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Development and analysis of a lithium carbon monofluoride battery-lithium ion capacitor hybrid system for high pulse-power applications

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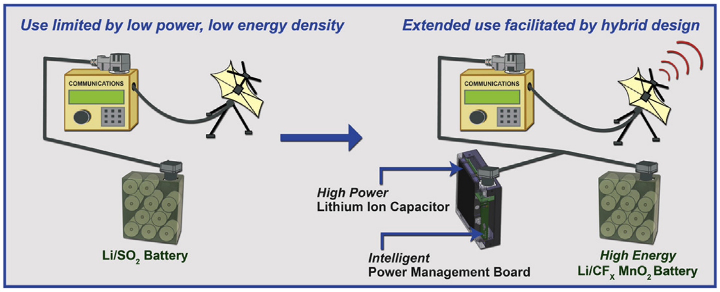
HIGHLIGHTS

- A power management board was developed to hybridize lithium batteries with LICs.
- Hybridization of high-energy density Li/CF_xMnO_2 batteries enables high-power use.
- The hybrid LiC-battery design reduces Li/CF_xMnO_2 battery operating temperatures.
- The hybrid LiC-battery design minimizes Li/SO_2 battery voltage delay.

GRAPHICAL ABSTRACT



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ABSTRACT

Although Li/CF_x and Li/CF_xMnO_2 have two of the highest energy densities of all commercial lithium primary batteries known to date, they are typically current-limited and therefore are not used in high-power applications. In this work, a Li/CF_xMnO_2 battery (BA-5790) was hybridized with a 1000 F lithium ion capacitor to allow its use for portable electronic devices requiring 100 W 1-min pulses. An intelligent, power-management board was developed for managing the energy flow between the components. The hybrid architecture was shown to maintain the battery current to a level that minimized energy loss and thermal stress. The performance of the Li/CF_xMnO_2 hybrid was compared to the standard Li/SO_2 battery (BA-5590). The hybrid was shown to deliver the same number of 100 W pulse cycles as two BA-5590 batteries, resulting in a weight savings of 30% and a volumetric reduction of 20%. For devices requiring 8 h of operational time or less, a 5-cell Li/CF_xMnO_2 hybrid was found to be a lighter (55%) and smaller (45%) power source than the existing two BA-5590 battery option, and a lighter (42%) and smaller (27%) option than 1½ BA-5790 batteries alone. At higher power requirements (>100 W), further weight and size improvements can be expected.

1. Introduction

Portable electronic devices often have load profiles that consist of intermittent pulses of high power separated by a much longer, more modest baseline-power demand. One of the mainstay

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batteries used by the military for such applications has been the lithium/sulfur dioxide (Li/SO_2)-based BA-5590 primary battery. With an energy density of ~200 Wh kg^{-1} (230 Wh L^{-1}) [1,2], the BA-5590 is noted for its ability to meet high-power requirements and to operate at low temperatures (−40 °C). However, major limitations of the BA-5590 for defense applications continue to be its weight and volume. The total weight of batteries required to complete a mission can be a logistics problem, thus reducing the fighting capability of the soldier. Additionally the military, similar to the consumer, desires miniaturized, less cumbersome devices. Reducing the weight and volume of the power source promotes user agility and would be of great value to the Marine Corps and the Army.

Alternative technologies with higher energy densities have been developed, such as lithium/carbon monofluoride (Li/CF_x) which have approximately twice the energy density of Li/SO_2 cells (Table 1). However to date, Li/CF_x technologies have not replaced the Li/SO_2 in military dominance due to their inability to meet the power demands required for numerous electronic devices. The limited high-rate performance of the Li/CF_x battery is thought to be the result of kinetic limitations associated with breaking C–F bonds and the poor electrical conductivity of the CF_x material creating high internal impedance during discharge [3,4].

