Dual-chemistry cathode system for high-rate pulse applications

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Abstract

A novel electrode design was developed and used to construct cells for high-rate pulsing applications. In this electrode design, a cathode material with high energy density, such as carbon monofluoride (CF_x), is sandwiched between two layers of current collectors that in turn are sandwiched between two layers of cathode materials with high power capability, such as silver vanadium oxide (SVO). Lithium cells constructed with such cathodes exhibited power capability similar to SVO cells, but with higher volumetric and gravimetric capacity. The advantages of both SVO and CF_x materials were efficiently utilized.
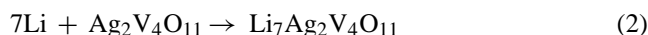© 2005 Elsevier B.V. All rights reserved.

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1. Introduction

A variety of implantable medical devices utilize batteries as their power sources to treat patients with a wide spectrum of illnesses [1]. The batteries used in these devices have to provide the required energy in a specific fashion depending on the type of device and the application. In some cases, only low power or current (microampere level) is needed throughout the service life, for example, implantable pacemakers. In some other situations, in addition to low-rate requirements, medium (milliampere level) to high power pulses (ampere level) are occasionally needed for a short duration to provide the medical treatment for the patients. Examples of such devices include implantable nuerostimulators, drug pumps, congestive heart failure (CHF) devices and cardiac defibrillators. All these applications present challenging and demanding requirements for the power source. The batteries must deliver enough energy to maintain a long device service life. Yet, the volume of the batteries must be small enough to allow reasonable device size for implant.

Historically, several primary lithium cell systems have been successfully used as power sources for implantable medical device applications, for example, Li/carbon monofluoride (CF_x) for medium rate applications [2] and Li/silver

vanadium oxide (SVO) for medium to high-rate applications [3]. The electrochemical reactions during discharge for these two systems are shown in equations (1) and (2):

$$x\text{Li} + \text{CF}_x \rightarrow \text{C} + x\text{LiF} \tag{1}$$

$$7\text{Li} + \text{Ag}_2\text{V}_4\text{O}_{11} \rightarrow \text{Li}_7\text{Ag}_2\text{V}_4\text{O}_{11} \tag{2}$$

These two systems have been demonstrated to be safe based on extensive safety tests and many years of experience in device applications. A comparison of these two technologies can be found in Table 1. The CF_x system energy density is around $300\,\text{Wh}\,\text{L}^{-1}$ higher than SVO, the self-discharge is low and the cell resistance is stable as a function of time. The SVO system has two orders of magnitude lower internal resistance and can be pulsed at currents exceeding $35\,\text{mA}\,\text{cm}^{-2}$ of electrode interface area. One of the notable advantages of the SVO system over CF_x is its stepped discharge voltage profile which is used to determine the battery's state-of-charge in order to predict when an implantable device will reach the end of its service life. It would be desirable to combine these two materials in a way that would take advantage of their different strengths.

The development of a power source system utilizing the combination of two different cathode materials has been studied in the past. One early investigation of mixing two types of cathode materials was reported by Marple [4] in 1987. In this paper, a mixture of MnO_2 and CF_x materials was pro-

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Table 1
Comparison of existing implantable battery technologies

Category	Li/SVO	Li/CF$_x$
Typical running voltage (V)	2.7	2.9
Energy density (Wh L^{-1})	730	1000
Typical current density (mA cm^{-2})	35	1
Typical internal resistance (BOL) (Ω)	0.250	40
Time-dependent internal resistance increase (%)	40–60 DOD	None
Self-discharge (% year^{-1})	1	<1
Stepped discharge curve	Yes	No

posed as cathode material in lithium cells. The presence of CF$_x$ improved the pulsing performance of the cell compared to pure MnO$_2$ electrode cells during the latter portions of discharge.

In 1992, Weiss et al. [5] disclosed a method of utilizing both SVO and CF$_x$ materials in a single cell system. In this system, SVO and CF$_x$ materials were physically mixed before being formed into cathodes. For medium-rate applications (normally achieved with the pure CF$_x$ system), the gain was the introduction of an end-of-service indicator and increased rate capability, while the energy density of the cathode was lowered relative to a pure CF$_x$ cell design. For high-rate applications (defibrillators), the gain of higher energy density due to the presence of CF$_x$ was partially cancelled by the loss of power capability (also due to the presence of CF$_x$) relative to that of the pure SVO cell design. Therefore, SVO/CF$_x$ mixture technology is most beneficial in medium to low-rate applications, rather than in high-rate applications.

