

Short communication

Hybrid cathode lithium batteries for implantable medical applications

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Abstract

Lithium batteries with hybrid cathodes of $\text{Ag}_2\text{V}_4\text{O}_{11}$ and CF_x have been developed that combine the best features of both cathode components. They can offer power density and energy density that are competitive with or superior to other developed battery chemistries, along with the stability and reliability needed for implantable medical applications. More than 100,000 have been used in human implants since introduction in 1999.

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1. Introduction

The earliest practical implantable cardiac pacemakers appeared in the late 1950s, powered by Zn/HgO batteries [1]. Throughout the 1960s most implanted pacemakers continued to use Zn/HgO batteries. Efforts were made in the late 1960s to introduce nuclear batteries based either on the Seebeck effect or the betavoltaic effect [2]. However, following the introduction of lithium/iodine batteries for cardiac pacemakers in 1972 [3,4], the usage swung rapidly toward electrochemical power sources based on lithium. Several lithium-based battery chemistries were introduced besides lithium/iodine including Li/SOCl₂, Li/Ag₂CrO₄, Li/CuS and Li/MnO₂. By the mid-1980s most of the industry had settled on lithium/iodine for implantable pulse generators (IPGs) requiring less than about 200 μW, notably cardiac pacemakers. IPGs that required power in the range 200–500 μW, such as implantable neurological stimulators, came to be powered mainly by Li/SOCl₂ batteries. Implantable cardioverter-defibrillators (ICDs) were initially powered by Li/V₂O₅ batteries.[5] Later most of the ICD industry adopted silver vanadium oxide [6–8] of composition $\text{Ag}_2\text{V}_4\text{O}_{11}$ as a de-facto standard.

The lithium/iodine system has provided small, simple, highly reliable power sources with power characteristics almost ideally suited to the requirements of cardiac pacing for more than three decades. The system provided energy density of about 1 Wh/cm³ at drains of less than about 100 μA in batteries of conventional construction. The system also provides predictable increases in electrical resistance to signal end-of-service [9]. However, in the late 1990s implantable cardiac devices began to have increased peak power requirements that challenged the power capability of conventionally designed lithium/iodine batteries. These include increased use of addressable memory to capture and store information about the electrical activity of the heart, faster and longer-range telemetry to transmit this information outside the body, and new sensors and therapies with higher power requirements. These new therapies include cardiac resynchronization and treatment of atrial fibrillation. Peak power requirements for these features can run into the milliwatt range, well outside the range of efficient discharge for conventionally designed lithium/iodine batteries.

Analysis of battery chemistries that had been used to power implantable devices showed several that met the need for higher power, but always with compromise of energy density or inadequate end-of-service warning. A new implantable lithium battery chemistry [10] has been developed to meet the power requirements of implantable devices with the

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new therapies and features without compromise [11]. This chemistry uses hybrid cathodes consisting of mixtures of silver vanadium oxide, $\text{Ag}_2\text{V}_4\text{O}_{11}$, and carbon monofluoride CF_x . $\text{Ag}_2\text{V}_4\text{O}_{11}$ is a cathode material with high power capability used most often to power implantable cardioverter-defibrillators. CF_x is a commercial cathode material with limited power capability and fairly abrupt end-of-service characteristics, but with very high capacity density. The blend of the two cathode materials gives a primary battery that has energy density equal to that of a lithium/iodine battery of identical form factor, with 40–50 times the power. The system supports a voltage-based indicator of depth-of-discharge and end-of-service and, in addition, reduces the mass of the battery almost by half, saving 5–10 g for a typical design.

Medtronic introduced the system in 1999 powering a device for treating atrial fibrillation. This was followed in 2000 with implant of a three-electrode IPG providing cardiac resynchronization therapy for treatment of congestive heart failure. The hybrid cathode battery system has since been introduced in other implantable devices including cardiac pacemakers, hemodynamic monitors and drug-delivery devices. The total number of implants powered by hybrid cathode batteries stood at more than 100,000 as of January 2005. In the future this chemistry is expected to find application in the full range of implantable device applications requiring primary batteries, including ICDs.

Alternatives to this mixed hybrid cathode system used since 1999 are reported to be under development. For example, a cathode system in which the silver vanadium oxide and CF_x are deposited in distinct layers and laminated to form the cathode has been described [12–14]. First implant of this system is expected in 2005 [15].

