Journal of Power Sources, 5 (1980) 3 - 13

PERFORMANCE AND RELIABILITY OF THE LITHIUM/IODINE BATTERY

C. C. LIANG and C. F. HOLMES
Wilson Greatbatch Ltd., 10,000 Wehrle Drive, Clarence, New York 14031 (U.S.A.)

Summary

The lithium/iodine –polyvinylpyridine battery, used as a power source in cardiac pacemakers, is discussed. Because of the critical nature of the use of this cell, rather stringent reliability and quality assurance procedures are carried out during design, manufacturing, and testing of these cells. The construction of the cells is carried out under careful quality control supervision. An intensive reliability program is initiated in early design stages and carried out through the useful life of the cells.

The cells currently produced show energy densities of approximately 0.75 W h/cc in a range of cell configurations with rated capacities from 1.3 - 3.0 A h. Since first implanted in late 1972, lithium–iodine cells have amassed an outstanding record of reliability in the clinical application. The construction, reliability procedures, and performance of the cells are discussed in this paper.

Introduction

The lithium/iodine–polyvinylpyridine (PVP) battery is a long life, low drain, solid electrolyte, primary cell which has seen extensive use as a power source for cardiac pacemakers. The anode is lithium, the cathode/depolarizer is an iodine–PVP charge transfer complex, and the electrolyte is lithium iodide, formed *in situ* during discharge. The iodine–PVP mixture contains excess iodine at unit thermodynamic activity and is an electronic conductor. The self-forming electrolyte/separator increases in thickness as the cell is discharged, causing a gradual rise in impedance. Near end-of-life the conductivity of the iodine–PVP complex drops markedly, causing a more rapid drop in loaded voltage and indicating approaching end of cell life.

The history, chemistry, discharge characteristics, and cell design aspects of this system have been discussed elsewhere in the literature [1 - 6]. Since its commercial introduction in 1972, over three hundred thousand of these cells (in various design configurations) have been implanted and have

TABLE 1

Specifications of Wilson Greatbatch Ltd. batteries

Model	Nominal dimensions (mm)	Nominal weight (g)	Nominal volume (cm^3)	Rated capacity (A h)	Energy density
755	33 × 9 × 40	33	9.5	3.0	227 W h/kg 0.79 W h/cm^3
762	45 × 9 × 28	30	8.6	2.5	208 W h/kg 0.73 W h/cm^3
761/15	45 × 8.6 × 15	17	4.6	1.3	190 W h/kg 0.71 W h/cm^3
761/23	45 × 8.6 × 23	27	7.6	2.5	230 W h/kg 0.82 W h/cm^3

amassed an outstanding clinical record of reliability. Over the past few years many improvements to cell design have been made by several organizations.

It is the purpose of this paper to discuss the current state of the art in cell design and construction as practiced by this company. Particular emphasis is given to the reliability and quality assurance program instituted to insure optimum performance of this critical item. Cell performance and estimates of self-discharge are also discussed.

Cell design and construction

The evolution of the design of the lithium–iodine cell has been discussed at a recent symposium [7]. Currently four models are produced for use in cardiac pacemakers. (This company also manufactures proprietary cells for certain customers. Because of non-disclosure agreements such cells are excluded from this discussion.) Basic properties of these cells are shown in Table 1.

A cutaway view of the model 761/23 cell is shown in Fig. 1. The cell consists of a central lithium anode around which the cathode material is poured. The anode lead is brought out through a hermetic glass-to-metal seal. The case itself acts as the cathode current collector.

Cell construction begins with the fabrication of an anode "subassembly". This subassembly consists of the battery lid, the glass-to-metal seal, the inner seal, the anode current collector, and a Halar strap which will surround the anode periphery to insulate it from the case. The inner seal, which must be impermeable to the cathode material, is a redundant double crimp design. An inner Halar isolator is crimped to the bottom of the glass seal by a stainless steel crimp. An outer Halar insulator is then crimped over this inner structure by an additional stainless steel crimp. Destructive analyses of sample cells thirteen months old indicated that no cathode material had permeated even this outer seal.

