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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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EVALUATION OF LITHIUM-VANADIUM OXIDE CELLS

HERBERT F. HUNGER ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

DECEMBER 1982

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INTRODUCTION

The Li/TiS_2 cell, employing stable electrolytes, is known to show a high energy density, good rate characteristics, and an excellent cycle life.

The search for cells with even higher energy densities has been going on for the past decade and several new cathode materials such as $Cr_{0.75}V_{0.25}S_2$ and V_6O_{13} have been suggested. With the latter compound, hermetically sealed Li/V_6O_{13} cells have been built. Their behavior, after one year of storage, is the subject of this report.

DISCUSSION

Cell Description

Two types of hermetically sealed cells (prismatic type and laboratory test cell) have been used in the evaluation. Four cells were delivered by EIC Corporation under Contract Number DAAK20-79-C-0267, for ERADCOM evaluation. A thorough description of the cells geometry is given in the Final Report.¹

The prismatic cell is made of

$$Li/1.5 \text{ M LiAsF}_{6} - 2 \text{ Me} - THF/Nonstoichiometric V}_{6013}(V0_{2.19})$$

and the laboratory test cell of

 $Li/1.5 \text{ M LiAsF}_6 - 2 \text{ Me} - THF/Stoichiometric V_60_{13}(V0_{2.16}).$

The specifications for both types are given in Table 1.

Discharge and Charge of the Prismatic Cell

The second discharge was performed after storage of the cells for 11 months at room temperature in the fully charged state. The prismatic cell discharged at 140 mA (0.5 mA/cm^2) from an open circuit voltage of 2.78 V to 1.9 V. The temperature on the outside of the can varied between 21 and 28°C (21°C was the average temperature of the air conditioned room; 28°C can be reached at the given current flow by a heating effect caused by the internal illumination of the dry box).

Since a periodically interrupted sine wave pulse current circuit² was used, both the ohmic iR free cell voltage and the cell voltage including the ohmic iR drop could be recorded. The discharge and charge currents were, consequently, interrupted sine wave current pulses with a frequency of 60 Hz.

¹K. M. Abraham, J. L. Goldman, M. D. Dempsey, and G. L. Holleck, "Exploratory Development of an Electrically Rechargeable Lithium Battery," Final Report, Contract DAAK20-79-C-0267 (ERADCOM), EIC Corp., October 1980.

²H. F. Hunger and J. E. Ellison, "Cathodic Reduction of Carbon-Fluorine and Carbon-Nitrogen-Fluorine Compounds in Organic Electrolytes," R&D Technical Report ECOM-4296, March 1975.

TABLE 1. SPECIFICATIONS OF Li/V₆0₁₃ CELLS

<u>``</u>

	Laboratory Cell	Prismatic Cell			
Cathode					
Composition	1.7g stoichiometric V ₆ 0 ₁₃ (70 w/o V ₆ 0 ₁₃ , 20 w/	16.1 g nonstoichiometric V ₆ 0 ₁₃ /o C, 10 w/o Teflon)			
Thickness	48 mil	60 mil			
Cathodes Per C	ell 2	7			
Cathode Area	2.54 cm X 3.81 cm X 4 = 38.7 cm ²	5.0 cm X 3.75 cm X 14 = 263 cm ²			
Lithium Electrod	<u>e</u>				
Composition	0.72g lithium (designed for 200 cycles)	5.18g lithium			
Ah	2.78	20.0			
Anode Area	38.7 cm ²	263 cm ²			
Electrolyte	∼10 ml ≃10g	22.7g			
Separator	2 layers Ce	elgard 2400			
Capacity	During first galvanostatic discharge at 20 mA (0.5 mA/cm ²) for Laboratory Cell and 140 mA for Prismatic Cell.				
	312 mAh (0.59e/V)	5.21 Ah (1.04e/V)			
	during first galvanostatic cha given above	arge at same currents as			
	304 mAh	4.39 Ah			
Cell Weight	128.5g (90% can)	125.2g (50% can)			

