constant temperature (± 0.1 °C) water bath.

Discussion

After 15.84 months on test, the 10.0 k Ω test cells reached end-of-life (1954 mV). A lithium assay test on the residual lithium indicated that approximately 2783 (± 21) mA h of discharge had occurred during life. Of this, 2774 mA h could be attributed to discharge testing, and the remaining 9 mA h to self-discharge and parasitic lithium discharge. Based on the total amount of lithium available in the cells, and assuming that the contribution to the total lithium loss from parasitic lithium discharge was negligible, this would give an estimated 0.0 - 0.8% self-discharge at the lithium anode per

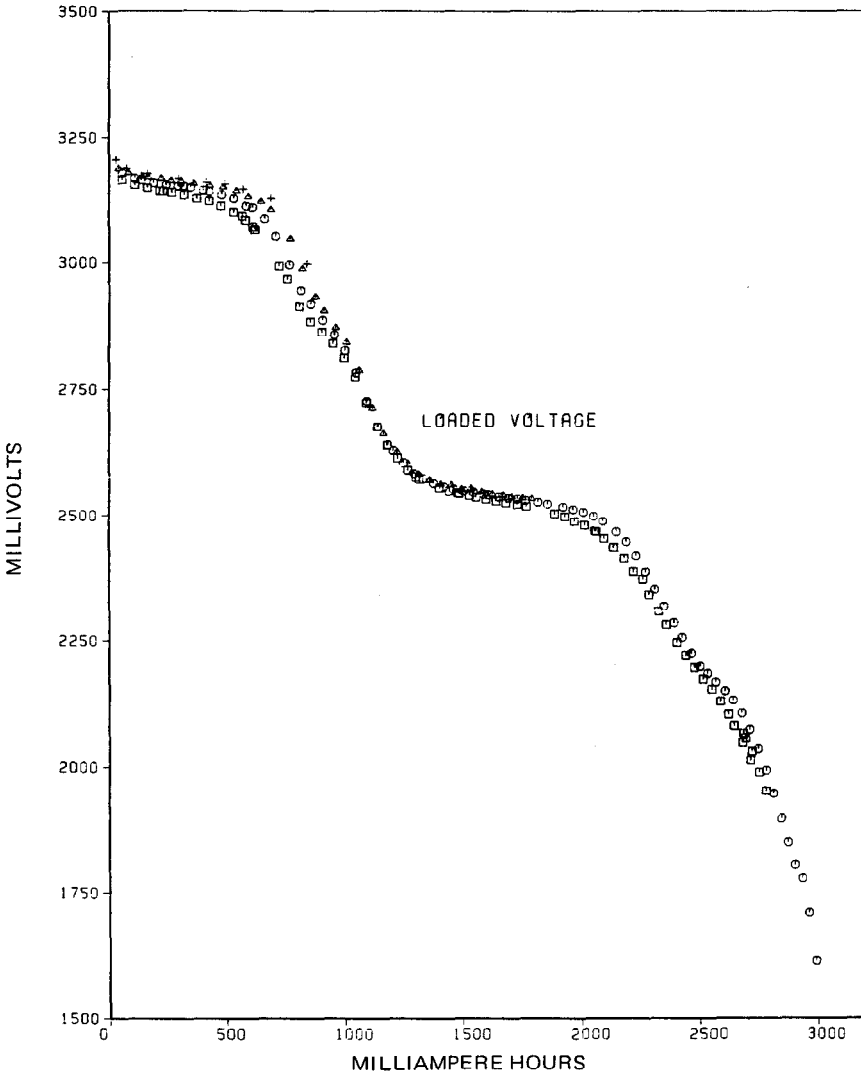


Fig. 2. Voltage as a function of depth of discharge (37 °C). □, 10.0 kΩ; ○, 20.0 kΩ; △, 38.3 kΩ; +, 80.6 kΩ.

year on test. This estimate is consistent with the value of 0.3 (± 0.1)% predicted from the calorimetry data on the room-temperature storage group after 25.54 months on test.

If it is assumed that all of the heat dissipating from the 10.0 kΩ test cells could be attributed to polarization and self-discharge, then microcalorimetry measurements under load and open-circuit would estimate 3.4 (± 1.5) and 3.1 (± 0.1)% self-discharge per test year, respectively. Neither of these estimations is consistent with the lithium-assay and storage-test results.