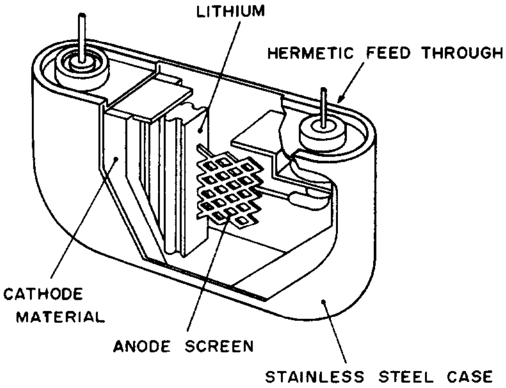

Fig. 1. Cutaway view of the model 761/23 cell.

Two pieces of lithium are pressed onto the anode screen and Halar insulator structure. The pressing fixture is a corrugated design, resulting in the formation of a corrugated anode as shown in Fig. 1. This corrugated design results in better lithium cohesion and the capability of sustaining considerably higher current drains because of the 30% increase in surface area.

The lithium anode is then coated with a solution of polyvinylpyridine dissolved in a volatile solvent which evaporates before cell construction. This coating of the anode has been shown to have a long-term beneficial effect on cell performance [7, 8].

The completed anode assembly is placed in the case and the lid is welded to the case. At this time the ferrule through which the cathode material will be poured into the cell is temporarily plugged, and the cell is leak checked with a helium mass spectrometer. After successfully completing this test the cell is filled with the cathode material. The molten iodine–PVP complex is poured into the cell through the fill ferrule in such a manner as to minimize air space in the cell. An inner plug is force-fit into the fill ferrule, and the outer plug is welded to the upper lip of the ferrule, hermetically sealing the battery. The cell is again checked for hermeticity.

Adherence to good manufacturing practices such as complete traceability of components is practiced during cell construction. The critical operations such as pressing and pouring are performed in a "super dry room" where the dew point is typically below − 50 °C. Inspections are performed after every major operation in cell construction.

Cell reliability

Because of the life-sustaining use of the lithium/iodine cell, rather extreme measures must be taken to insure the quality and reliability of the product. Certain aspects of the system contribute to an inherent reliability.

For example, the separator/electrolyte is formed *in situ* and is self-healing. Were a crack to develop in the lithium iodide separator, intrusion of cathode material would result in an immediate reforming of the separator as long as enough lithium remains to react with the cathode material. The solid electrolyte also contributes to a low self-discharge. No gas is evolved during the cell reaction, and no gross overall changes in volume occur under normal discharge conditions. This means the cell can be hermetically sealed.

In spite of the inherent "forgivability" of the Li/I_2 system, an intensive Q.C./reliability program is underway to insure that the cell will perform according to specifications for the required time period. This program begins with early coordination between reliability engineers and development engineers on new cell designs.

Materials compatibility testing is initiated on all new candidate cell components. Critical new parts such as glass seals are subjected to intensive qualification testing to insure serviceability and long-term performance.

New cell designs are subject to an extensive, formal qualification testing program. The two purposes of the design qualification program are to characterize the performance of new cell designs and to demonstrate that such designs will perform reliably for the length of time intended. The testing program subjects candidate cells to stresses far beyond those encountered in normal cell life. After each phase of testing the cells are nondestructively analyzed according to well-documented procedures. This nondestructive analysis includes visual examination, dimensional analysis, radiographic examination, electrical testing, and hermeticity testing. The candidate cells are then divided into two groups. One group is subjected to detailed destructive analysis and the other group is placed on real-time electrical testing as part of a continuous long-term monitoring program. These long-term tests continue throughout the life of the battery and serve as a check of the conclusions drawn from the qualification program.

Figure 2 is a schematic diagram of the qualification testing program. Cells actually used in the testing are typically those from the first production run of the model, *i.e.*, cells made by production personnel as opposed to prototypes constructed by the engineering staff. A portion of these cells is destructively analyzed before any testing to establish a base line for the destructive analysis of cells subjected to stress tests. The remainder of the test block goes through environmental testing and electrical testing as shown on the diagram.

Environmental testing includes the subjection of the cells to temperature extremes, thermal shock, mechanical vibration, mechanical shock, pressure, and moisture levels beyond conditions which the cells would experience in normal use. Destructive and nondestructive analyses characterize the effects of these stresses on the battery.

Electrical characterization includes two-month testing under a constant load of 100 kΩ at both 37 and 60 °C, moderate and severe accelerated discharge testing, and associated microcalorimeter studies. These tests provide an electrical characterization of the cells for future reference. Long-term testing is carried out for the life of the cell.