In 1999, Spillman and Takeuchi [6] reported a new concept of utilizing a two cell system for implantable cardiac defibrillator applications. An SVO cell provided high power therapy only, while a CF$_x$ cell provided energy for the low power therapy and circuitry applications. This battery system maintains the advantages of both SVO (rate capability, EOL indicator) and CF$_x$ (high capacity and energy density) systems, but requires the careful capacity balance of the two cells such that both the SVO cell and the CF$_x$ cell reach the end of service life at the same time.

In 2003, Gan and Takeuchi [7] described an SVO cell and a CF$_x$ cell connected in parallel during discharge. Under low-rate discharge, the cell with the higher voltage was preferentially discharged. Under high-rate pulsing discharge conditions, the SVO cell provided most of the current. After the high current pulse ended, the SVO cell exhibited a lower potential than the CF$_x$ cell. Under these conditions, the SVO cell was charged by the CF$_x$ cell until the cell potentials were equilibrated. However, there is some concern about the potential for lithium dendrites to form when charging lithium cells.

In all attempts mentioned above, the goal of combining a high energy density cathode material and a high-rate cathode material to fully utilize the advantages of both systems was only partially achieved.

2. Experimental

Experimental cells were built according to Fig. 1 with $n = 5$ by first preparing a cathode assembly by pressing CF$_x$ material ($x = 1.03$) in a matrix of binder and conductive additive between two titanium screens. Silver vanadium oxide (Ag$_2$V$_4$O$_{11}$) material in a matrix of binder and conductive additive was pressed on both sides of the assembly to provide a cathode having the configuration

Fig. 1. Conceptual drawing of dual-chemistry cathode cell for high-rate applications.

SVO/screen/CF$_x$/screen/SVO. The capacity ratio of SVO to CF$_x$ was typically 0.55. The cathode assembly was heat-sealed inside a polyethylene separator.

Six cathode plates were combined with an anode prepared from a lithium metal ribbon applied to a nickel current collector. The anode was heat-sealed in a polyethylene separator and the cell assembly was placed in a stainless steel can. A header containing the cathode terminal surrounded by a glass-to-metal seal was laser welded to the can. The cell was filled with an electrolyte consisting of 1 M LiAsF$_6$ in PC:DME (1/1, v/v) and was close-welded to provide a hermetic cell.

For testing, the cells were fitted with a resistor to simulate the quiescent drain of a medical device except where noted. The resistance was chosen to provide the desired test length. For pulse testing, the cells were pulsed 12–20 times during the duration of the cell discharge at even intervals. Each pulse event consisted of four 10-s pulses separated by a 15-s rest except where noted. All testing was done at 37 °C.

3. Results and discussion

A new electrode design concept aimed at maintaining the advantages of both SVO and CF$_x$ has been disclosed in 2003 [8,9], as shown in Fig. 1. The cathode is composed of two layers of SVO, two layers of current collector and one layer of CF$_x$ sandwiched together. This design is well suited for high-rate applications that require ampere level pulses. This electrode concept could presumably be used with other materials as well [8]. This report focuses on application of the cathode design concept using SVO and CF$_x$ in batteries for high-rate implantable medical devices.

3.1. Dual-chemistry cathode concept

Power sources for implantable medical devices should meet several key requirements:

(a) *Safety*: They must be safe under all reasonable conditions.
(b) *Energy density*: They should have high energy density to provide the required longevity and maintain small device size.
(c) *Power*: They should have high power capability to maintain short capacitor charge time (defibrillator applications).
(d) *Predictability*: The long-term cell performance should be predictable under various discharge conditions.
(e) *Shelf life*: They should have long shelf life with a low self-discharge rate.
(f) *End of service indicator*: They should have a stepped voltage discharge profile.