Because more heat dissipation occurs in the discharge test cells than can be attributed to polarization and self-discharge, an investigation into the contributions to the total heat dissipation was conducted on the 10.0, 20.0, 38.3, and 80.6 k Ω test cells. For a given voltage under load (V , mV), voltage under open circuit (V_{oc} , mV), constant resistive load (R , Ω), and test temperature (T , degrees Kelvin), the following thermodynamic relationship was used:

$$Q_t (\mu\text{W}) = Q_r + Q_p + Q_s + Q_{sd} + Q_x$$

where: Q_t represents the total heat dissipation as measured by the micro-calorimeter; Q_r , the heat dissipation attributed to the load inside the micro-calorimeter chamber = V^2/R ; Q_p , the heat dissipation attributed to polarization

$$= \frac{(V_{oc} - V)V}{R} = \frac{\eta V}{R};$$

Q_s , the heat dissipation attributed to entropy

$$= -\left(\frac{TV}{R}\right)\left(\frac{dV_{oc}}{dT}\right);$$

Q_{sd} , the heat dissipation attributed to self-discharge; Q_x represents the heat dissipation attributed to non-Faradaic contributions and/or parasitic side reactions, and where Q_r , Q_p , and Q_s are the contributions dependent on the discharge reaction.

The Q_p contribution was calculated using the electrical data gathered during discharge. Open-circuit measurements were taken on a regular basis, after two to six days of stabilization, and provided the η values. Figure 3 presents a sample graph of averaged loaded voltage data and averaged η voltage data as a function of test DOD. The grid lines at 850, 1700, and 2550 mA h correspond to the points of one, two, and three electron equivalents per mole of $\text{AgV}_2\text{O}_{5.5}$, respectively, in the discharge reaction.

Removing the Q_r and Q_p contributions from the total dissipation gave an estimate of net heat dissipation. Figure 4 presents a sample graph of averaged voltage data and averaged net heat dissipation as a function of DOD. Both the load and open-circuit calorimetry data are included in the Figure. In order to break down the contributions to the total heat dissipation further, the Q_s , Q_{sd} , and Q_x factors were calculated for the 10.0, 20.0, 38.3, and 80.6 k Ω test cells at four different DODs. Using the temperature coefficients calculated for the cells at 0, 27, 53, and 88% DOD, Q_s values were obtained. The Q_{sd} contribution was then estimated using the data from the room-temperature storage group, and was found to average 3.5 (± 2.0) μW throughout life.

Table 1 summarizes the Q contributions to the overall heat dissipation of the test cells at the four different DODs. The Q_x contribution was calculated by removing the estimated Q_s and Q_{sd} values from the net heat dissipa-

