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OAK RIDGE NATIONAL LABORATORY

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CRADA Final Report
for
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DEVELOPMENT OF A THIN-FILM BATTERY POWERED HAZARD CARD AND OTHER MICROELECTRONIC DEVICES

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CRADA No. ORNL 94-0285
with
Research International
for
Development of a Thin-Film Battery Powered Hazard Card and Other Microelectronic Devices
Final Report

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Solid State Division

Abstract

The objective of this project is to develop several types of microelectronic devices including a personal hazardous monitor, that could be powered by thin-film rechargeable lithium batteries developed at the Oak Ridge National Laboratory. Work performed at ORNL included designing and fabricating thin film lithium cells with amorphous V_2O_5 cathodes that could meet or exceed the requirements of Research International's devices. Work performed at Research International included designing prototype devices and testing them with the batteries made at ORNL.

Objective

This project was ained at the development of microelectronic devices including a personal hazardous monitor, that could be powered by thin-film rechargeable lithium batteries developed at the Oak Ridge National Laboratory.

Benefits to DOE Missions

This project aided in the advancement of ORNL's thin-film rechargeable lithium batteries and enhanced the prospects the commercialization of this technology. The primary device developed, a personal hazard gas sensor or "Hazard Card", was designed to detect low levels of specific, toxic organic molecules and to sound an alert when the concentration reached dangerous levels. The card could be used, for example, by workers involved in decontamination and decommissioning of DOE facilities.

Work Performed

Hazard Card

Two designs for the hazardous gas sensor, the "Hazard Card", were considered (Appendix 1). For both designs, the minimum operating voltage is 2.5 V. In the preliminary design, the quiescent operating current was about 10 μA, and the liquid crystal display and the alarm required pulses of 29 μA and 49 μA, respectively. For 24 h of operation, the battery is required to deliver 248 μAh of capacity above 2.5 V. In the final design, the quiescent current drain for continuous operation of the sensor and flickering LED display is 20 μA, and the audible alarm requires 68 μA. For continuous operation of the sensor and display for 8 h and for 5 soundings of the audible alarm for 60 s each, the battery is required to deliver 166 μAh above 2.5 V. The requirements for both designs were to be met after 1000 cycles.

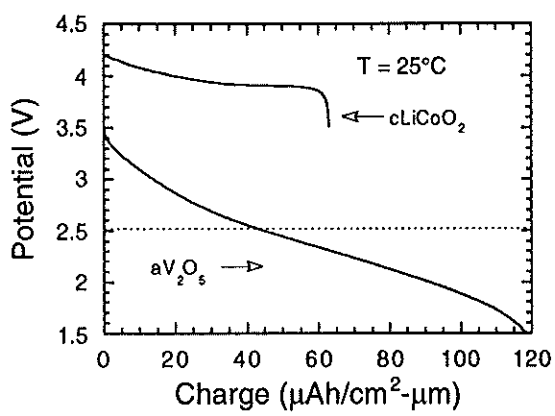

Fig. 1. Low current (1 $\mu A/cm^2$) discharge curves for thin-film lithium batteries with amorphous V_2O_5 and crystalline $LiCoO_2$ cathodes.

At the time this project began, our experience with thin-film cathode materials was limited to amorphous vanadium oxide. We deposited the V_2O_5 films by reactive dc magnetron sputtering of V in Ar + 15 % to 20 % O_2. The as-deposited films had an O/V ratio of 2.5 (±0.1) as determined by Rutherford backscattering and Auger electron spectroscopy, and they were observed to be amorphous in electron diffraction measurements. A graph of specific capacity vs. voltage for a Li-aV_2O_5 cell discharged at a low current shown in Fig. 1. Although Li-aV_2O_5 batteries have a high specific capacity of ~120 $\mu Ah/cm^2$-μm between 3.5 V and 1.5 V, less than half of this capacity is available at potentials above 2.5 V. Recently, a new battery designed for the Hazard Battery that is based on $LiCoO_2$ cathodes will have much higher specific capacity above 2.5 V (Fig. 1) than the Li-aV_2O_5 cell developed in the early stages of this project.