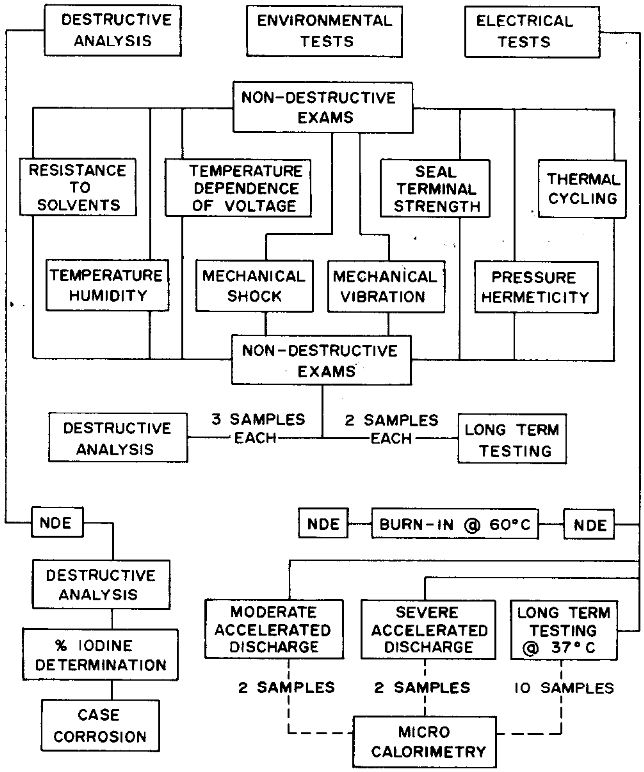

Fig. 2. Flow chart of cell qualification plan (NDE, nondestructive examination, includes 10X visual examination, electrical measurements, radiographic examination, dimensional analysis, and hermeticity testing).

In addition to the qualification testing of candidate cell designs, individual parts from new vendors are subjected to qualification testing. These tests can range from simple dimensional analysis for some parts to extensive stress testing and destructive analysis for critical components such as glass-to-metal seals.

During production, cells are subjected to an extensive quality assurance/ reliability program. The program begins with incoming inspection of all parts. Stainless steel components are subjected, on a lot sample basis, to in-house determination of percent. carbon, grain size analysis, and testing for sensitization (chromium carbide precipitation). Anode leads and screens are checked for tensile strength and hardness. Glass seals are checked for hermeticity, and lot samples are pulled to destruction to determine seal strength. Polyvinylpyridine is subjected to water analysis and infrared spectrophotometry to determine purity. Vendor certifications are checked against requirements for all components. Throughout the manufacturing process inspection sites are stationed where all subassemblies are checked for quality. One battery in fifty is subjected to metallurgical weld analysis. All welds in the sample battery are cross-sectioned, mounted, polished, and subjected to metallographic analysis [9]. Samples and results are kept for permanent records. A team of reliability technicians performs routine destructive analysis of an additional four percent. of all cells to look for potential problems in materials or construction. Permanent records are kept of the results of this analysis.

After completion of the manufacturing process all cells undergo extensive nondestructive analysis. The cells are checked for hermeticity with a helium mass spectrometer. The maximum allowable indicated helium leak rate is 2×10^{-8} cc/s. Each cell is examined under a 10X microscope for defects in welds, glass seals, or cosmetic appearance. The cells are then placed on a burn-in test for two months. The cells are kept at 37 °C under a constant load of 100 kΩ. During this time six readings of voltage and impedance (1 000 Hz) are taken. Computer printouts of these data and associated statistical analysis are kept for permanent records. Cells to be shipped must meet specified limits for electrical measurements. A representative sample of two percent. of all cells is kept in-house for life testing under the above conditions. After electrical testing the cells are X-rayed. The cells are subjected to a humidity test consisting of a 10 h exposure to 100% humidity at 49 °C. After this test the cells are subjected to a final visual examination under a 10X microscope before packing for shipment to pacemaker manufacturers.

The life testing samples are monitored on a monthly basis. Voltage and impedance (1 000 Hz) measurements are tabulated and examined. Cells are also visually examined on a regular basis for dimensional changes, degradation of glass seals, or other external indications of problems. Selected older cells are destructively analyzed to look for potential problems and assess long-term materials compatibility.

The quality assurance/reliability program is designed to begin in the early stages of cell development, to continue throughout the production of the cells and maintain a monitoring function even after the cells are no longer produced, for as long as the life of each cell model.