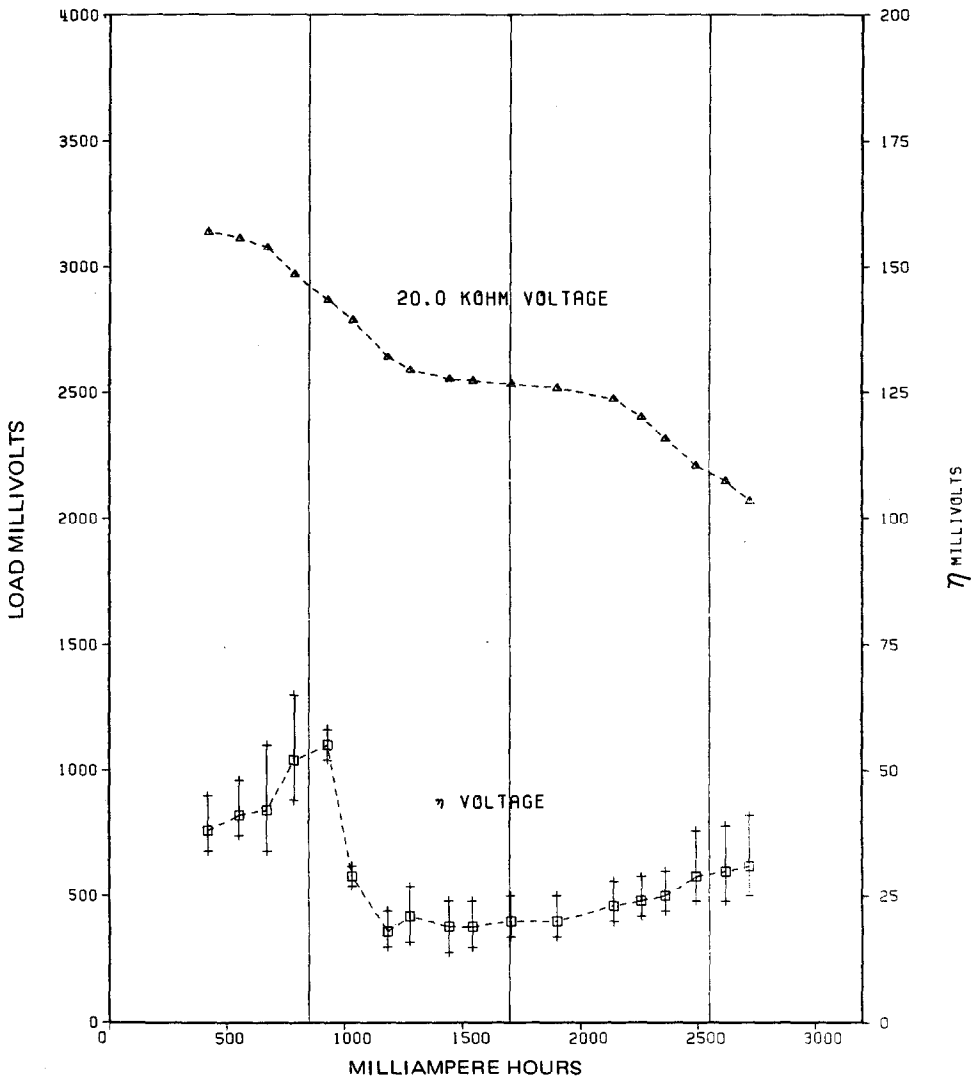


Fig. 3. Voltage and η voltage as functions of depth of discharge.

tion of the battery. By comparison with the Q_r and Q_x contributions, the Q_p , Q_s , and Q_{sd} factors are negligible.

Table 2 presents the estimated percent self-discharge per year based on the load microcalorimetry measurements, the open-circuit microcalorimetry measurements, and the lithium analysis. The differences found between the discharge test estimates and the storage/lithium assay estimates are attributed to non-Faradaic contributions and/or parasitic side reactions (Q_x).