As a consequence of internal cell resistance, which is due mainly to the cathode, the capacity delivered depends on the thickness and area of the cathode, the current density, and the temperature. Examples of the effect of current density and temperature are shown in Fig. 2. In order to obtain a data base for design of the Hazard Card battery, work at ORNL during the early months of the project focused on the behavior of 1 cm^2 sized cells with cathodes of different thicknesses under different loads and cycling conditions.

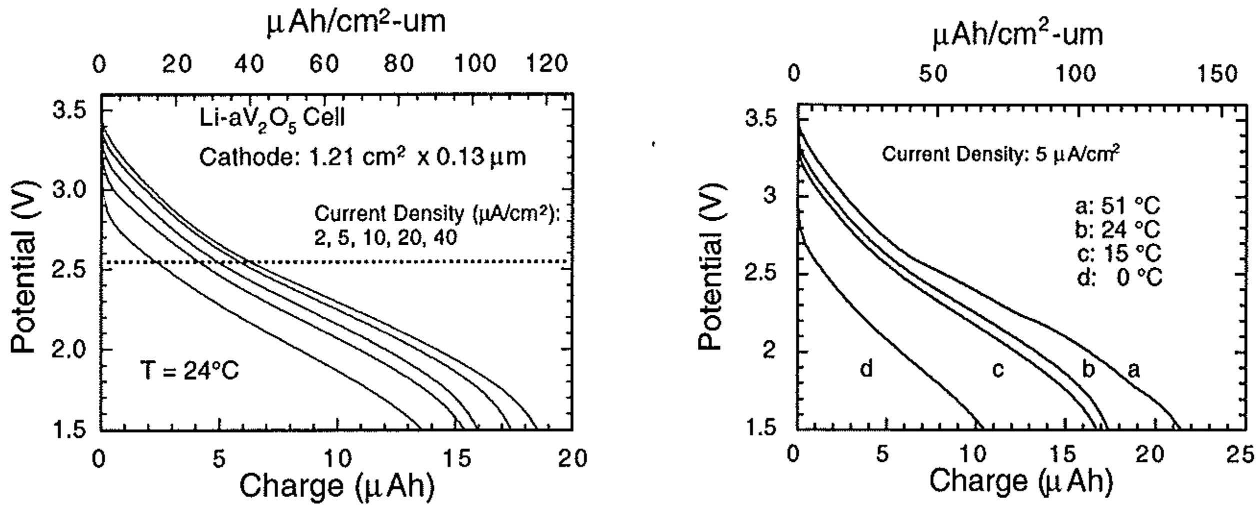

Fig. 2. Discharge of a Li-aV_2O_5 battery at different current densities at 24°C and at different temperatures for a current density of 5 µA/cm^2.

The space allocated to the Hazard Card battery was one side of a 2" × 4" substrate; the reverse side was to be occupied by the sensor and circuitry in the final product. From the results of the experiments with small cells, we expected that a battery with a cathode of 9 cm^2 and about 1 µm thick should deliver the energy and power required by the device after 1000 cycles. The layout of the prototype battery is shown in Fig. 3. Because the area of the battery is large relative to the flux from our the 2" diameter magnetron sputter guns, the thickness of the current collector, cathode, and electrolyte films varied by about 20% from the edge to the center of the films. However, this non uniformity had no evident effect on battery performance. Based on a specific capacity of 120 µAh/cm^2-µm, the average cathode thickness was about 1 µm.