In order to understand the performance of the dual-chemistry cathode system, it is useful to examine the electrochemical characteristics of SVO and CF$_x$. Fig. 2 represents the discharge curves for pure SVO and pure CF$_x$ cathodes. SVO is characterized as having two distinct discharge
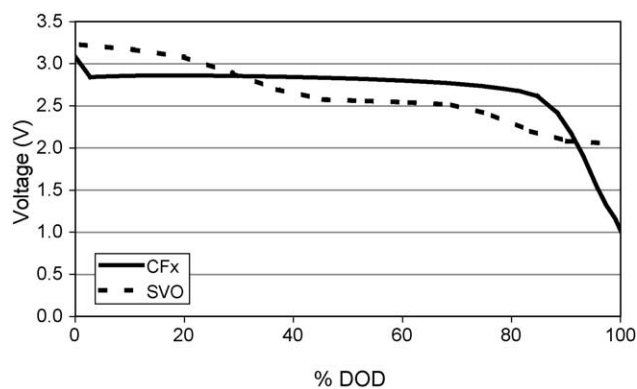
Fig. 2. Representative constant resistive load discharge of Li/CF$_x$ and Li/SVO cell.

plateaus—one at 3.2 V and other at 2.6 V [10]. The plateau at 3.2 V is reported to correspond to reduction of Ag^{1+} and V^{5+}. The 2.6 V plateau is believed to be the result of reduction of V^{5+} and V^{4+}. The electrochemical reaction of SVO has been reported to be reversible [11]. CF$_x$ has one discharge plateau at 2.8 V, which is located between the two SVO plateaus from a potential standpoint.

In the dual-cathode concept, one would expect the highest voltage plateau (3.2 V SVO plateau) to be discharged first under light loads since CF$_x$ can deliver only minimal current at this potential. Under heavy pulsatile loads, the cell potential will drop low enough to allow for the participation of CF$_x$, but SVO would be expected to carry most of the load since it delivers more current at a given overpotential and is located closer to the anode. Once the first SVO plateau is exhausted and the cell reaches 2.8 V, CF$_x$ reduction would be expected to provide the majority of the low-rate energy requirements. When pulsed with high current, the cell voltage will drop such that both materials can accept some of the current. Again, it is expected that SVO will provide most of the energy under heavy load. Once the heavy load is removed, SVO would be expected to have a lower potential than the CF$_x$. It is hypothesized that lithium ions and electrons will then migrate along the resulting potential gradient from SVO to CF$_x$ until an equilibrium is achieved. When the CF$_x$ material is exhausted, the SVO material will again provide the majority of the energy.

Fig. 3 represents the discharge curve of a dual-cathode cell with SVO and CF$_x$ cathode materials according to the cathode design described by Fig. 1. It is apparent that there are three discharge plateaus in the background curve, which is described by the pre-pulse voltage. The first is at 3.2 V, the second at 2.8 V and the third is at 2.6 V. These plateaus can be assigned as discharge of SVO, CF$_x$ and SVO, respectively, based on theoretical considerations supported by the individual discharge curves given in Fig. 2.

This stepped discharge curve is advantageous for an implantable medical application because the background potential of the cell, which is primarily thermodynamically controlled, provides a good indication of the cell's state-
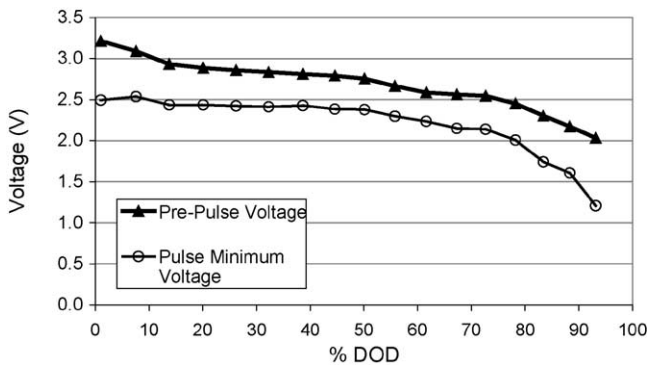
Fig. 3. Pulsatile discharge test of dual-chemistry cathode cell. Cells were discharged over 18 months. The pulse current was $22\,\mathrm{mA\,cm^{-2}}$ of cathode surface area. The minimum voltage for the first pulse of the train is shown.

of-charge. This allows the physician to have a replacement indicator before the cell is no longer functional in the device. The SVO:CF$_x$ system provides two replacement indication points—one between the CF$_x$ plateau and the second SVO plateau and other after the second SVO plateau. The selection of which point is most appropriate depends on the requirements of the device as well as the SVO:CF$_x$ capacity ratio in the particular cell design. Hence, the ability to adjust the SVO:CF$_x$ capacity ratio is another advantage of the dual-chemistry cathode concept (Fig. 2).

