# Parasitic reactions and the balance of materials in lithium batteries for implantable medical devices

Ann M. Crespi and Paul M. Skarstad

*Medtronic, Inc., 6700 Shingle Creek Parkway, Minneapolis, MN 55430 (USA)*

## Abstract

The parasitic reactions that occur in lithium/silver vanadium oxide cells have been investigated by microcalorimetry. Reactions between lithium and components of the electrolyte are the biggest contributors to heat output. The rate of parasitic reaction of lithium needs to be known to ensure that the batteries are not anode-limited. This parameter is one of many included in a calculation of the balance of materials in the cell. This calculation ensures the proper balance of electrodes and electrolyte solution in a constrained volume and also determines electrode dimensions.

## Introduction

Implantable medical batteries must operate reliably and predictably for a period of many years. An indicator of approaching end-of-service is especially important in these batteries. In general, the battery system is chosen such that the voltage declines gradually at end-of-service, allowing the voltage to be used as an indicator. For cells with lithium anodes, this scheme works only if the cells are cathode-limited. Parasitic reactions that consume the electrodes can change the balance of the cell in a way that depends on time and electrode dimensions. The rates of parasitic reactions must be characterized and incorporated into the design of the cell in order to ensure predictable performance.

Rates of parasitic reactions in lithium/silver vanadium oxide batteries with a liquid organic electrolyte are deduced from the heat output as measured by microcalorimetry. The heat output has been assigned to each electrolyte by measurements on partial cells containing only lithium or only partially-lithiated silver vanadium oxide electrodes, and cells with variable anode areas and cathode capacities. These measurements have been translated into rates of parasitic anode and cathode reaction. The loss rates in large part determine the electrode balance of a cell.

## Experimental

Cells were constructed in hermetically-sealed stainless-steel cases with the terminals exiting the cell through glass-to-metal seals. Three types of cells were made. Cells with two lithium electrodes were case-neutral, with one feedthrough for each electrode. Cells with partially-lithiated silver vanadium oxide electrodes, also case-neutral, were constructed with three feedthroughs, one for each of two silver vanadium oxide electrodes, and another for a sacrificial lithium electrode. The cells were discharged

such that all of the lithium was depleted and the silver vanadium oxide electrodes reached the composition $Li_{0.8}Ag_2V_4O_{11}$. Cells with lithium and silver vanadium oxide electrodes were constructed with the case at the lithium potential. The electrodes were configured with one, two, or three rectangular cathode plates and a single strip of anode interwoven between the cathode plates. The loading on the cathode plates was varied from 27 to 83 mg silver vanadium oxide per $cm^2$. The cells were discharged to a cathode composition of $Li_{0.13}Ag_2V_4O_{11}$.

All electrodes were encased in a microporous polypropylene separator. The electrolyte solutions were 1 M $LiClO_4$ or $LiAsF_6$ in a mixture of propylene carbonate and 1,2-dimethoxyethane, 1:1 by volume. The solvents were obtained from Fluka, dried over 3 A molecular sieves, and filtered through a millipore filter. The $LiAsF_6$ was purchased from Aldrich, and the $LiClO_4$ was from Fluka. The concentration of water in the electrolyte solution was less than 40 ppm. The cathode consisted of a mixture of silver vanadium oxide, carbon, and Teflon pressed onto a titanium screen. The silver vanadium oxide has the formula $Ag_2V_4O_{11}$ [1, 2].

Heat output was measured using a Model 4233 microcalorimeter from Hart Scientific. For measurements under constant current discharge fine copper wire was soldered to the terminals of the cells. The wires exited the calorimeter through small grooves in the covers of the sample chamber.

## Results and discussion

The heat output of cells with two lithium electrodes was measured under conditions of no current drain, constant current, and following a high-current pulse. The parasitic heat output is calculated from the total by subtracting the heat due to polarization and entropic factors (see equation below) [3, 4]. For this symmetrical cell, $\Delta s$ is zero.

$$\dot{q}_{total} = \left(\frac{I_F}{nF}\right) T \Delta s + (E_L - E^0)I_F + \left(\frac{I_c}{nF}\right) \Delta H_{parasitic} = \dot{q}_{entropy} + \dot{q}_{polz} + \dot{q}_{parasitic} \qquad (1)$$

Under constant current conditions, the parasitic heat output increases with increasing current density over the range studied, as seen in Fig. 1. After a high-current pulse, the cell also experiences a period of elevated heat output due to parasitic reactions, as seen in Fig. 2. This excess heat is mostly dissipated within 2 h. The elevated heat output is likely due to the disruption of a protective film on the lithium, allowing an accelerated rate of reaction with the electrolyte solution. The heat output from the cells containing $LiAsF_6$ was higher than for those containing $LiClO_4$.

