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THE LITHIUM–IODINE CELL FOR MEDICAL AND COMMERCIAL APPLICATIONS

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Summary

The lithium–iodine solid electrolyte pacemaker cell is described along with other versions of the cell intended for watches, CMOS memories and oil well data logging applications. Process modifications are mentioned which can increase the current density of the system from 1 $\mu A/cm^2$ in pacemaker cells to 60 $\mu A/cm^2$ in button cells for watches and D cells. A 14 ampere-hour D cell is described which can supply 10 mA at room temperature or up to 500 mA at 130 °C.

Introduction

The $Li/LiI/I_2$, P2VP* solid electrolyte cell was conceived in 1968 by workers at Catalyst Research Corporation and first reported in 1970 [1]. Several organizations have studied and improved the system over the past decade [2 - 5]. Since the first implantation in 1972, the lithium–iodine cell has become the standard power source for the pacemaker industry [6]. More than 500 000 have been manufactured and more than 400 000 implanted since 1972. The failure rate for these cells is vanishingly small and certainly less than that of the electronics. Although the pacemaker version of the cell is limited to a few microamperes per square centimeter, recent developments have led to increases in power density by a factor of five. These cells are suitable for electronic watches (analog and LCD), volatile CMOS memory protection, and a variety of other electronic devices which require low to moderate power. They are also well suited for operation at 100 - 170 °C, a range where few if any other chemistries will operate reliably for an extended period.

Even more recent improvements in component processing have led to an additional improvement by a factor of five in current density, allowing

*P2VP is an abbreviation for poly (2-vinylpyridine).

Fig. 1. Some pacemaker and button lithium–iodine cells. Large button cell is 23 mm in diameter.

cells to be discharged at 60 $\mu A/cm^2$ at room temperature. It is now possible to produce "D" size lithium–iodine cells which will deliver 0.8 - 1.0 W h/cm^3 at low currents and power densities as high as 1 - 2 mW/cm^3.

Another advantage of the system is its stability. The open circuit voltage is stable for more than ten years, allowing it to be used as a reference in electronic circuits. The self-discharge rate is extremely low (less than 5% in ten years) which means that once in place, cells will deliver rated capacity no matter how infrequently they are actually used. With microelectronic circuit power requirements diminishing, this low self-discharge advantage becomes significant. Systems can be permanently deployed without costly battery maintenance schedules. Often, the cost of replacing batteries far outweighs the cost of the batteries themselves.

Cell geometry and chemistry

Several cell configurations are shown in Fig. 1. The button cells on the right are intended for watch and printed circuit (P.C.) board applications,

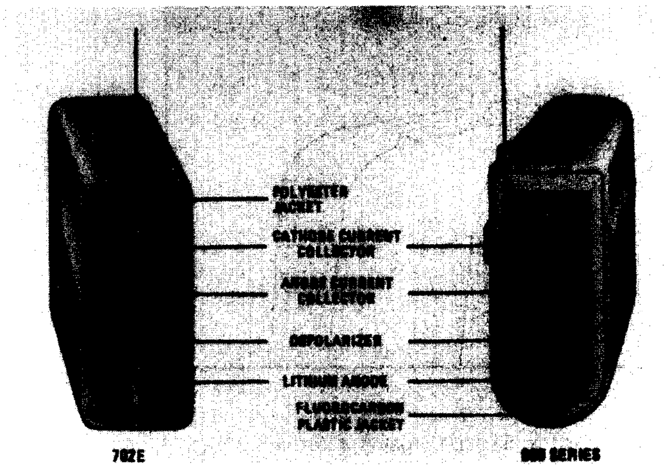


Fig. 2. Cross-section of inner assemblies of two typical pacemaker cells before encasement in hermetically sealed 304 stainless steel enclosures.

while the larger cells are used for pacemakers. A cross-sectional view of two typical pacemaker cells is shown in Fig. 2. Representative discharge curves are shown in Fig. 3 for the 810A/16 pacemaker cell. It is the second cell on the left in Fig. 1.

Designs such as these have gained wide acceptance in the pacemaker industry; more than 80% of the pacemakers manufactured in 1978 will use lithium–iodine cells.