Fig. 3 also contains the minimum loaded voltage when the cell was pulsed using a current of $22\,\mathrm{mA\,cm^{-2}}$ of cathode surface area. The loaded voltage curve is similar in shape to the background curve indicating the observed dc resistance of the cell did not change much as a function of depth-of-discharge. The loaded cell voltage is 2.0–2.5 V. This is well above the voltage requirement for an implantable cardiac defibrillator. The consistency of the loaded voltage as a function of depth-of-discharge is desirable because this results in consistency in the time it takes for the battery to deliver the energy necessary to charge the capacitors in the device. Consistently, short charge times maximize the effectiveness of the device.

3.2. Comparison of dual-cathode and SVO cell discharge performance

Fig. 4 presents a comparison between the dual-chemistry cathode and pure SVO, which is the current state-of-the-art technology for high-rate implantable applications. The comparison shown is for the two technologies in the same size and shape container. The dual-chemistry cell delivered more capacity than did the pure SVO cell owing to the contribution of the high energy density CF$_x$ material. In fact, at a background voltage of 2.1 V, the dual-chemistry cell delivered 475 mAh more capacity, which is a 21% improvement over the pure SVO cell. At the same time, the voltage drop during pulsing was roughly the same for the two cathode types. Thus, the cathode design allowed for the preservation of the rate capability of SVO while at the same time taking advantage of the energy density of CF$_x$. The preservation of
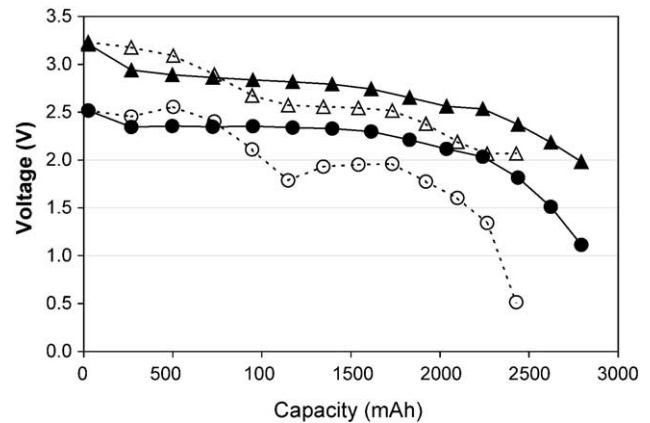

Fig. 4. Pulsatile discharge test of dual-chemistry cathode cell (closed symbols) and SVO cell (open symbols). The SVO was discharged over 24 months and the dual-chemistry cell was discharged over 20 months. The pulse current was $22\,\mathrm{mA\,cm^{-2}}$ of cathode surface area. The minimum voltage for the first pulse of the train (circle) and the pre-pulse voltage (triangle) are shown.

rate capability in the dual-chemistry cell is interesting since the amount of SVO in the concept cell is considerably less than in the SVO cell.

It is evident that the loaded voltage was 300–500 mV higher from 750 mAh to the end-of-life for the dual-chemistry cell. This was partially the result of the higher background voltage. The higher loaded voltage during the last two-thirds of discharge will result in higher power and faster energy delivery, which is beneficial in a therapeutic sense.

At a capacity of 1200 mAh, the pure SVO cell experienced its maximum voltage drop. It is characteristic of the SVO cell system to experience an increase in resistance at the onset of the second discharge plateau. The data shown in Fig. 4 represent the minimum loaded voltage for each pulse, which typically occurs at the end of each pulse. In the 1200 mAh region, the pulse minimum voltage is actually found at the beginning of the pulse owing to a voltage delay phenomena common to lithium battery systems. The amount of voltage delay observed increases as the discharge time increases. This stability issue is undesirable because in some cases the resistance increase is not entirely reversed by further pulsing, making prediction of cell performance challenging. It is, therefore, notable that the resistance in the dual-chemistry cathode system is more constant during discharge. The reduction in time-based resistance growth will result in more predictable cell performance.