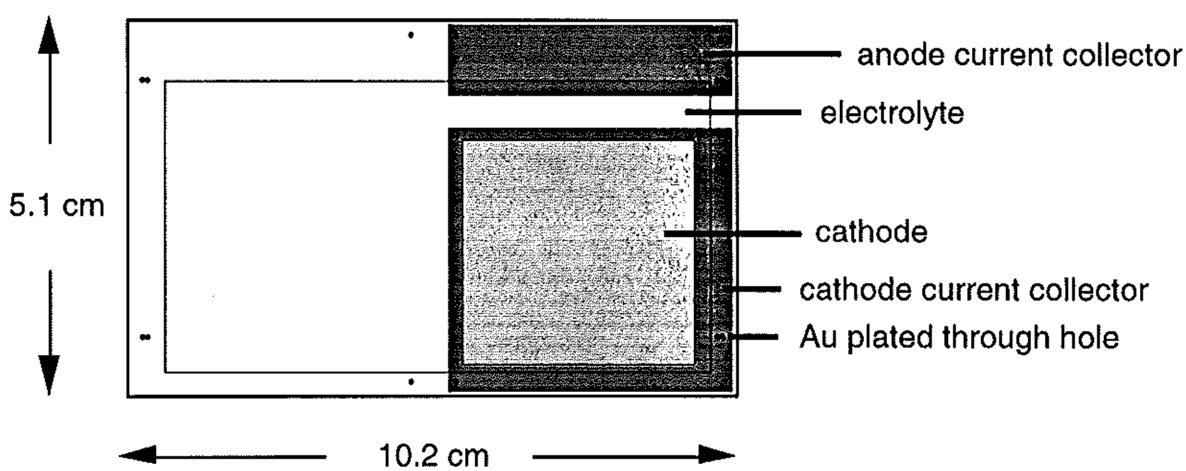

Fig. 3. Layout of the Hazard Card Battery. Lithium anode and protective coating not shown.

A complete duty cycle of one of the prototype batteries operating under quiescent conditions of the final Hazard Card design is shown in Fig. 4. As can be seen, this battery could supply 20 μA for 8 h for operation of the sensor and display, and there remained sufficient capacity to supply 68 μA for about 2.5 h of operation of the alarm, far longer than specified (Appendix 1). The charging circuit of the Hazard Card is based on contactless optical coupling using photodiodes and has a maximum output current of about 30 μA. This is sufficient to fully charge the battery in less than 6 h following 8 h of normal operation of the Hazard Card. From extensive cycling experiments with 1 cm^2 Li-aV_2O_5 cells, we can predict that for the duty cycle of Fig. 4, the capacity of the Hazard Card battery will decrease about 0.04% with each cycle. Therefore, the battery which had a starting capacity of 330 μAh above 2.5 V, will be able to supply over 190 μAh or just over 10% more capacity than required to operate the Hazard Card after 1000 cycles. In order to provide a more comfortable margin of extra capacity, the cathode thickness could be increased by at least 50% without compromising performance. There is also ample room on the substrate for increasing the active area of the battery.

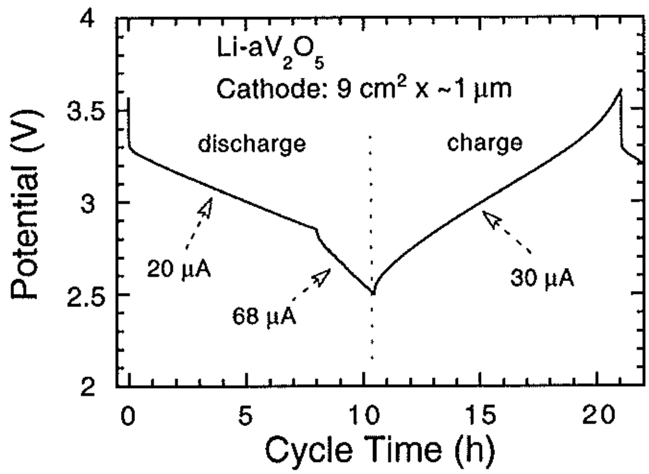

Fig. 4. One duty cycle of the Li-aV_2O_5 Hazard Card battery.

SRAM Backup

Research International has proposed several potential applications such as a personal identification badge in which a thin-film battery is used to retain memory in SRAM chips. A study to demonstrate memory backup was recently completed using 1 MB and 2 MB PCMCIA cards. When removed from the computer, the current loss corresponds to a drain through a constant load of 1–2 MΩ, and we observed that memory is retained at voltages as low as 1.5 V. The result of one experiment is shown in Fig. 5. The battery, consisting of two Li-aV_2O_5 cells connected in parallel had a capacity of about 1.6 mAh between 3.5 V and 1.8 V. At the 1.8 V cutoff, the battery could hold memory in the 2 MB card for about 25 days.