Cell performance

The discharge characteristics of the Li/I_2 cell have been discussed in terms of cell chemistry and electrical properties of the components [5, 6]. The discharge can be discussed in terms of three "phases". In the first phase of discharge, occurring throughout approximately 75% of cell life, there is a gradual rise in cell impedance with a corresponding slight drop in voltage, due to the buildup of the lithium iodide electrolyte. The second phase of discharge occurs when the ratio of iodine to PVP drops to a point such that the electrical conductivity of the I_2–PVP complex begins to decrease more substantially. The load voltage begins to drop more rapidly, though the open circuit voltage (OCV) remains near the theoretical value of 2.8 V. Finally, in the third phase, the load voltage has dropped substantially, and

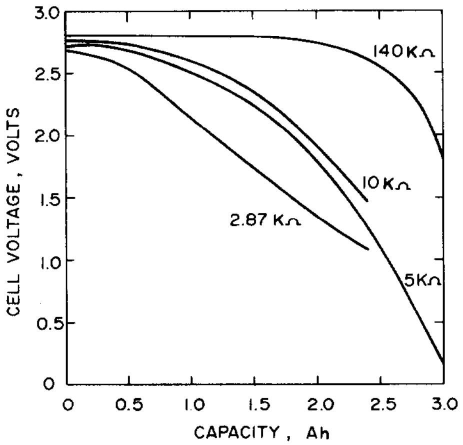

Fig. 3. Discharge profiles of the model 755 cell at various constant loads.

the OCV also drops. This drop in OCV occurs because the iodine remaining in the cathode material is no longer at unit thermodynamic activity but is bound to the PVP. The cells are designed to be cathode limited to provide the gradual end of life characteristic desirable in the clinical application.

A normal current drain for the Li/I_2 cell is around 30 μA. It would therefore require over ten years of testing to complete the discharge of a cell under real time conditions. Therefore, cells are tested by accelerated discharge techniques. The cells are discharged under heavy current drains of about 450 and 225 μA (*i.e.*, under constant loads of 5 or 10 kΩ) to predetermined levels, where the voltage under typical application loads (say 140 kΩ) is then measured. By this cyclic procedure the estimated discharge curve under normal load can be determined and verified by real time testing.

Figure 3 shows the discharge curves (37 °C) for the model 755 cell (rated at 3 A h) under various constant loads. The curve for 140 kΩ load was obtained by the cyclic procedure described above; the other curves are real time measurements. It should be pointed out that three years of real time testing at pacemaker load follows the curve obtained by the cyclic procedure. In fact, early prototype model 755 cells have shown average voltage drops of less than 10 mV in over three years of testing at 100 kΩ constant load. Figure 3 also indicates that at an average drain rate as high as 400 - 450 μA (5 kΩ load) the discharge efficiency is higher than 70% to a cutoff voltage of 1.5 V.

The precoating of the lithium anode with polyvinylpyridine markedly improves the electrical performance of the cell. Originally introduced to result in more uniform initial cell characteristics, this precoating has proven to have long-term effects on cell performance in both real time and accelerated discharge testing. Figure 4 demonstrates this phenomenon. The Figure shows discharge profiles at constant 10 kΩ load (ten times normal

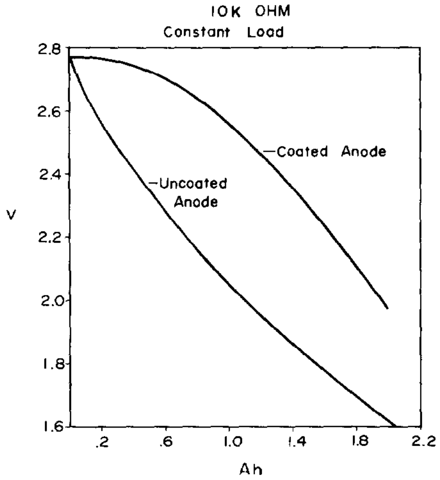

Fig. 4. Comparison of discharge profiles between model 755 cells with coated and uncoated anodes.

current load) for two model 755 cells, one a normal cell and the other an otherwise identical cell with uncoated anode. The exact reason for this difference is not certain at present, but may be due to an increased conductivity of the lithium iodide electrolyte. Destructive analysis of coated and uncoated cells reveals marked differences in morphology, crystal growth, and even color of the lithium iodide formed in such cells. The difference in lithium ion conductivity between LiI formed in coated and uncoated cells is at least one order of magnitude throughout most of the cell life, as calculated from voltage profiles.