The heat output was also measured, under open-circuit conditions, in the cells that contained only partially-lithiated silver vanadium oxide electrodes and electrolyte. The heat output was quite low for such cells (1 $\mu W/A$ h), indicating that a parasitic loss of the cathode is not important, or the reactions have a low enthalpy.

The heat output was measured under open-circuit conditions for cells with lithium and silver vanadium oxide electrodes. The electrolyte in these cells was $LiAsF_6$. As seen in Fig. 3, the heat output of these cells is proportional to the area of the anode and independent of the cathode capacity. The rate of parasitic loss of anode capacity is proportional to area and can be quantified, based on some assumptions about the nature of the parasitic reactions.

A number of researchers have characterized reaction products of lithium with $LiAsF_6$, propylene carbonate, and 1,2-dimethoxyethane on lithium surfaces. Aurbach et al. [5–7] have characterized films on lithium surfaces that were generated by contact
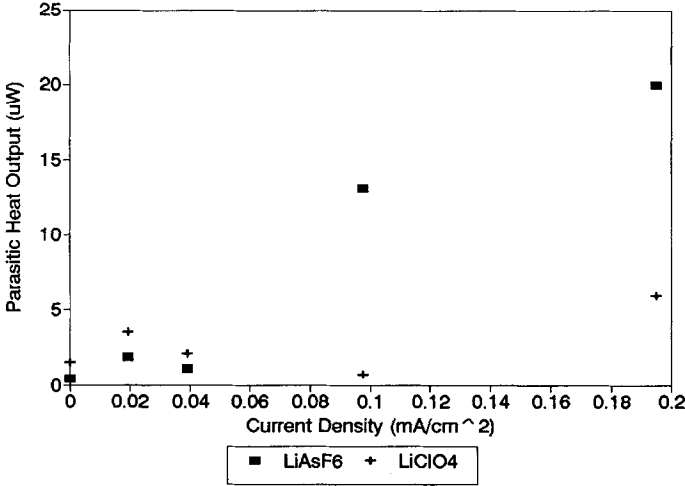
Fig. 1. The effect of current on parasitic heat output in a cell with two lithium electrodes. The electrolytes are 1 M LiClO₄ or 1 M LiAsF₆ in propylene carbonate and 1,2-dimethoxyethane, 1:1 by volume.
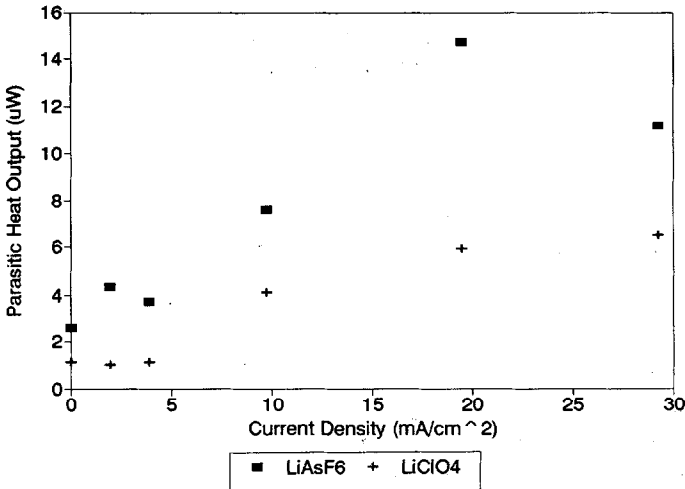


Fig. 2. The effect of a 5 s high-current pulse on subsequent parasitic heat output of the same cells described in Fig. 1.

