High Rate Li/CF_x-MnO_2 Hybrid Technology

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Abstract: *EaglePicher Technologies has developed a hybrid Li/MnO_2-CFx technology capable of delivering high energy at high discharge rates and very low temperatures. Performance of the hybrid chemistry has been validated at up to 4C discharge rates and at temperatures between -55°C and 60°C. These cells deliver a nominal specific energy of >400 Wh/Kg at room temperature, which is >50% above current Li-ion cells. In addition to the advantage in specific energy, the Li/MnO_2-CFx hybrid technology offers advantages in shelf-life and maintenance costs (no need for re-charge prior to use) over Li-ion batteries.*

This technology is suitable for applications requiring a combination of high power and high energy such as single use UAVs and hypersonic applications. This presentation will provide a general overview of recent developments on the hybrid technology at EaglePicher. In addition, testing results from our pouch cells, 2/3A cells and corresponding battery packs will be discussed.

Keywords: carbon fluoride; manganese dioxide; battery.

Introduction

Lithium/Carbon fluoride (Li/CF_x) is an attractive primary power source, because of its high specific energy, low self-discharge (less than 1% per year), excellent thermal stability, wide operating temperature range (-40 to 85°C), and improved abuse tolerance over other lithium systems. However, the obstacles that prevent a wider market penetration of Li/CF_x chemistry are its initial voltage delay at low temperature, thermal management issue at high discharge rates, and its material cost. Several approaches have been used to address these issues, including a partial substitution of CF_x by manganese dioxide to form hybrid cathode [1-2]. Using web-coating process similar to that in lithium-ion battery production, EPT has developed CF_x-MnO_2 hybrid cathode, which not only maintains all the favorable advantages of Li/CF_x but also provides the highest specific energy and excellent performance in wide temperature range as compared to other lithium primary chemistries.

This paper provides a general overview of recent developments on hybrid chemistry technology at EaglePicher Technologies, and discusses results from our work on pouch cells, cylindrical cells and corresponding batteries packs.

Experimental

The materials and cathode process were described previously [3-5]. Carbon fluoride (CF_x) and electrolytic manganese dioxide (MnO_2) used in this work were commercially-available materials. The hybrid cathodes were processed using EPT's advanced web coating equipment similar to that used in lithium-ion technology. The cathode composition and formulation were optimized to achieve high electrode density with enhanced rate capability.

Results and Discussion

EPT has developed a high-power and high-rate lithium primary cell technology that includes a web-coated CF_x/MnO_2 hybrid cathode and proprietary electrolyte formulations through extensive efforts over the last several years. The addition of MnO_2 in the cathode reduces the heat generation, eliminates voltage delay, and lowers the overall cathode material cost. The web coating process enables thinner cathodes with improved rate capability. The choice of carbon type used as the conducting additive and its distribution within the cathode structure, as well as an optimized cathode porosity further enhance the cell rate capability. In order to extend the operating temperature of the Li/CF_x-MnO_2 hybrid cell without sacrificing the rate capability, an electrolyte with low viscosity, low melting-point solvents and optimal lithium salt concentration was developed. This hybrid technology has been evaluated in both cylindrical and prismatic cells configurations. In this paper, we will discuss the performance of the hybrid Li/CF_x-MnO_2 pouch and cylindrical cells for high-rate applications in an extended temperature range.

High-Rate Hybrid Pouch Cell Development

Pouch cells with this hybrid chemistry were developed to maximize cell discharge rate capability, while maintaining the high energy density. The advantages for pouch cells include flexibility in size design, high specific energy, and inexpensive packaging material compared to hard case cells. The pouch cell format also offers improved packaging efficiency for prismatic battery packs. The historic limitations for pouch cells include leakage and swelling due to gassing and CF_x electrode expansion during discharge [6]. Among these limitations, the major challenge for hybrid pouch cells is cell swelling due to the well-known swelling behavior of the CF_x cathodes during discharge; the higher the amount of CF_x in the hybrid cathode, the higher the extent of swelling tends to be. The swelling will not only affect the battery integrity, but also will negatively impact the battery discharge performance in the pouch cell format. These limitations can be addressed through optimization of the electrolyte formulation, the choice of suitable CF_x materials, pouch material selection, and pouch sealing techniques. Figure 1 shows a picture of the first generation high-rate hybrid pouch cell (LCF-136) developed at EaglePicher.

Figure 1. Li/CFx-MnO_2 Pouch Cell

The chemistry and design of the EaglePicher pouch cells were optimized by selecting the proper cathode active material, cathode composition, carbon conductive additives, and binder. Also, for the active materials, the ratio of the amount of MnO_2 to CF_x was optimized in terms of its effect on swelling, heat generation, and energy density requirement for the high-rate battery. The cathode loading was optimized according to the process capability, energy density, and power requirements for the battery. Cathode porosity was also optimized based on its effects on cathode swelling and energy density requirement for the battery.

Performance of the LCF-136 pouch cell was validated at up to a 2C rate for a wide range of temperatures. Figure 2 illustrates the performance of pouch cells at different rates at -40°C. In the figure, it is demonstrated that the cells exhibit a good rate capability at -40°C, delivering 85 to 95% discharge efficiency. Another characteristic of the curves is that the higher the rate, the higher the cell discharge efficiency at -40°C. This is explained by the heat effect of the battery. The higher discharge rate will generate greater amounts of heat, making the battery discharge at a warmer temperature, thus working at a higher voltage, and delivering higher capacity and energy [7].