2. Description and characteristics of hybrid cathode batteries electrolyte

Most commercial Li/CF_x cells use electrolyte consisting of LiBF_4 dissolved in γ -butyrolactone to minimize secondary intercalation reactions known to cause swelling when CF_x is used with many other commonly used lithium battery electrolytes. $\text{Ag}_2\text{V}_4\text{O}_{11}$ cells for ICDs use a high-conductivity electrolyte containing 1 M LiAsF_6 dissolved in equal volumes of propylene carbonate and dimethoxyethane. Electrolyte composition can affect solubility of $\text{Li}-\text{Ag}_2\text{V}_4\text{O}_{11}$ discharge products, leading to undesirable side reactions, particularly for high-rate ICD batteries. However, stability of impedance is important for medium-rate applications as well. Thus, a key element of hybrid-cathode battery technology is selection of an electrolyte composition that gives stable performance over the long service life.

Proprietary electrolyte compositions have been developed that produce batteries with long-term electrical and dimensional stability required for all applications from pacing and monitoring applications requiring less than $50 \mu\text{W}$ to ICD pulses requiring 5–10 W. Different formulations have been

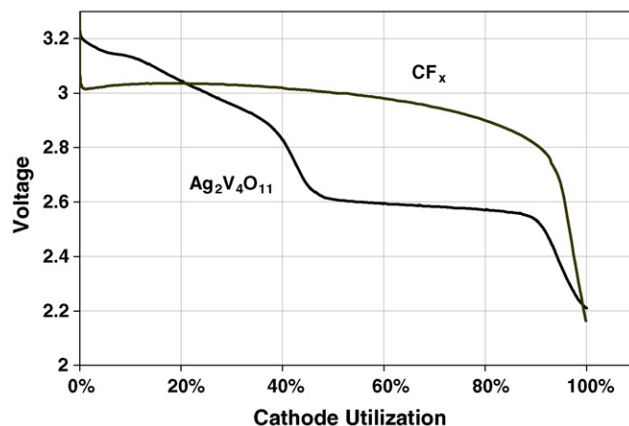


Fig. 1. Discharge voltage of $\text{Li}/\text{Ag}_2\text{V}_4\text{O}_{11}$ cell and Li/CF_x cell at $2 \mu\text{A}/\text{cm}^2$.

developed for medium-rate and for ICD applications. These formulations have been tested extensively under application conditions and at elevated temperature. Voltage, resistance and deliverable capacity have been shown to be stable and predictable in long-term discharge experiments. In the case of medium rate electrolyte, 100% of theoretical cathode capacity was delivered over periods as long as 6 years, indicating no detectable loss of cathode capacity to parasitic reactions.

3. Variation of voltage with degree of lithiation

The voltage curves for $\text{Ag}_2\text{V}_4\text{O}_{11}$ and CF_x versus Li are shown in Fig. 1. The voltage curve of hybrid cathode behaves like a superposition of the two in proportion to the starting composition of the mixture. CF_x by itself reacts with one equivalent of lithium per formula unit at 2.9–3.0 V in a single heterogeneous reaction. $\text{Ag}_2\text{V}_4\text{O}_{11}$ reacts with up to six chemical equivalents of Li per formula unit at potentials between 3.1 and 2.2 V. The open-circuit voltage curve of $\text{Ag}_2\text{V}_4\text{O}_{11}$ [16] consists of two voltage plateaus, each followed by a voltage ramp. Each plateau contributes two electrochemical equivalents, and each ramp contributes one electrochemical equivalent to the overall reaction. The plateaus lie at 3.1 and 2.6 V and bracket the CF_x potential of about 2.9 V. The voltage under load shown in Fig. 1 shows a gradual decline on the first plateau; this is typical of discharge of $\text{Ag}_2\text{V}_4\text{O}_{11}$, even at low background discharge rates $<1 \mu\text{A cm}^{-2}$. As a hybrid-cathode battery discharges at very low rates, the $\text{Ag}_2\text{V}_4\text{O}_{11}$ will first discharge some of its capacity, followed by the CF_x and then the remaining $\text{Ag}_2\text{V}_4\text{O}_{11}$ capacity, as shown in Fig. 2.

At significantly higher rates, as in a defibrillation pulse, the more rapid discharge kinetics of $\text{Ag}_2\text{V}_4\text{O}_{11}$ may cause it to discharge in preference to CF_x , shifting and blurring the boundaries between CF_x and $\text{Ag}_2\text{V}_4\text{O}_{11}$ discharge somewhat. If the current is relaxed following such a high-current episode, the CF_x recharges the $\text{Ag}_2\text{V}_4\text{O}_{11}$ back to the composition at which the two materials have equal potentials.