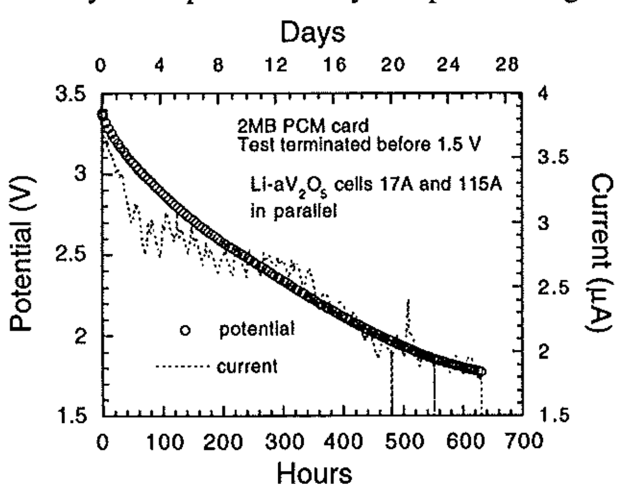

Fig. 5. Voltage and current supplied by the Li-aV_2O_5 battery to a 2MB PCMCIA card.

Conclusions

It was demonstrated in this project that thin-film rechargeable lithium batteries can meet the power requirements of a variety of microelectronic devices. During the course of this research, thin-film batteries with crystalline $LiCoO_2$ cathodes have been developed. A new design for a Hazard Card battery that is based on four Li-$LiCoO_2$ cells is illustrated in Fig. 5. As shown in Fig. 1, crystalline $LiCoO_2$ has a significantly larger specific capacity than aV_2O_5 for operation above 2.5 V. The battery illustrated occupies just over one-half of one side of the substrate. Each battery with a 4 $cm^2 \times 1$ μm thick $LiCoO_2$ cathode can deliver about 240 μAh of charge between 4.2 V and 3.8 V. The voltage range and capacities that could be achieved with different combinations of parallel and series connections are given in Table 1. With the capability of 4 V, 8 V, or 16 V operation, the battery offers possibilities for new circuit designs with different types of sensors.

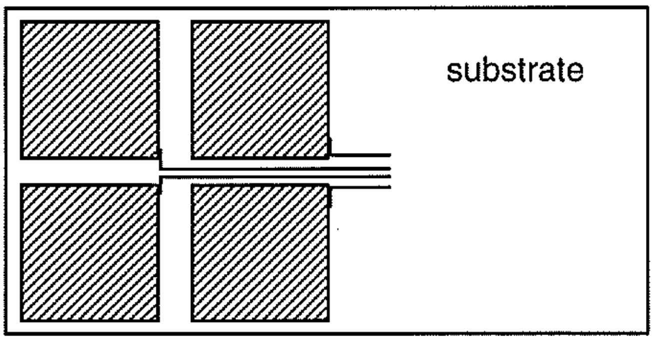

Fig. 5. Proposed four-cell Li-$LiCoO_2$ battery for the Hazard Card.

Table 1. Future Prototype Battery for Hazard Card

Connection	Voltage Range	Capacity (μAh)
4 cells in parallel	4.2–3.0	960
Series combination of 2 cells in parallel	8.4–6	480
4 cells in series	16.8–12	240

Future Work and Commercialization Possibilities

Research International has not revealed any plans to pursue development of the Hazard Card and no future work has been planned. However, the prospects for commercialization of ORNL's thin film rechargeable battery technology are good. A prototype manufacturing project is currently under way at a large U. S. company, and an in-line system for high volume production of thin film batteries is being designed.

Inventions

Listed below are issued patents and one invention disclosure that resulted totally or in part from this CRADA project.

“Protective Lithium Ion Conducting Ceramic Coating for Lithium Metal Anodes and Associate Method,” J. B. Bates, U.S. Patent No. 5,314,765 (May 24, 1994).