Since the lithium iodide electrolyte has a low electronic conductivity and a low iodide ion conductivity, the self-discharge rate of this battery should theoretically be very low. Early claims by manufacturers of this cell rated the self-discharge at "less than 10 percent. in ten years". With the advent of microcalorimetry as a practical tool for determining internal heat dissipation in batteries, more precise estimates of self-discharge can be made. Use of microcalorimetry in battery analysis has been discussed in pacemaker reliability workshops [10 - 13], in the Power Sources Symposium [14] and, recently, in a detailed paper by Untereker [15]. In his paper, Untereker determined the relation between depth of (accelerated) discharge and heat dissipation for a proprietary, two-cell lithium–iodine battery (the Wilson Greatbatch Limited model 742). He then estimated the fractional loss of energy from self-discharge to be 12% over the life of the battery. It should be noted that the assumption was made that all heat output was due to the direct combination of Li and I_2. According to Untereker, other experiments have proven that parasitic processes such as curing of epoxy and polyester contribute substantially to heat output observed early in life. Even so, the estimate of 12% is in reasonable agreement with the 10% specification of the manufacturer.

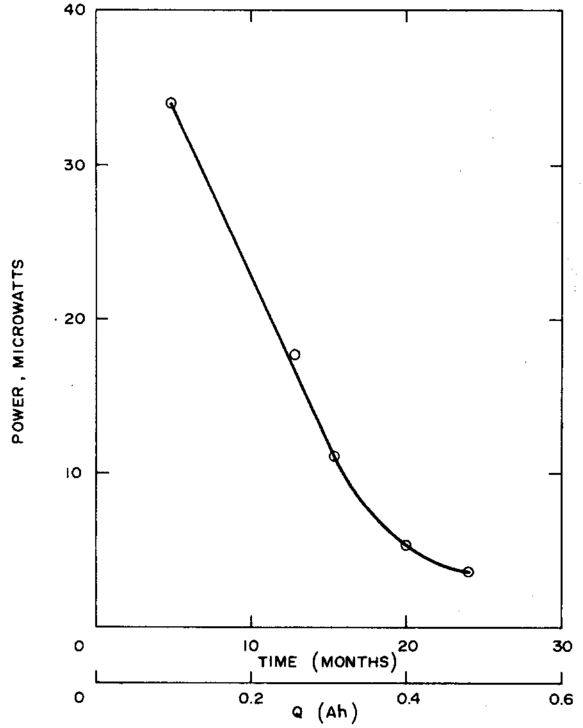

Fig. 5. Calorimetric power *vs.* time on test (and depth of discharge) for a series of model 755 cells on real-time life testing. Each point represents at least five cells. Measurements made at 37 °C under open circuit conditions.

Since over two years of life testing of standard production-quality model 755 cells has taken place, it is now possible to estimate heat output, and therefore self-discharge, for cells under real-time discharge conditions. For this experiment, groups of cells which had been on constant (100 kΩ) load test for selected periods ranging from 4.9 months to 24 months were measured in a Tronac Model 351RA microwattmeter. Cells were chosen at random from normal production cells on test as life samples. Early prototypes and cells judged electrically inferior from the initial two-month burn-in test were excluded.

Figure 5 shows the results of this experiment. Each point represents an average of at least five cells, all of the same serial number range and all having been on life test for the period indicated (time $t = 0$ is taken to be the end of burn-in testing). A total of 30 cells were measured. The averages range from a high of 34 microwatts for cells on test for 4.9 months to a low of 3.5 microwatts for cells on test for two years. If one assumes that cells continue to show powers of 3.5 microwatts for the next eight years (microcalorimetric measurements of cells on accelerated discharge indicate that this is a pessimistic assumption), an estimate of self-discharge over a ten year period can be made. A lithium–iodine battery loses 9.95×10^{-11}

ampere hours of capacity per microwatt-second of energy loss. Extrapolating to zero time and integrating the area under the curve in Fig. 5, a total of 0.18 A h capacity loss in 10 years is estimated. This represents 6% of the rated capacity of 3.0 A h. Since the model 755 is a single cell, this value is in reasonable agreement with Untereker's result for the two-cell model 742 and is considerably less than original estimates of 10% in ten years.

Regular examination of long-term test cells, and destructive analyses of selected older cells, have demonstrated that the physical integrity of the batteries on a long-term basis is excellent. Glass-to-metal seals and welds have held up well during long-term testing.