3.3. Long-term stability of dual-chemistry system

The stability of the system is substantiated by Fig. 5, which shows the long-term discharge results for the dual-chemistry system. The plot compares the discharge results for tests ranging from 18 to 42 months. There was virtually no difference in performance for the first eight pulse trains owing to the stability of CF$_x$ material. There was 50 mΩ of time-based resistance increase at the ninth pulse train. This corresponds
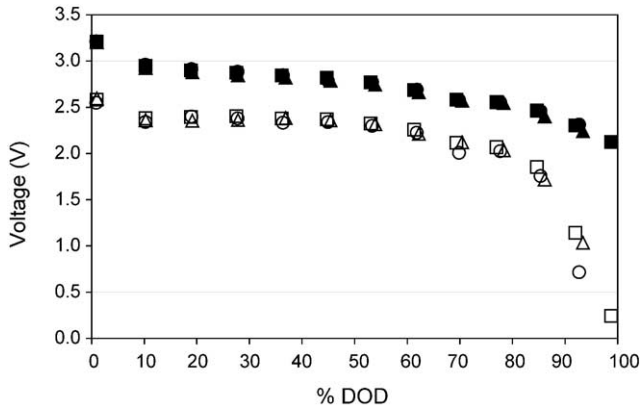
Fig. 5. Pulsatile discharge test of dual-chemistry cathode cell. Cells were discharged over 18 (▲), 30 (■) and 42 (●) months. The pulse current was 22 mA cm^{-2} of cathode surface area. The minimum voltage for the first pulse of the train is shown (open symbols).
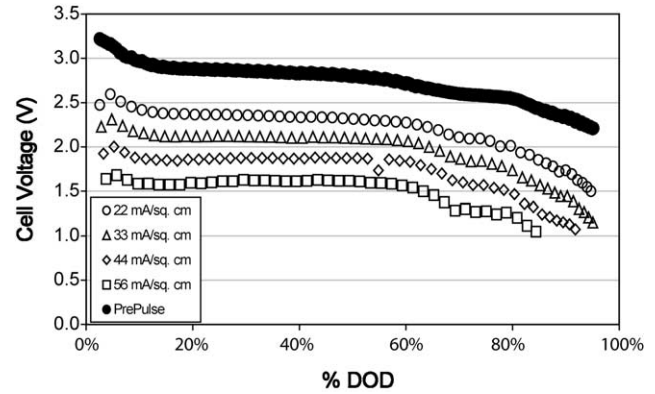

Fig. 6. Pulsatile discharge test of dual-chemistry cathode cell. One 10-s pulse was applied every 23 h with current density alternating between 22, 33, 44 and 56 mA cm^{-2}. The minimum voltage for each pulse is shown. No constant resistive load was used.

to the onset of the second discharge plateau of SVO and is related to the resistance increase seen in pure SVO cells. The magnitude of the resistance increase was minimized in the dual-cathode system and was observed to be fully reversible as seen by examining the results for the tenth pulse train in which all three test lengths gave similar loaded voltages. The improved stability in this region can be attributed to the reduced amount of SVO material present in the dual-chemistry cell.

It can also be seen in Fig. 5 that the background voltage curves overlay well. Throughout life, the 42 months discharge load resulted in slightly higher background voltage. While the lighter load would be expected to result in higher voltage in this test, it is noteworthy that the relationship still held at the end of discharge. This indicates that the amount of self-discharge in the system over 42 months was <2%. Any significant self-discharge would have been expected to result in a shortening of the overall discharge curve as the test length increased. The self-discharge observed here is characteristic of the self-discharge of the CF$_x$ system and is less than that typically observed for the SVO system.

3.4. Power capability of dual-chemistry system

It was previously seen in Fig. 4 that the power capability of the dual-chemistry cathode is similar to that of the pure SVO system. The power capability is further demonstrated in Fig. 6, which shows the performance at current densities up to 56 mA cm^{-2}. At the highest current density tested, the cell maintained greater than 1.5 V throughout most of discharge. Since no background load was used during this test, all of the capacity was removed by pulsing. If one assumes that the SVO material provided much of the pulse energy, these results suggest that the CF$_x$ material served to "re-charge" the SVO since the theoretical cell capacity was achieved. In addition, the CF$_x$ plateau is clearly visible in Fig. 6.