This remarkable acceptance is to a large extent the result of the unusual chemistry of this solid-electrolyte system. Its reliability is high because its modes of failure are slow. It cannot suffer from separator rupture since the lithium iodide layer is self-healing. It neither swells nor shrinks nor produces gases during discharge.

The cell is composed of three layers; lithium, lithium iodide and a cathode containing P2VP with a large excess of iodine.

For pacemaker cells, this material is used in a plastic form, prepared by heating iodine and P2VP at temperatures between 100 and 200 °C for several days. An alternate method of preparing the depolarizer involves blending iodine and P2VP and pressing the powders into a pellet without heating. This method is used to prepare cathode pellets for button-type watch cells and results in an improvement in current density by a factor of five [7].

The resistance of the plastic depolarizer is a function of iodine content. This relationship is shown in Fig. 4. A typical cell might contain 6 molecules of iodine for each monomer unit in P2VP. During discharge, iodine is extracted until this ratio is reduced to 2 or 1.5 and the resistance of the cell increases beyond its useful range.

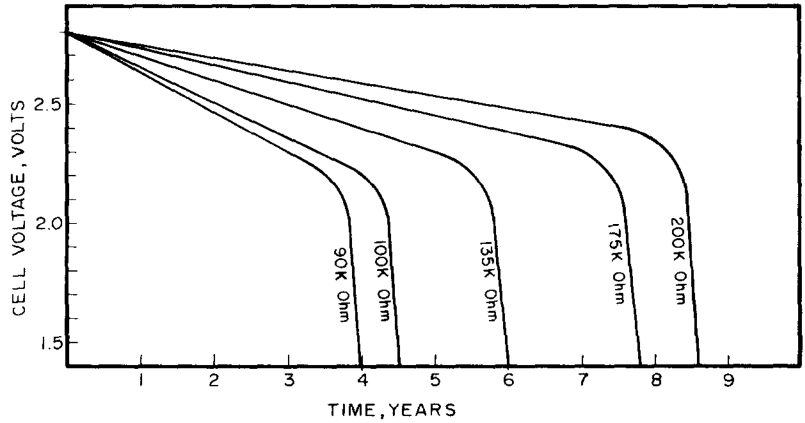


Fig. 3. Projected discharge curves for the 810A/16 pacemaker cell. Cell is 45 mm wide, 16 mm tall and 10 mm thick.

On contact of anode and cathode, a thin layer of lithium iodide is formed *in situ*. The thickness of the lithium iodide increases as iodine from the cathode diffuses through the electrolyte to react thermochemically at the anode. This process, the self-discharge reaction, slows as the thickness of the electrolyte hinders iodine diffusion. Cell resistance rises concomitantly with increasing lithium iodide thickness at a rate proportional to the square root of time — a relationship typical for such a process.

The self-discharge process, after a few years, reaches a point where only a few microwatts can be measured in a microcalorimeter for a cell of 20 cm^2 electrode area. For a cell 10 cm^3 in volume, this implies a loss in capacity of less than 5% in ten years, at 37 °C.

When the cell is discharged, the voltage declines nearly linearly as the resistive LiI layer increases in thickness. The overall cell reaction can be represented as

$$2Li + P2VP \cdot nI_2 = 2LiI + P2VP(n-1)I_2. \qquad (1)$$

This linear decline continues until the resistance of the iodine-depleted depolarizer becomes significant. At that point, a "knee" in the curve is seen. The characteristics of this knee are such that pacemaker designers can typically set their electronics to provide a six-month warning time of impending cell exhaustion. It is for this reason that all pacemaker cells are cathode limited.