Materials compatibility of the cell components has proven to be excellent during long-term testing. Of particular interest was the compatibility of the 304L stainless steel case to the iodine–PVP cathode mixture. Studies by an independent laboratory have concluded that cells made in the absence of excess moisture show negligible corrosion of the stainless steel case after up to 26 months of load testing at 37 °C, *i.e.*, corrosion not exceeding 25 microns in depth after 26 months (new cases, typically, have gouges from the tooling in this range). Moreover, lack of correlation of wall thickness with age strongly suggests that whatever microcorrosion occurs does so shortly after cell construction and is self-limiting [16].

A recent analysis and examination in this laboratory of an early prototype model 755 cell (serial number 26) after 36 months at 37 °C confirmed and extended this finding. Metallographic, scanning electron microscopic, and dimensional examination revealed corrosion to a depth of less than 25 microns after three years. This corrosion appears as general etching and micropitting in the "fill line" area of the cell, *i.e.*, at the interface between the cathode material and the air space above it in the cell. The bulk of the case interior showed essentially no corrosion. Indeed, the original draw marks were visible on the cell case interior. Metallographic cross-sectioning revealed intergranular corrosion no greater than ten microns. The weld integrity was excellent.

Conclusion

The lithium/iodine cells (produced by this company) have proven to be a reliable and effective power source for cardiac pacemakers. This is due to an inherent reliability of the system coupled with an intensive quality assurance/reliability program that begins with cell design and continues throughout cell life.

In terms of electrical behavior, self-discharge, and mechanical integrity/materials compatibility, the cell design has proven adequate for the critical medical use for which it was intended. Indeed, pacemaker failure due to premature battery depletion or failure, which was responsible for half the clinical pacemaker explants in 1970, has been reduced to statistically insignificant levels today.

References

1 F. Gutman, A. M. Herman and A. Rembaum, *J. Electrochem. Soc., 114* (1967) 343.

2 W. Greatbatch, J. Lee, W. Mathias, M. Eldridge, J. Moser and A. Schneider, *IEEE Trans. Biomed. Eng., BME-18* (1971) 317.

3 J. Moser, Solid state lithium–iodine primary battery, *U.S. Patent No. 3 660 163* (1972).

4 R. T. Mead, Solid state battery, *U.S. Patent No. 3 773 557* (1973).

5 F. E. Kraus and A. A. Schneider, *Proc. 27th Power Sources Symp., 1976,* The Electrochemical Society, Princeton, N.J., p. 144.

6 W. Greatbatch, M. Mueller and C. Holmes, *Fall Meeting, Electrochemical Society, 1977,* published by The Electrochemical Society, Princeton, N.J., Abstract No. 21.

7 R. T. Mead, C. F. Holmes and W. Greatbatch, *Proc. Symp. on Cell Design and Optimization,* The Electrochemical Society, Princeton, N.J., Vol. 79-1, p. 327.

8 R. T. Mead, W. Greatbatch and F. Rudolph, Lithium–iodine battery having coated anode, *U.S. Patent No. 3 957 533* (May) (1976).

9 C. F. Holmes, *Qual. Prog.,* (Jan.) (1979) 21.

10 E. J. Prosen and J. C. Colbert, *Reliability Technology for Cardiac Pacemakers III, Natl. Bur. Stand. (U.S.) Spec. Publ., 400 - 50,* (1979) 23.

11 R. M. Hart and L. D. Hanson, *Reliability Technology for Cardiac Pacemakers III, Natl. Bur. Stand. (U.S.) Spec. Publ., 400 - 50,* (1979) 10.

12 D. Untereker, *Reliability Technology for Cardiac Pacemakers III, Natl. Bur. Stand. (U.S.) Spec. Publ., 400 - 50,* (1979) 17.

13 W. S. Holmes, *Reliability Technology for Cardiac Pacemakers III, Natl. Bur. Stand. (U.S.) Spec. Publ., 400 - 50,* (1979)6.

14 C. F. Holmes, W. S. Holmes, R. L. McLean and W. Greatbatch, *Proc. 28th Power Sources Conf., 1978,* The Electrochemical Society, Princeton, N.J., p. 226.

15 D. F. Untereker, *J. Electrochem. Soc., 125* (1978) 1 907.

16 W. R. Brown, An examination of Wilson Greatbatch Limited Model 755 cells after load testing, *Calspan Corporation Report, April 1978.*