The second discharge curve is shown in Figure 1. There are two distinct portions in the discharge curves with two different slopes. The total discharge time to 1.9 V was 24.5 hours corresponding to $0.7e^-$ /Vanadium atoms or to 0.7 Li atoms intercalated per Vanadium atom. The first region ends at about $0.3e^-$ /V, the second region starts between 0.4 and $0.5e^-$ /V. A current density of 0.5 mA/cm^2 leads to an iR drop of about 0.1 V. The ohmic cell resistance R Ω increased during discharge from 0.67Ω to 1.43Ω . Since there are no other changes in the system, this must be caused by the intercalation of 0.7 atoms of lithium per vanadium atom. This increase in ohmic cell resistance is shown in Figure 1. The increase is fairly linear and proportional to the number of lithium atoms intercalated (+ $0.057 \Omega/0.1e^-$).

The second charge of the prismatic cell from 2.16 to 3.0 V at 140 mA (0.5 mA/cm^2) and within a temperature range of 22 to 27°C took 27.5 hours corresponding to $0.77e^{-}/V$. The second charge curve is also shown in Figure 1. The measured cell voltage includes the ohmic iR drop. The charge curve shows an initial plateau between 2.3 and 2.35 V up to a charge of $0.3e^{-}/V$. Thereafter, a steep rise to 2.6 V is observed, followed by a steady increase to 3.0 V.

Charge Retention of the Prismatic Cell Type

The prismatic cells were cycled once galvanostatically, shortly after fabrication. Then they were stored for 11 months in the fully charged state at room temperature. The second cycle was measured thereafter. The results of the first two cycles are compared in Table 2.

TABLE 2. CHARGE RETENTION OF PRISMATIC CELL (NS V₆0₁₃)

EVENTS	Ah	e /V	% OF ORIGINAL CAPACITY
FIRST DISCHARGE	5.21	1.04	100
FIRST CHARGE	4.39	0.88	84.26
SECOND DISCHARGE	3.48	0.70	79.29
SECOND CHARGE	3.88	0.77	88.33
FIRST CHARGE SECOND DISCHARGE SECOND CHARGE	4.39 3.48 3.88	0.88 0.70 0.77	84.26 79.29 88.33

A capacity loss of 15.74% is observed after the first discharge. This corresponds to an intercalation level of $\text{Li}_{0.16}\text{V}_6\text{O}_{13.14}$. The actual capacity loss after one year of storage is only 4.97%. The capacity increase after the second charge (60 Hz interrupted sine wave pulse current) is 9.04% over that of the second discharge and exceeds the capacity of the first charge by 4.07%. A beneficial effect caused by the charging method cannot be excluded as one possibility.

The excellent capacity retention after one year of storage exceeds considerably that of nickel-cadmium and nickel-zinc cells which retain only about 50% of their capacity after one year of storage. This decay is mainly due to the NiO(OH) electrode.



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Energy Per Weight and Volume (Prismatic Cell)

The energy per weight and volume data of the prismatic cell with nonstoichiometric $V_6O_{1,3}$ are given in Table 3.

TABLE 3. ENERGY PER WEIGHT AND VOLUME (PRISMATIC CELL NS V_60_{13})

183 Ah/kg of Reactants
88 Ah/kg of Reactants plus Electrolyte
62 Ah/kg of Cell Component Weight
139 Wh/kg of Cell Component Weight
70 Wh/kg of Total Cell Weight
0.078 Ah/cm³ of Can Volume
0.18 Wh/cm³ of Can Volume

The ampere-hours measured during the second charge were used as a basis for the cell capacity (3.88 Ah). An average discharge voltage of 2.25 V was estimated from the second discharge data.

We obtained 183 Ah/kg of reactants and 70 Wh/kg of total cell weight, including can weight. This is equal to 32 Wh/lb. These data are for a 27.5 hour rate (0.5 mA/cm^2) after one year of storage.

The electrode package volume is 5.0 cm X 3.7 cm X 1.8 cm = 33.75 cm³. Based on this volume, we obtain 0.11 Ah/cm³ or 0.26 Wh/cm³. Based on the can volume 5.5 cm X 5.0 cm X 1.8 cm = 49.5 cm³, we obtain 0.18 Wh/cm³.