Button cells

The S23P-15 button cell is shown in Fig. 1 at the upper right corner. Its size, construction and performance are given in the data sheet shown as Fig. 5. This cell represents a first stage improvement in power density over the typical pacemaker cell. Like the pacemaker cell, it is hermetically sealed,

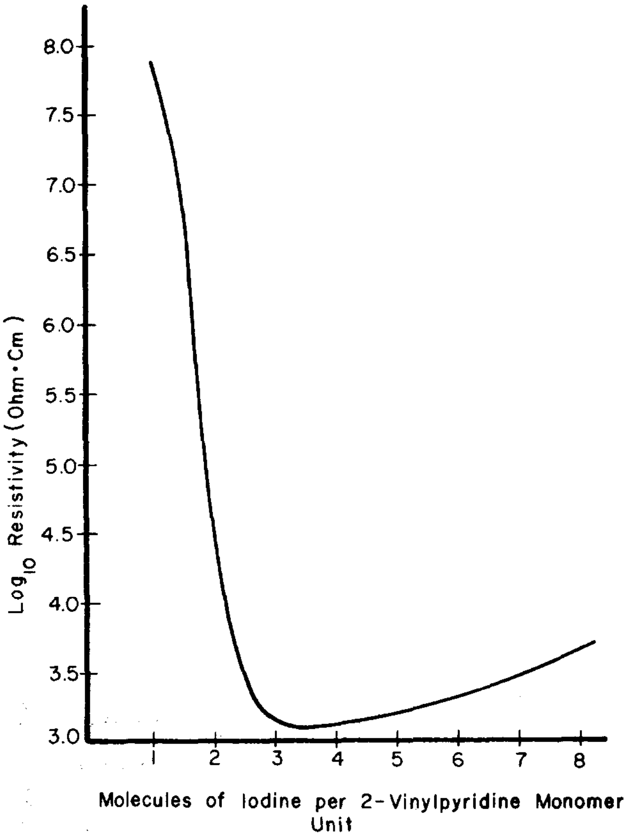
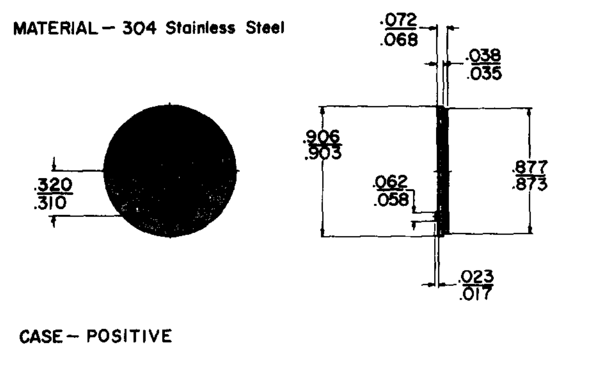


Fig. 4. Resistivity of P2VP–I_2 depolarizer as a function of iodine content.

allowing the cell to be used in close proximity to electronic components. Its dimensional stability is excellent with less than 3% swelling during discharge. This is especially important if the cell is to be used in a watch or soldered to a P.C. board. For watch application, an important feature of the cell is its thinness (as little as 1.5 mm). The diameters of available lithium–iodine watch cells range from 27 to 19 mm. Other models will soon be available with diameters of 11 mm and less. The low self discharge of the pacemaker cells is preserved in these versions of the lithium–iodine chemistry even at 50 °C, the operating temperature of many electronic modules.

If the cell is to be used for standby power for volatile memories, it should be capable of supplying 2 V at 0.5 - 20 μA for each 1K memory chip. Important cell characteristics for such an application include not only low self discharge but also long operating life and high reliability. The cell should be capable of being treated like any other electronic component, *i.e.*, soldered to the printed circuit board with the expectation that the cell will last the life of the device. Lithium–iodine button cells fulfill these requirements and, in fact, are already being used in devices such as cash registers to protect volatile information.



CONVERSIONS	
INCHES	MM
.017	.43
.023	.58
.035	.89
.038	.97
.058	1.47
.062	1.57
.068	1.72
.072	1.83
.310	7.87
.320	8.13
.873	22.17
.877	22.28
.903	22.94
.906	23.01

WEIGHT	3.8 Grams	* SELF DISCHARGE	0.02 Ah Maximum in 10 Years at 25°C
NOMINAL VOLTAGE	2.8 Volts — Open Circuit	CONSTRUCTION	Hermetically Sealed, Laser Welded Case. Glass-to-Metal Terminal Seal
CURRENT	0–20 Microamperes at 25°C Pulsing Allowable up to Several Hundred Microamperes	OPERATING TEMP	0–50°C Nominal −10°C at Reduced Drain Rates
NOMINAL CAPACITY	120 Milliampere Hours		