3.5. Flexibility of cell design

Fig. 7 shows a dual-chemistry cathode cell subjected to an accelerated pulsing test. In this test, cells with SVO:CF$_x$ capacity ratios ranging from 0.15 to 1.24 were discharged over 33–108 h. The cells with more CF$_x$ took longer to discharge in this test because they typically had more capacity per unit of electrode interface area. This test demonstrates the ability of the dual-chemistry cell to be discharged quickly while still retaining its power capability. It is reasonable to consider whether repeated pulsing can exhaust the SVO material resulting in loss of the cell's ability to deliver high current pulses. It is important that the CF$_x$ participate at a rate that can keep up with the demands of repeated pulsing. Fig. 7 demonstrates that the CF$_x$ material seems to function well in this cathode design even when the cathode is mostly composed of CF$_x$ (SVO:CF$_x$ capacity ratio = 0.15).
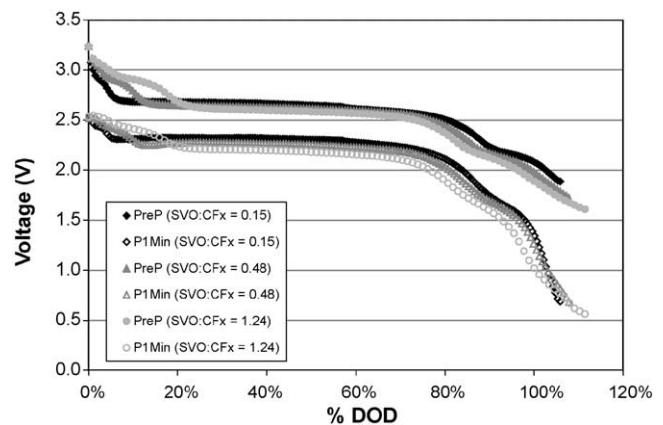

Fig. 7. Accelerated pulse test. Cells were pulsed at 25 mA cm^{-2} of electrode interface area. A four-pulse train was applied every 30 min with a 10-s pulse length and 15 s between pulses. The voltage prior to the first pulse of each train and the minimum voltage for the first pulse of each train are depicted. Three different cell designs were used with an SVO:CF$_x$ capacity ratio range of 0.15–1.24. No background load was used.
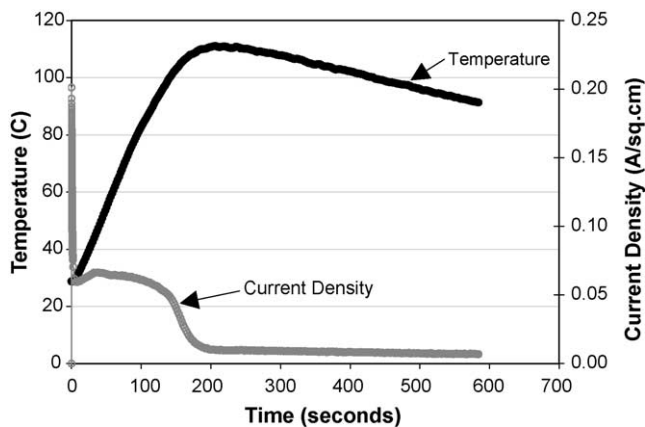
Fig. 8. Cell response to an external short-circuit on a beginning-of-life cell with a circuit resistance less than 10 mΩ. The temperature was measured on the case wall. The current density is expressed per unit of electrode interface area.

An examination of the pre-pulse curve in Fig. 7 shows the effect of changes in the SVO:CF$_x$ capacity ratio. It is apparent that the 3.2 V SVO plateau becomes longer as the SVO:CF$_x$ capacity ratio increases. Cells with more SVO would also be expected to have a shorter CF$_x$ plateau and a longer 2.6 V SVO plateau, but this cannot be seen in this test because the CF$_x$ plateau is polarized such that it overlaps with the 2.6 V SVO plateau.

3.6. Safety of cell system

Fig. 8 shows the results of a short-circuit test on a dual-chemistry cathode cell. The current initially spiked to 200 mA cm^{-2}, but dropped to 60 mA cm^{-2} by 10 s. At 150 s, the current dropped off to 10 mA cm^{-2} mostly as a result of the shutdown separator. The temperature increased linearly to 110 °C until 200 s (just after the proposed separator shut-down) and then began to slowly decrease. The cell did not vent or leak. The performance of the cell in this abusive test was similar to existing high-rate medical battery technology.

4. Conclusion

A new dual-chemistry cathode concept has been developed. The use of SVO and CF$_x$ in the cathode provides a cell which maintains the rate capability of SVO with increased energy density and stability and decreased self-discharge. The desirable attributes of SVO and CF$_x$ were realized whereas the disadvantages were minimized. The performance of the resulting cell meets all of the requirements for high-rate implantable medical batteries.

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