Discharge and Charge of the Laboratory Cell

Like the prismatic cells, the laboratory cells were cycled once after fabrication and then remained fully charged for 11 months on shelf. Then the second discharge was performed at a current of 20 mA (0.5 mA/cm^2) from an open circuit voltage of 2.78 V to a cell voltage of 1.9 V over a temperature range of 20 to 27°C.

The discharge curves are shown in Figure 2. The upper curve is without the ohmic drop, the lower curve includes the ohmic iR drop. The discharge took 15 hours and $0.57e^{-1}$ /Vanadium atom were obtained for the stoichiometric vanadium oxide. Figure 2 also shows the second charge curve. The second charge at 20 mA (0.5 mA/cm^2) from about 2.1 V to 3.0 V over the temperature range 20°C to 26°C took about 13 hours. The ohmic resistance increase during the second discharge is also shown in Figure 2.

In Figure 3 the second discharge of stoichiometric (S) and nonstoichiometric (NS) V_6O_{13} are compared. A discharge plateau between 2.15 and 2.08 V accounts for the higher e⁻/V of the nonstoichiometric V_6O_{13} (0.7e⁻/V) versus 0.57e⁻/V for the stoichiometric V_6O_{13} . From Figure 3 it can be seen that the cell polarization, excluding the ohmic iR drop, is less for the stoichiometric oxide up to about 0.5e⁻/V as compared to the nonstoichiometric V_6O_{13} . Better rate characteristics should be expected from the stoichiometric V_6O_{13} . From Figure 3 a rate increase of 73 percent of the stoich'ometric oxide over the nonstoichiometric oxide was computed.



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The charge retention of the laboratory cell is shown in Table 4. The second discharge after one year of storage showed a capacity loss of only 1.3%. The third partial charge nearly restored the capacity to that one of the first charge.

TABLE 4. CHARGE RETENTION OF LABORATORY CELL (S V_60_{13})

EVENTS	Ah	<u>e⁻/V</u>	% OF ORIGINAL CAPACITY
FIRST DISCHARGE	0.312	0.59	100
FIRST CHARGE	0.304	0.57	97.45
SECOND DISCHARGE	0.30	0.567	96.15
SECOND CHARGE	0.26	0.49	83.33
THIRD PARTIAL CHARGE		0.573	97.13

The capacity of the laboratory cell corresponds to 149 Ah/kg of reactants. The amount of lithium in the cell is about 10 times the stoichiometric amount required (cathode limited system) since the cell is designed for 200 cycles. If the lithium amount is reduced by 50 percent, we would obtain 180 Ah/kg which comes close to the figure for the nonstoichiometric V_{60}_{13} in Table 3.

The Open Circuit Potentials of V6013 Cathodes

The open circuit potentials of V_6O_{13} cathodes measured against a lithium reference electrode are identical with the open circuit voltages of Li/V_6O_{13} cells. They are a function of the state of charge of such cells and can be used directly to determine the prevailing state of charge of the cell.

In Figure 4 the open circuit potentials of stoichiometric and nonstoichiometric $V_{6}O_{13}$ versus lithium are plotted as a function of e^-/V atom or Li atoms/V atom. The potentials were measured during interruptions in the charge or discharge processes (partial or complete charge or discharge) after a constant potential was attained which occurred usually after resting overnight. The curves for both oxides are practically identical up to $0.5 e^-/V$. Above that value the two oxides behave differently. The stoichiometric oxide continues the potential decline observed after $0.4 e^-/V$. The nonstoichiometric oxide exhibits a plateou extending to $0.7 e^-/V$. In the case of TiS₂ or MoO₃ the whole intercalation range is linear. Nonlinear behavior is an indicator of different phases or compounds formed during the intercalation process.