* Measured by Microcalorimetry

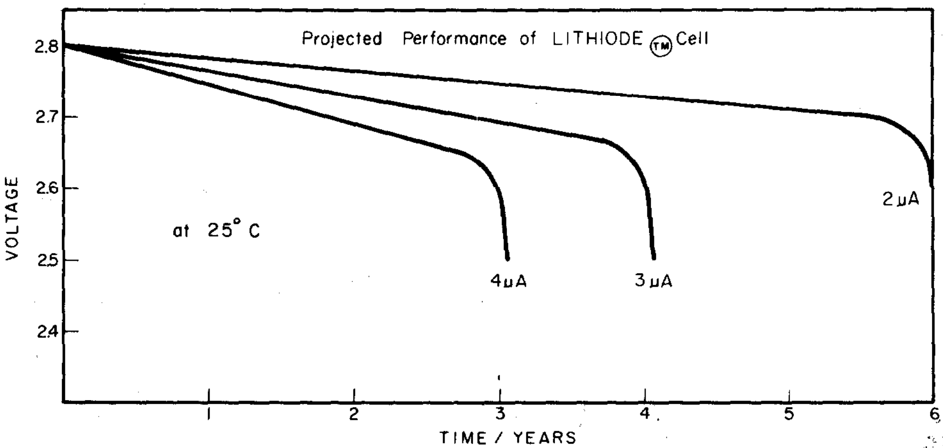


Fig. 5. Specifications for the S23P-15 watch cell.

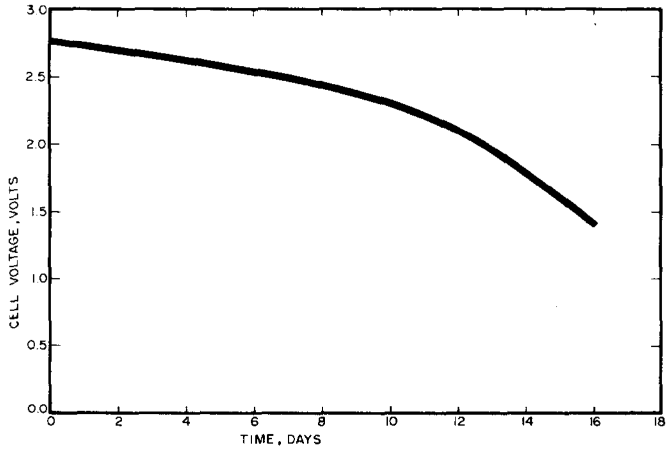


Fig. 6. Experimental S23P-15 button cell showing increased power density (10 kΩ, 25 °C).

A cell like the S23P-15 can be manufactured easily, allowing it to be cost competitive with standard silver oxide watch cells, particularly when the cost of replacing such conventional cells is taken into account. Moreover, the cost of servicing a standby cell used for volatile memory protection can be much higher than replacing a simple watch cell.

The most recent cathode improvements have resulted in a version of the S23P-15 with a discharge curve as shown in Fig. 6. Calculations based on this curve show an energy density of 0.41 W h/cm^3 and a power density of 0.85 mW/cm^3 (cell volume is 0.72 cm^3).

D cell

Using the same cathode processing techniques as the cell of Fig. 5, a D cell can be constructed which will perform as shown in Fig. 7, when discharged at 25 °C. Curve 1 was recorded over a period of 70 days during which time the cell delivered 14 ampere-hours with an energy density of 0.75 W h/cm^3. At lighter loads the energy density of the cell would increase to near 1.0 W h/cm^3. At temperatures other than 25 °C, the cell would function efficiently at currents shown in Fig. 8.

Specially constructed D cells can be prepared which will withstand temperatures up to 175 °C. At 130 °C, for example, cells have been discharged for many weeks at 10 mA, with pulses up to 500 mA at voltages above 2.5. This performance suggests high temperature applications such as oil well data logging where the temperature of a well four kilometers deep will reach 160 °C. Few, if any, conventional cells can withstand weeks above 100 °C. A prime candidate for this environment may be the lithium–iodine solid electrolyte cell which can withstand substantial shock, vibration, and even short circuiting at these temperatures without venting, leaking, swelling or exploding.