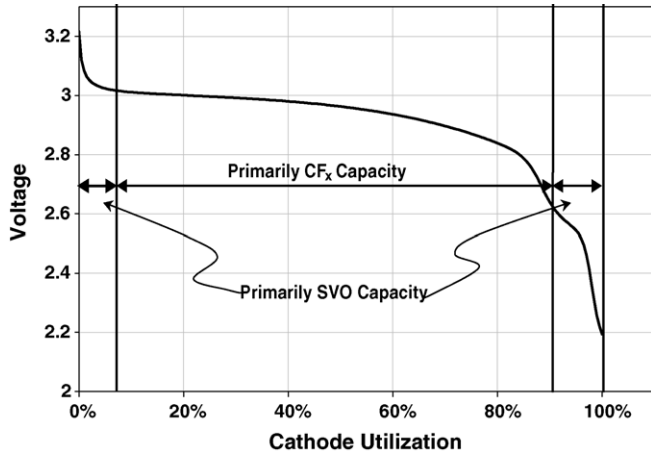


Fig. 2. Discharge voltage of a Li/CF_x-Ag₂V₄O₁₁ medium-power hybrid cathode cell at 2 μA/cm².

The composition of the hybrid mixture can be chosen based on the application, enhancing the capacity with a greater proportion of CF_x or enhancing the power capability and end-of-service characteristics with more Ag₂V₄O₁₁. For low- and medium-rate applications the composition can be chosen such that 85–90% of the battery capacity comes from CF_x. Discharge curves in Fig. 3 show the variation in operating voltage with current density over the range of current density 3.8–30.1 μA cm⁻². In this composition range efficiently designed medium-rate hybrid cathode batteries can match lithium/iodine in energy density at about 1 Wh cm⁻³. Discharge data for hybrid cathode and iodine cells with identical form factor are shown in Fig. 4.

For ICD applications, a higher proportion of Ag₂V₄O₁₁ is required to give adequate power. The composition is still chosen with CF_x as the major component, contributing 65–75% of the total capacity. High-power ICD batteries designed with hybrid cathodes maintain nearly uniform power capability throughout the discharge lifetime of the battery. This means that charge times for ICDs remain constant and low,

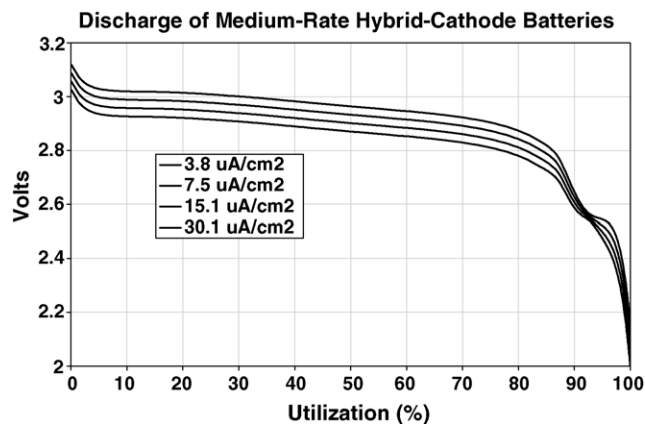


Fig. 3. Comparison of discharge characteristics of medium-power hybrid cathode cell and lithium/iodine cell of same form factor. Note falloff in delivered capacity of iodine cell at 1 mA.

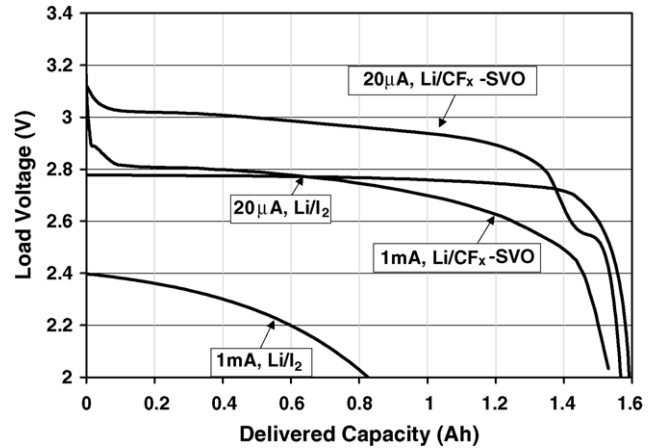


Fig. 4. Voltage of medium-power hybrid cathode cells at range of current densities.

as with ICD batteries balanced for three-electron reduction of Ag₂V₄O₁₁ [17]. However, the energy density is enhanced more than 50% relative to such “charge-time-optimized” ICD batteries.

4. Comparison with other implantable battery systems

Models have been developed, using techniques previously reported in these Symposia, describing both design of practical hybrid cathode batteries and the expected long-term discharge behavior. These have been developed for both the medium-power and high-power hybrid cathode battery systems. Corresponding models for the iodine and two SVO systems have been described previously at these Symposia [9,18,19] and elsewhere [16]. In all cases the models incorporate data from cell discharge experiments lasting at least 5 years and as long as 7 years. These models were used to explore the relationship between power capability and energy density for these battery systems for a region of design space accessible with current design and manufacturing technology.