The Rate Characteristics of Stoichiometric V₆0₁₃ Cathodes

The rate characteristics of $\text{Li/V}_{60_{13}}$ cells were measured with laboratory cells (stoichiometric $V_{60_{13}}$) after one year of storage. A step discharge was used to determine the rate characteristics. The cell was discharged in consecutive steps for about one minute each at given current densities and the cell voltage (without and with the ohmic iR drop) was measured at the end of each one minute discharge scep. The chosen current densities were 0.25, 0.33, 0.50, 1.00, 2.50, 4.00, and 8.00 mA/cm². In Figure 5 both cell voltages are plotted against the current density. A cell voltage of 1.9 V is reached during this type of step discharge at 8 mA/cm². This has to be considered the practical rate limitations of the cell





around room temperature. The current densities were chosen for the following reasons. In a design study (Appendix A) to replace nickel cadmium batteries by a rechargeable lithium battery of the type described in this report, it was found that the following current densities were significant. A current of 0.33 mA/cm^2 corresponds to the receiving mode of a radio set and 2.5 and 8.0 mA/cm² to two transmitting modes. The required duty cycles are 9:1. The laboratory cell underwent Program 1, at 0.33 mA/cm^2 (13 mA), followed by Program 2, at 8 mA/cm² (810 mA). The actual duty cycles were 9:1 min., 37:1 min., 10:1 min., 40:1 min., and 10:1 min., until 1.9 V cell voltage were reached. The cell voltages (plus and minus ohmic iR drop for Program 2) versus time of operation are shown in Figure 6. In this discharge about 25 percent of the total cell capacity were taken out.

Based on a rate capability of 8 mA/cm^2 , which would correspond initially to 2.12 A at 2.33 V in the prismatic cell design, a power per weight ratio of 39 W/kg of total cell weight can be estimated. For the 1.9 V cutoff level, 32.2 W/kg can be calculated.

The rate capability of laboratory cells after one year of storage was also determined below room temperature. Figure 7 shows the cell voltage versus log of current and current density of a laboratory cell at 26.5° C and at 0° C. The method used to obtain the current voltage curves was again the one minute step discharge described previously. In such a step discharge at 26.5° C, 8 mA/cm² can be reached at 1.9 V (+ iR). At 0.0°C, only 2.5 mA/cm² can be reached or 31.25% of the rate capability at room temperature. Other electrolytes than 1.5 M LiAsF₆ - 2M-THF have to be employed if lower temperature operation is required.

One approach to increase the rate capability of the cells is the addition of a co-solvent to the electrolyte. In some cases, synergistic effects increasing the electrolyte conductance and improving the rate capability of the cells are observed.³

In Figure 8 five minute step discharges of the following cells are compared:

L1/0.5M L1AsF₆ - DME/MoO₃ L1/1.5M L1AsF₆ - 2M-THF/V₆O₁₃ L1/1.0M L1AsF₆ - DME (75 V%) - PC (25 V%)/MoO₃

Figure 8 shows a plot of the cell voltages minus the ohmic iR drop versus the current density. The beneficial effect of the synergistic effect caused by the addition of a co-solvent to a single solvent electrolyte is shown by comparing a DME electrolyte with a DME-PC electrolyte. Similar improvements can be expected for the 2M - THF electrolyte by addition of a proper co-solvent. This would not only increase the rate capability at room temperature but also the low temperature operation.

SUMMARY AND CONCLUSIONS

Hermetically sealed Li/V_6O_{13} cells (prismatic and laboratory cell type) were evaluated after one year of storage at room temperature. The original capacity of the prismatic cells was 4 to 5 Ah and that of the laboratory cell about 300 mAh.

³H. F. Hunger, "Electrolytes for Rechargeable Lithium Batteries," R&D Technical Report DELET-TR-81-17, September 1981.



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Figure 6. Laboratory Cell (S V_60_{13}). Discharge (Program 1 and 2).

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From discharge and charge curves it was found that nonstoichiometric $V_{6}O_{13}$ could intercalate about 0.7 lithium atoms per vanadium atom at low rates of discharge (0.5 mA/cm²) while stoichiometric $V_{6}O_{13}$ could accommodate only 0.57 lithium atoms per vanadium atom. The intercalation process can be followed by a linear increase in ohmic resistance proportional to the number of lithium atoms intercalated.

The charge retention of both cell types was excellent. The capacity loss after one year of storage was only 4.97% for the prismatic cell and only 1.3% for the laboratory cell. Charging with a 60 Hz interrupted sine wave pulse current has apparently a beneficial effect in restoring the capacity to about that of the original charge.