with solutions of lithium salts, including $LiAsF_6$, in propylene carbonate, ethers (including 1,2-dimethoxyethane) and mixtures of propylene carbonate and ethers. The lithium alkyl carbonates were formed upon contact with propylene carbonate, and lithium alkoxides formed upon contact with ethers. Some possible reactions are listed below, along with enthalpies of reaction. Some of the enthalpies of formation were estimated using the group additivity method [8]. Enthalpies of reaction are normalized per equivalent of lithium consumed. A two-electron reduction to lithium carbonate and propene is also a possibility [9]. The hexafluoroarsenate anion may also be reduced
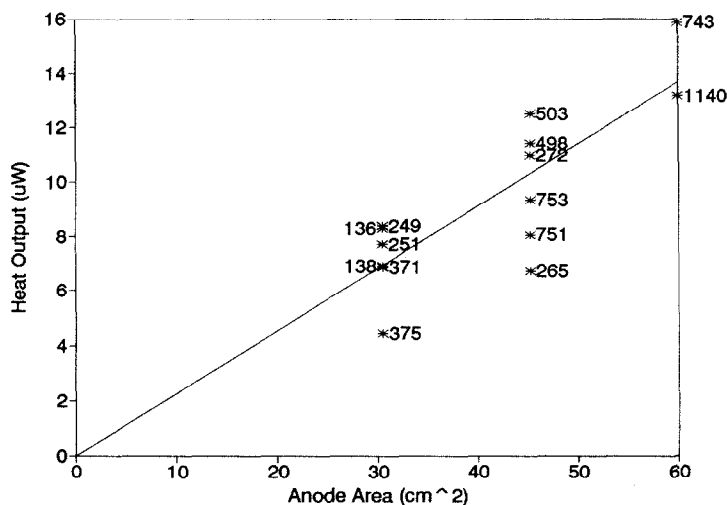
Fig. 3. Heat output of lithium/silver vanadium oxide cells as a function of lithium surface area with linear regression. The labels are cathode capacities in mA h. The electrolyte is 1 M LiAsF$_6$ in propylene carbonate and 1,2-dimethoxyethane, 1:1 by volume.

by lithium. Koch [10] has suggested that LiAsF$_6$ is reduced to AsF$_3$ which subsequently reacts with alkoxides on the surface of lithium to form a brown film.

The estimated enthalpies of reaction ($\Delta H_{rxn}$) per equivalent of lithium consumed are:

|  | Estimated $\Delta H_{rxn}$(kJ/eq Li) |
|---|---|
| $C_4H_6O_3 + Li + 1/2H_2 \longrightarrow CH_3CH_2CH_2OC(O)OLi$ | $-377$ |
| $C_4H_6O_3 + Li \longrightarrow CH_2{=}CHCH_2OC(O)OLi + 1/2H_2$ | $-251$ |
| $CH_3OCH_2CH_2OCH_3 + 2Li \longrightarrow 2LiOCH_3 + C_2H_2$ | $-261$ |
| $C_4H_6O_3 + 2Li \longrightarrow Li_2CO_3 + C_3H_6$ | $-295$ |
| $LiAsF_6 + 2Li \longrightarrow AsF_3 + 3LiF$ | $-365$ |

The extent to which each of these reactions occurs is unknown in the cells described here. Other reactions may also occur that produce heat but do not consume lithium, such as reactions of AsF$_3$ with alkoxides. Nevertheless an estimate of $-300$ kJ/eq Li is useful in estimating the rate of loss of lithium in parasitic reactions. Using the slope obtained from a linear regression of the data in Fig. 3 (0.23 $\mu$W/ cm$^2$), the rate of loss of lithium is 0.65 mA h/cm$^2$ per year. The slope of this line decreases with increasing storage time, presumably because of passivation of the lithium surface. However, when used to power an implantable cardiac defibrillator, the batteries are periodically subjected to high-current pulses which regenerate the reactive lithium surface.

Parameters such as the rate of loss of anode capacity are incorporated into a calculation that determines the optimal contents of the cell. A system of four nonlinear equations (eqns. (2)–(5)) has developed for a volumetrically-constrained system. Equations (2)–(4), which describe conservation of volume, electrode balance, and electrolyte requirement relate purely to materials balance, and eqn. (5) incorporates a dimensional

constraint, electrode loading. A second system of equations has been developed incorporating a model of the electrode configuration and constraining dimensions to give dimensions of the electrodes. The two systems are solved iteratively for the capacity of each electrode ($Q_+$ and $Q_-$), the volume of electrolyte ($V_{el}$), and the dimensions of the electrodes.