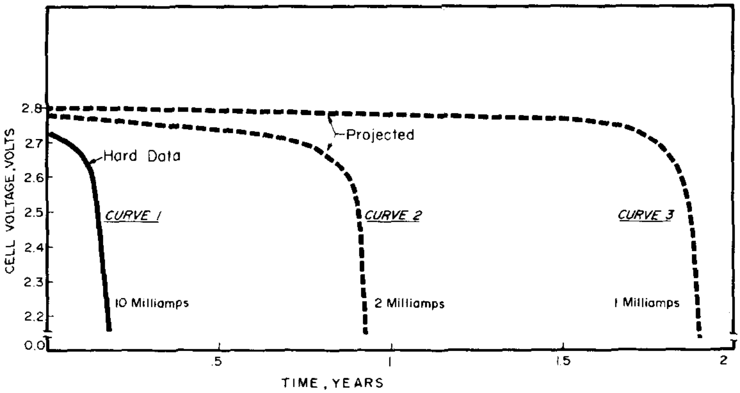


Fig. 7. Lithium–iodine D cell discharge curves (25 °C). Curve 1 shows 14 A h delivered in 70 days.

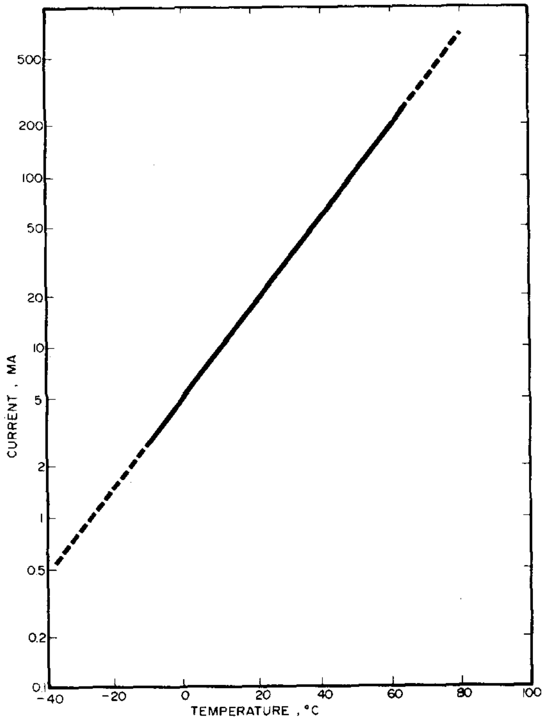


Fig. 8. Continuous current capability of a lithium–iodine D cell as a function of temperature.

Safety

With conventional cells, a breach in the separator can cause overheating from internal shorting. With this solid-electrolyte system, such a mechanism is forbidden due to the self-healing nature of the solid-electrolyte separator.

External shorting can also cause serious internal heating in many conventional systems. Because of the inherent internal resistance of this lithium–iodine system, short-circuit current is limited. Even with a high surface area cell such as the D cell version of this chemistry, external short circuits at 150 °C result in only 3 degrees rise in external case temperature, even after 1.5 hours of testing.

If the cell is heated significantly above the melting point of lithium (180 °C), sufficient heat is evolved to cause the gases within the hermetic enclosure to expand and rupture the case. Such rupture will occur, however, with overheating of most, if not all, conventional and lithium cells which are tightly sealed.

Conclusions

The lithium–iodine cell is the first lithium cell to capture a major share of a specific market — more than 80% of today's pacemakers are powered by this system. With improvements in internal resistance, the cell will not be limited to such low current drain applications, but can find use in a wide variety of commercial applications where current densities of 60 $\mu A/cm^2$ are acceptable. In fact, room temperature current densities as high as 1 mA/cm^2 should not be ruled out for this chemistry.

The intrinsic safety of this self-limiting system overcomes the most frequently stated objection to a commercial lithium battery. Its low self-discharge and ruggedness make it suitable for a wide range of applications. At moderately high temperatures (< 170 °C), it is one of the few systems which will perform reliably for an extended period.

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