Fig. 5 shows the relationship between power density and energy density for cells of the two hybrid-cathode systems and for corresponding cells of several other important implantable lithium battery chemistries, including iodine and two forms of silver vanadium oxide.

The two silver vanadium oxide systems differ in the form of silver vanadium oxide used. The two forms are crystalline, single phase Ag₂V₄O₁₁ [8], termed “CSVO”, and silver vanadium oxide of the same composition made by low-temperature decomposition of AgNO₃ in the presence of V₂O₅ [6], termed “DSVO”.

CSVO and DSVO are similar in power capability for approximately three electrochemical equivalents of reaction, but differ significantly in the rate of a time-dependent growth of resistance for reaction beyond three equivalents [16]. The plots for six-equivalent balance assume a 6-year service life.

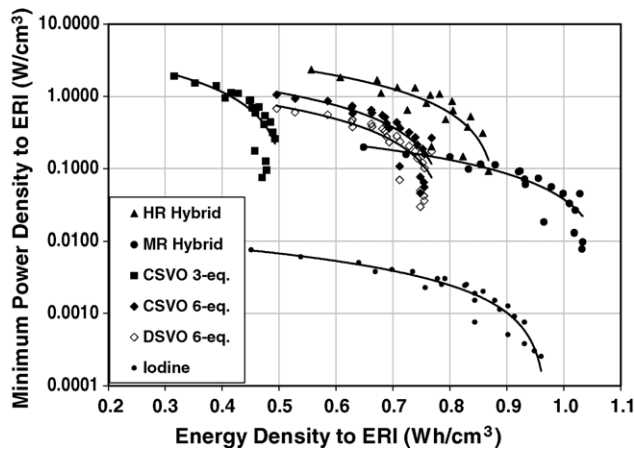


Fig. 5. Ragone plots of medium-power and high-power hybrid cathode cells systems compared with other implantable battery systems, silver vanadium oxide (CSVO and DSVO) and lithium/iodine.

Longer service life would increase the difference between CSVO and DSVO on this plot. Both three-equivalent balance and six-equivalent balance are presented for CSVO.

For non-iodine systems calculations were made assuming cases with external footprint dimensions $2.245 \text{ cm} \times 3.01 \text{ cm}$ and thicknesses of 0.75, 1.0, 1.25 and 1.50 cm. Prismatically coiled electrodes fit within these cases with 1, 3, 5, 8 and 10 turns. Two layers of $25 \mu\text{m}$ separator were assumed. For each system an “elective replacement indicator” (ERI) voltage was chosen appropriate to the system such adequate capacity remained after this point to operate an ICD for at least three months. Background voltage and minimum pulse voltage for the fourth pulse in a train of four 60-J pulses were calculated as functions of discharged capacity. These were used to calculate the cell impedance for pulses of this magnitude. From this the impedance-matched pulse power density (power per unit external case volume) was calculated as a function of discharged capacity. Likewise energy density to ERI was calculated from capacity and average background voltage to ERI. For each cell design the minimum value of impedance-matched power density to ERI versus the energy density to ERI is shown in Fig. 5.

For iodine cells an encasement with similar footprint dimensions was chosen, with thicknesses of 0.3, 0.6 and 0.9 cm. Baseline anode area was calculated for a two-sided central-anode design, and this area was enhanced by factors of 3, 5, 8 and 10. Lithium excess was taken to be proportional to anode area. None of these designs was capable of supporting a defibrillation pulse, so ERI was taken to be at 90% of the capacity delivered to 2.0 V. Only the design with baseline electrode area has ever been constructed, but the calculations do accurately reflect the performance expected of an iodine battery built with the enhanced areas as well. Impedance-matched power for the iodine system was based on 1 kHz impedance, representing a pulse of short duration. The comparison between iodine and the other systems may not be exact in these calculations, but Fig. 5 does show the large disparity in power density between iodine and the other systems.

Fig. 5 also shows the advantageous energy density with competitive power density of high-power hybrid relative to other high-rate systems. It also shows the advantageous power density and competitive energy density of medium-power hybrid relative to iodine.

5. Conclusion

Lithium batteries with hybrid cathodes of $\text{Ag}_2\text{V}_4\text{O}_{11}$ and CF_x combine the best features of both cathode components. They can offer power density and energy density that are competitive with or superior to other developed battery chemistries, along with the stability and reliability needed for implantable medical applications.

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