Over the years, numerous attempts to increase the rate capability of the Li/CF_x electrochemistry and thereby increase operational life have had limited success. CF_x is an intercalation compound formed by the reaction between carbon powder and fluorine gas. This process forms strong covalent C–F bonds with sp^3 hybridization that induces charge localization and results in a significant reduction in electrical conductivity as the value of x increases [5]. Approaches to solving the issue of low electrical conductivity to improve rate capability while maintaining a high energy density include: partial carbon fluorination so that any unreacted carbon can serve as a conductor between the CF_x particles [6,7], carbothermal treatment of the CF_x that results in the formation of sub-fluorinated CF_x [8], and pretreatment of CF_x using a “solvated electron” reduction method to obtain a thin layer of graphitic carbon coating on the CF_x particle surfaces [9]. Additional material approaches to improving poor-rate performance have included blending CF_x with more conductive cathode materials such as manganese dioxide (MnO_2), with the expectation that an optimized cathode mixture ratio would provide enhanced cell rate capability while maintaining the high energy density advantage of CF_x [10]. These studies demonstrated promising improvements in cathode rate capability, though none were at a level required for future high-power portable devices. Thus batteries composed of CF_x cathode materials still cannot deliver their full capacity under high-power conditions, making them an unsuitable replacement for the low energy density Li/SO_2-based batteries in military applications.

A hybrid battery-capacitor architecture containing both a high-energy device (battery) and a high-power device (capacitor) is a potential solution to address the unmet military need for light, miniaturized devices that can provide a series of intermittent high-power pulses superimposed over a steady, low-power baseline. Combining a battery with a capacitor allows the capacitor to support the high-power transients, thus lowering the battery discharge current and improving energy utilization. In a CF_x battery-capacitor hybrid, each component would operate under optimal discharge rate conditions: short-duration, high-power pulses are supplied by the capacitor, and the CF_x battery operating at low to moderate discharge rates fulfills the baseline power demand. During periods of low-power events, the CF_x battery would re-charge the capacitor.

Several studies have indicated success in utilizing hybrids with capacitors to improve the usable capacity of primary lithium and non-lithium batteries in applications requiring high-power pulses. However, few have focused on providing such augmentation while minimizing weight and volume – key for military applications. Most previous investigations have used electrochemical double layer capacitors (EDLCs) for the high-power component. Atwater et al. observed a significant improvement in a primary zinc-air battery using a simplistic hybrid design consisting of the battery and an EDLC in parallel with no interface electronics [11]. The hybrid zinc-air achieved double the number of high-power pulses compared to the battery alone. Penella et al. [12] observed a 33% improvement in runtime with a primary, silver oxide-zinc battery when hybridized with an EDLC and more recently, Cain et al. [13] noted a 46% increase in retrievable energy from a primary Li/MnO_2 battery. A larger number of studies have also focused on hybridizing secondary (rechargeable) batteries with EDLCs. For example, Cain et al. observed a 40% increase in capacity with a lithium ion rechargeable battery in the above study [13]. Others have also investigated hybridization of lithium ion batteries with EDLCs as a method to increase cycle life and improve operating temperature performance, in addition to extending battery run time [14–19]. These enhanced properties are particularly relevant for electric, hybrid electric and plug-in vehicles where high-power surges can lead to excessive cell heating, battery degradation and safety concerns. To determine the viability of a hybrid system for these and other applications, significant experimental work, mathematical simulations, and investigations to improve power/energy management have been conducted [e.g., 20–21]. Though these studies have successfully demonstrated improved battery performance, a thorough analysis of the weight and size of the devices has often been neglected.

The benefits of a hybrid battery-EDLC power source, unfortunately, are not without consequences. Enhanced battery performance can be at the expense of the overall system’s weight, volume and complexity [22–24]. These repercussions are particularly damaging for portable applications when long (>30 s) high-power

Table 1
Comparison of lithium primary D-cell technologies.

	Li/SO_2	Li/MnO_2	Li/CF_x	Li/CF_xMnO_2
Capacity at 2 A (Ah)	7.5	11	19	16
Open Circuit Voltage (V)	3.0	3.3	3.0	3.3
Nominal Voltage (V)	2.8	3.0	2.6	2.6
Operating Temperature (°C)	−60 to +70	−40 to +72	−20 to +90	−40 to +85
Weight (g)	85	115	69	81
Specific Energy (Wh/Kg) @12 V	255	287	716 (Al case)	514 (Al case)
Manufacturer, Number	SAFT, LO 26SX[a]	Ultralife, U10013[b]	Spectrum Brands, BR-20[c]	Eagle Picher, LCF-133[d]

[a] Saft specifications document 31033-2-1005 (October 2005).
[b] Ultralife specifications document UBI-5099, Rev F20 (October 2010).
[c] Rayovac marketing data sheet 123-BA02A (March 2016).
[d] Eagle Picher preliminary technical data sheet for Li-CF_x/MnO_2 hybrid.