Volumetric constraint:

$$V_+ + V_- + V_{el} + V_{inert} = V_{available} \tag{2}$$

or

$$\bar{V}_+ Q_+ + \bar{V}_- Q_- + V_{el} + \bar{V}_{inert} A = V_{available}$$

Electrode balance:

$$\left(1 + \frac{r_{par.} \times 24}{I_{app} \times 8766}\right) Q_+ - Q_- = 0 \tag{3}$$

Electrolyte requirement:

$$(\bar{V}_{+pores} + \bar{V}_{void}) Q_+ + \bar{V}_{par} Q_+ A + \bar{V}_{seppores} A - V_{el} = 0 \tag{4}$$

Electrode loading:

$$Q_+ - \bar{Q}_+ A = 0 \tag{5}$$

The volumetric constraint requires that the sum of the volumes of the cathode, anode, electrolyte, and inert materials such as separator and current collectors equal the available volume ($\bar{V}_{+or-}$ = solid volume of cathode or anode per unit capacity and $\bar{V}_{inert}$ = solid volume of separator and current collectors per unit area). The available volume is the internal volume minus any volume allowed for void space. The electrode balance depends on a rate of loss of anode capacity ($r_{par.}$), normalized to area ($A$), and the application current ($I_{app}$). A rate of loss of cathode capacity would also be
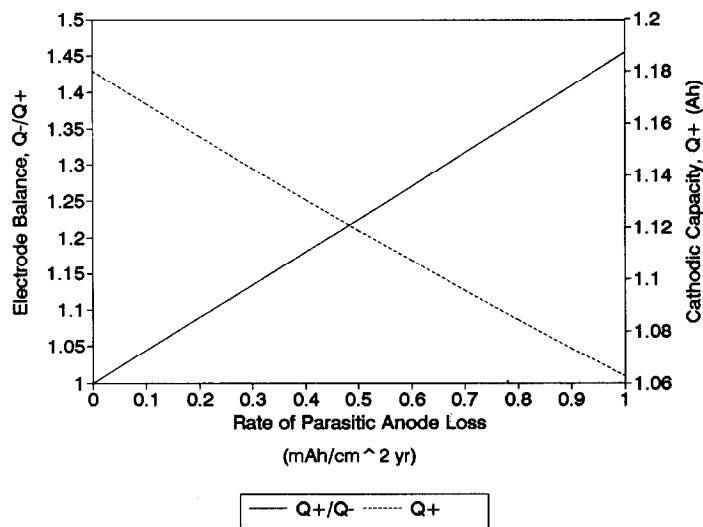


Fig. 4. The calculated effect of the rate of parasitic loss of anode capacity on the electrode balance and the capacity of the cathode.
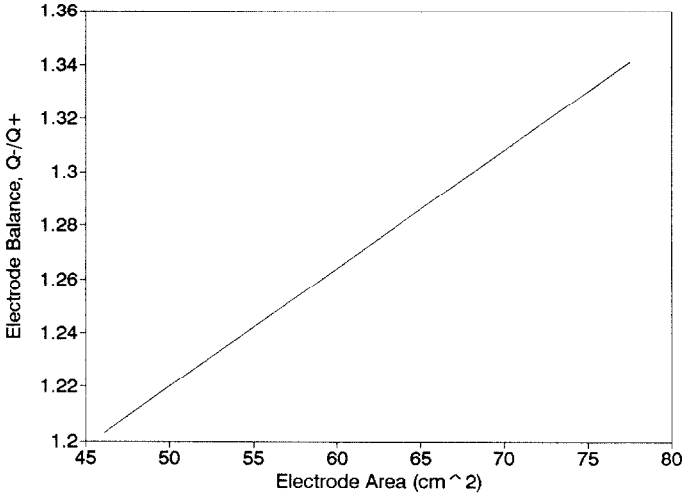
Fig. 5. The calculated effect of the area of the electrodes on the required electrode balance for a fixed cell volume.
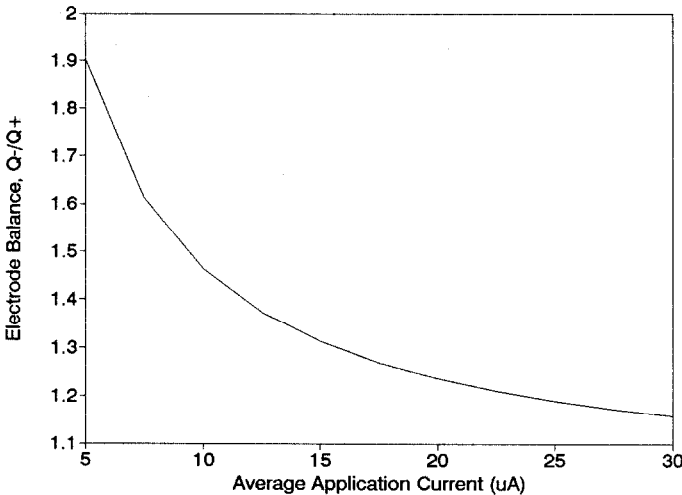