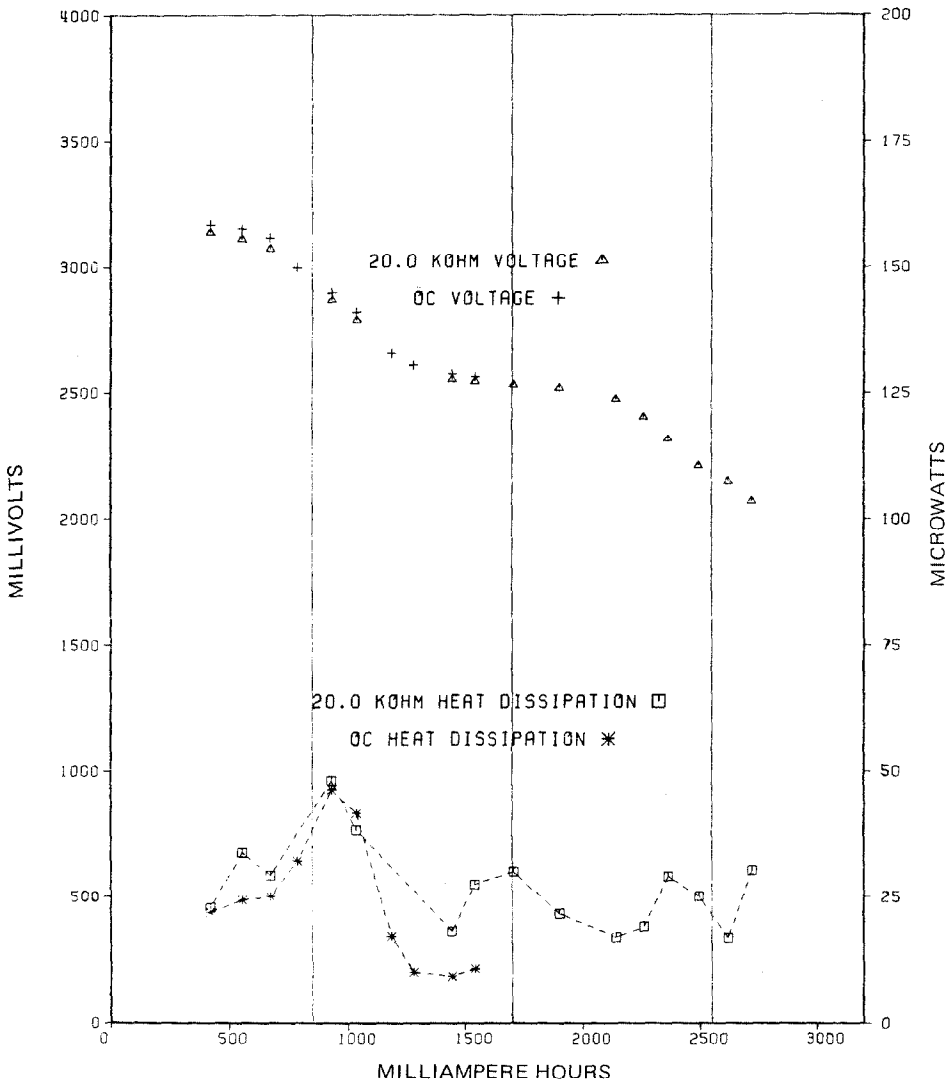


Fig. 4. Voltage and heat dissipation as functions of depth of discharge.

Conclusions

If it is assumed that all of the heat dissipating from the SVO discharge test cells can be attributed to polarization and self-discharge, then microcalorimetry measurements under load would estimate 3.4% self-discharge per test year for the 10.0 kΩ cells, 2.5% for the 20.0 kΩ cells, 1.4% for the 38.3 kΩ cells, and 0.5% for the 80.6 kΩ cells. Assuming that the contribution to total lithium loss from parasitic lithium discharge is negligible, the calorimetry data from the storage cells and the lithium-assay results from the 10.0 kΩ test cells estimated 0.0 - 0.8% self-discharge per year on test. Contribu-

TABLE 1
Contributions to total heat dissipation

Test load (k Ω)	Depth of discharge (%)	Q_t (μ W)	Q_r (μ W)	Q_p (μ W)	Q_s (μ W)	Q_{sd} (μ W)	Q_x (μ W)
10.0	0	—	—	—	—	—	—
	27	888 \pm 13	790	14	13	4	67
	53	665 \pm 13	626	9	17	4	9
	88	499 \pm 14	448	8	8	4	31
20.0	0	—	—	—	—	—	—
	27	467 \pm 13	411	8	6	4	38
	53	353 \pm 14	321	3	8	4	17
	88	248 \pm 14	214	3	4	4	23
38.3	0	269 \pm 14	261	2	1	4	1
	27	254 \pm 14	229	2	3	4	16
	53	190 \pm 1	170	1	4	4	11
80.6	0	136 \pm 1	125	1	0	4	6
	27	131 \pm 1	118	1	2	4	6

TABLE 2
Estimations of percent self-discharge per year

Test load (k Ω)	Average test (mths)	Average EOT (mV)	Average EOT (mA h)	% SD per year load (μ cal)	% SD per year OC (μ cal)	% SD per year assay
strg	25.54	—	—	—	0.3 \pm 0.1	—
10.0	15.84	1954	2774	3.4 \pm 1.5	3.1 \pm 0.1	0.3 \pm 0.5
20.0	31.03	1920	2835	2.5 \pm 1.4	—	—
38.3	27.58	—	—	1.4 \pm 1.0	—	—
80.6	27.58	—	—	0.5 \pm 0.1	—	—

EOT = End-of-test measurement.

% SD = Percent self-discharge at the lithium anode.

tions to the total heat dissipation from polarization and entropy were found to be negligible for the SVO system. The excess heat dissipated from the discharge test cells was therefore attributed to non-Faradaic contributions and/or parasitic side reactions.

References

- 1 C. C. Liang, M. E. Bolster and R. M. Murphy, *U.S. Pat. 4,310,609* (1982) and *4,391,729* (1983).
- 2 P. Keister, R. T. Mead, S. J. Ebel and W. R. Fairchild, *31st Power Sources Symp., Cherry Hill, NJ, June, 1984*, pp. 331 - 338.
- 3 E. S. Takeuchi and P. Keister, *Electrochem. Soc. Mtg., Las Vegas, NV, October, 1985*, pp. 195 - 196.