The energy to weight and volume ratios of the prismatic cell after one year of storage are 139 Wh/kg of cell components or 70 Wh/kg of total cell weight and 0.18 Wh/cm³ of can volume.

The open circuit potentials of the cells are a function of the degree of intercalation (lithium atoms per vanadium atom) and can be used directly to determine the state of charge of the battery.

The stoichiometric V_6O_{13} permits a higher rate than the nonstoichiometric oxide. The rate limitation of the cell lies around 8 mA/cm² for intermittent pulse current at room temperature. Continuous performance with high cell capacities could be demonstrated at 0.5 mA/cm².

The maximum power per weight ratio of a stoichiometric V_6O_{13} cell can be estimated at 39 W/kg after one year of storage.

The practical rate capability of the stoichiometric V_6O_{13} is, however, only 2.5 mA/cm² at 0.0°C. This is 31 percent of the rate at room temperature.

APPENDIX A

Design Study of a Rechargeable Lithium Battery (RLB)

In the next two tables (Tables A and B) the results of the design study are summarized.

Table A compares the characteristics of a conventional, vented nickel-cadmium battery with a RLB design. The RLB has 14 cell packages in series to give the required voltage. Each cell package consists of 7 single cells in parallel to provide the required current. The design is based on a cutoff voltage of 1.5 V for the single cell. The three power levels are for the transmitting and receiving mode of the radio set. At about the same weight as the nickel-cadmium battery, the RLB has three times the capacity or hours of operation. At the time of the design study, data for low temperature operation (-40°C) were not available. Over 200 deep discharge cycles have been obtained with Li/V_6O_{13} cells.

TABLE A. COMPARISON BETWEEN NICKEL-CADMIUM BATTERY AND RECHARGEABLE LITHIUM BATTERY

	Ni-Cd Battery (BB-651/U)	Rechargeable Lithium Battery					
NUMBER OF CELLS	24 Cells in Series	7 Cells in Par./14 C.Ps in Series					
VOLTAGE	20-32 V	20-35 V					
CURRENT (POWER)	$5-8A$ $6.5\overline{A}$ (160 W) $1.6 - 2.5A$ $2.05\overline{A}$ (50 W) $0.22 - 0.35A$ $0.28\overline{A}$ (6 W)	8 mA/cm ² (1.5 V _e Design) 2.5 mA/cm ² 0.33 mA/cm ²					
DUTY CYCLE	9:1	Same					
DIMENSIONS	4"x5"x13"/10.16x12.7x33 cm	10x12x20 cm					
VOLUME	260 cu in (4,260 cm ³)	$2,400 \text{ cm}^3$					
WEIGHT	12.5 - 13.5 #(5.67 - 6.12 kg)	6.3 kg					
CAPACITY	5.5 Ah	16.8 Ah					
OPERATING TIME	6 Hours High Power 12 Hours Low Power	18.3 Hours 36.6 Hours					
	1-2 Hours -40°C	5.6 Ah Expected					
CYCLES	1000 Cycles	200+ Cycles					

Table B shows Rechargeable Lithium Battery Design Characteristics, describing the electrodes, single cells, cell packages, and battery.

> TABLE B. RECHARGEABLE LITHIUM BATTERY DESIGN CHARACTERISTICS Electrode Area: 120 cm² = 10 x 12 cm Current Density: 8 mA/cm²; V_e = 1.5 V Cathode Thickness: 50 mils (0.127 cm); Capacity: 20 mAh/cm² Lithium Electrode: 15 mils; Capacity: 60 mAh/cm² Cell Thickness: 0.2 cm 7 Cells in Parallel Per Cell Package. Thickness: 1.4 cm Cell Package Weight: 310 g 14 Cell Packages in Series = Battery Battery Component Weight: 4.3 kg Can & Seal Weight: 2.0 kg Wh/kg Cell Components: 103 (47 Wh/1b) Wh/kg Battery: 71 (32 Wh/1b) W/kg Battery: 25 Wh/cm³ Battery: 0.186

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