Fig. 6. The calculated effect of the average application current on the required electrode balance for a fixed cell volume.

included in a general equation, but in this case it is not significant. The volume of electrolyte $(V_{el})$ required is enough to fill the cathode pores throughout discharge $(\bar{V}_{+\,pores}Q_+)$, fill the void space produced during discharge due to the volume of reaction $(\bar{V}_{void}Q_+)$, account for parasitic reactions with a negative volume of reaction $(\bar{V}_{par}Q_+A)$ and fill the pores of the separator $(\bar{V}_{seppores}A)$. The expression for electrode loading simply relates the cathode capacity and area.

This calculation was developed specifically for lithium batteries with liquid organic electrolytes. One key parameter in this calculation is the normalized rate of parasitic

reactions of the anode ($r_{\text{par,-}}$), the estimation of which is described above. This parameter can depend on the application conditions, as seen in Figs. 1 and 2. Other parameters, such as the rate of loss of electrolyte in terms of loss of volume ($\dot{V}_{\text{par}}$), can also be estimated from calorimetric data.

Some examples of the effect of parasitic reactions on the balance of materials in the cell appear above. The discharge lives of these cells are in the range of 5 to 10 years. Figure 4 shows the effect of $r_{\text{par,-}}$ on the electrode balance and the cathodic capacity for a cell of a given volume at a selected average current density, which in this case is quite low (0.25 $\mu$A/cm$^2$). Figure 5 shows how the required lithium excess increases as the area of the lithium electrode increases, due to increased parasitic losses. The effect of application current, which is inversely proportional to cell lifetime, appears in Fig. 6.

## Conclusions

The rates of parasitic loss of anode capacity has been estimated for lithium/silver vanadium oxide cells with liquid organic electrolyte. This loss rate is incorporated into a calculation that determines the cell balance and dimensions of internal components.

## Acknowledgements

## References

1　E. S. Takeuchi and P. Piliero, *J. Power Sources, 21* (1987) 133–141.
2　C. C. Liang, E. Bolster and R. M. Murphy, *US Patent No. 4 310 609.*
3　D. F. Untereker, *J. Electrochem. Soc., 125* (1978) 1907–1912.
4　P. M. Skarstad, in B. B. Owens (ed.), *Batteries for Implantable Biomedical Devices,* Plenum, New York, 1986, pp. 234–239.
5　D. Aurbach, M. L. Daroux, P. W. Faguy and E. Yeager, *J. Electrochem. Soc., 134* (1987) 1611–1620.
6　D. Aurbach, M. L. Daroux, P. W. Faguy and E. Yeager, *J. Electrochem. Soc., 135* (1988) 1863–1871.
7　D. Aurbach and Y. Gofer, *J. Electrochem. Soc., 138* (1991) 3529–3536.
8　S. W. Benson (ed.), *Thermochemical Kinetics,* Wiley–Interscience, New York, 1976.
9　G. E. Blomgren, in J.-P. Gabano (ed.), *Lithium Batteries,* Academic Press, New York, 1983, p. 22.
10　V. R. Koch, *J. Electrochem. Soc., 126* (1979) 181.