“Thin-Film Battery and Method for Making Same,” J. B. Bates, N. J. Dudney, G. R. Gruzalski, and C. F. Luck, U.S. Patent No. 5,338,625 (Aug. 16, 1994).

"Method for Making an Electrolyte for an Electrochemical Cell", J. B. Bates and N. J. Dudney, U. S. Patent No. 5,512,147 (Apr. 30, 1996).

“Packaging Material for Thin-Film Lithium Batteries,” J. B. Bates, N. J. Dudney, and K. A. Weatherspoon, U.S. Patent No. 5,561,004 (Oct. 1, 1996).

“Rechargeable Lithium Battery for Use in Applications Requiring a Low to High Power Output”, J. B. Bates, U. S. Patent No. 5,569,520 (Oct. 29, 1996).

"Method for Making an Electrochemical Cell", J. B. Bates and N. J. Dudney, U. S. Patent No. 5,567,210 (Oct. 22, 1996).

“Rechargeable Lithium Battery for Use in Applications Requiring a Low to High Power Output,” , J. B. Bates, U. S. Patent No. 5,569,520 (Oct. 29, 1996).

“An Electrolyte for an Electrochemical Cell,” J. B. Bates and N. J. Dudney, U.S. Patent No. 5,597,660 (Jan. 28, 1997)..

“Rechargeable Lithium Battery for Use in Applications Requiring a Low to High Power Output,” U. S. Patent No. 5,612,152 (Mar. 18, 1997).

Patent on new inorganic anode material for thin-film rechargeable lithium-ion batteries is in preparation for U. S. and foreign filing.

APPENDIX 1

Power Specifications and Battery Characteristics for the Hazard Card

Battery Design Specifications	Preliminary Design	Final Design
Voltage		
Nominal, V	3	3
Max, V	6	6
Min, V	2.5	2.5
Load (Discharge)		
Quiescent, μA	10.3	20
Total Pulse-1, μA	28.5	
Pulse-1 time, s	90	
Total Pulse-2, μA	48.6	68
Pulse-2 time, s	10	60
Total pulses/cycle	1	5
Discharge cycle time, h	24	8
Number of cycles	1000	1000
Battery Life		
Nominal, years	3	3
Capacity		
Quiescent, μAh/cycle	247	166
Pulse-1, μAh/cycle	0.71	
Pulse-2, μAh/cycle	0.14	
Total Capacity, μAh/cycle	248	235
Dimensions		
(Dia. or) Width, cm	2.00	3.00
Length, cm	4.00	3.00
Area (foot print), cm^2	8.00	9.00
Active film thickness, μm, max	10	10
Substrate thickness, typ.	100–500	100–500
Temperature		
Nominal, °C	25	25
Max, °C	55	55
Min, °C	0	0

Appendix 2

Tasks and milestones from the CRADA statement of work:

Laboratory Tasks

1. Fabricate Li-V_2O_5 thin-film batteries onto substrates supplied by RI.
2. Characterize the structure of each cathode in the early stages of the project.
3. Cycle each battery several times under conditions that mimic the application.
4. Investigate the cause of any battery failure experienced by RI.

Research International Tasks

1. Design and fabricate prototypes of the "Hazard Card".
2. Supply substrates for the thin-film batteries and sufficient technical information to allow realistic battery testing to be performed at ORNL.
3. Integrate batteries into devices.
4. Test the performance of devices powered by thin-film batteries.

Deliverables

The following reports and abstracts are required to be delivered under Article XI of the CRADA:

1. an initial nonproprietary abstract suitable for public release;
2. other abstracts (final when work is complete, and others as substantial changes in scope and dollars occur);
3. an annual progress report containing no Proprietary Information or Protected CRADA Information so the report can be openly distributed;
4. an final report; and
5. other topical/periodic reports where the nature of the research and magnitude of dollars justify.

Major Milestones

- Design and fabricate prototype devices (RI).
- Fabricate and test thin-film Li-V_2O_5 batteries to meet device requirements (ORNL).
- Test and evaluate battery-powered devices.
- Prepare quarterly reports.
- Prepare a final report.

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