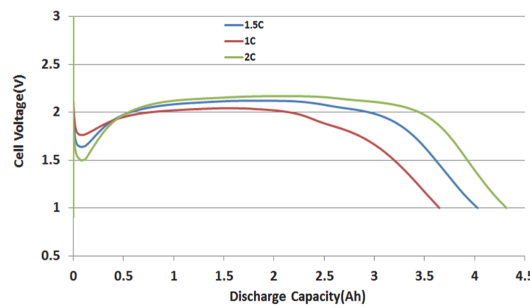

Figure 2. LCF-136 Rate Capability at -40°C

A manufacturing line for the LCF-136 has been installed and is in operation at our Joplin facility. The cells and battery packs have been fully qualified for different applications.

In recent years, Eaglepicher has developed a second generation high rate pouch cell (LCF-145) with increased rate capability for more demanding applications. Performance of the LCF-145 cell has been validated up to a 7C rate for a wide range of temperatures. Figure 3 shows the discharge curves of pouch cells at 20W rate (~3C rate) at various temperatures. As can be seen in the figure, the LCF-145 cells show a high discharge efficiency over the -40°C to 60°C temperature range.

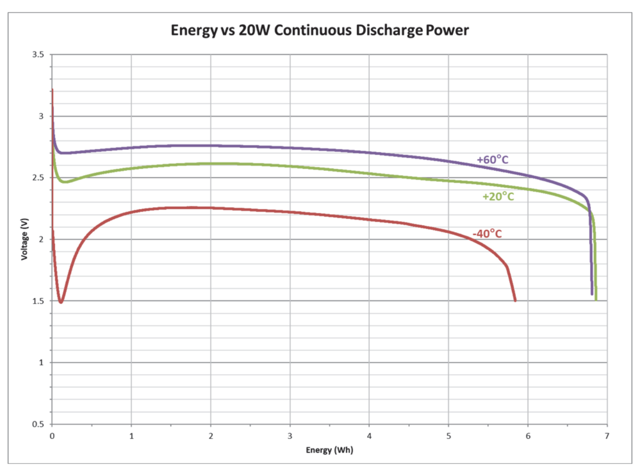

Figure 3. Discharge Performance of LCF-145 Pouch Cell at Various Temperatures

Figure 4 shows the performance of single LCF-145 pouch cells (in a 3-cell pack) under a simulated UAV profile. The discharge profile includes a 7C discharge rate during take-off and a 2C discharge rate during cruise discharge. It can be seen in the figure that the cell demonstrated the power capability required for this type of application. Several battery packs have recently been developed for different applications including UAVs.

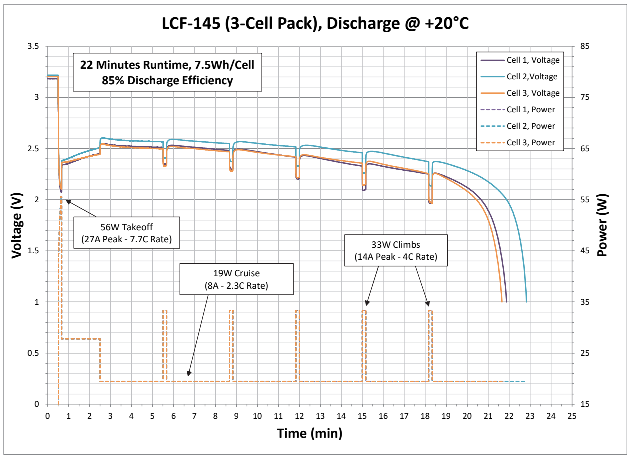

Figure 4. Performance of a LCF-145 pouch cell under a simulated UAV discharge profile

Small cylindrical cells (2/3A and 1/3A cells) have also been recently developed/qualified for hypersonic applications using the high rate hybrid chemistry. Table 1 shows the performance parameters of Eaglepicher's current high rate cylindrical cells and pouch cell products.

Table 1. Eaglepicher's High Rate Products

Product #	LCF-136	LCF-136HR	LCF-145	LCF-144	LCF-314
Electrochemistry	Li/CF_x-MnO_2	Li/CF_x-MnO_2	Li/CF_x-MnO_2	Li/CF_x-MnO_2	Li/CF_x-MnO_2
Form Factor	Prismatic Pouch	Prismatic Pouch	Prismatic Pouch	Cylindrical (2/3A Size)	Cylindrical (1/3A Size)
Exterior Construction	Aluminum-Polymer Laminate	Aluminum-Polymer Laminate	Aluminum-Polymer Laminate	Nickel-Plated Steel	Nickel-Plated Steel
Nominal Voltage (V)	2.6	2.6	2.6	2.6	2.6
Mass (g)	29.5	29.5	24.0	15.5	11.3
Dimensions (mm)	56.5 (H) x 50.0 (W) x 6.5 (T)	58.0 (H) x 49.8 (W) x 6.5 (T)	58.0 (H) x 49.8 (W) x 5.2 (T)	16.5 (Ø) x 32.0 (H)	16.5 (Ø) x 19.0 (H)
Storage Temperatures (°C)	-40°C to +85°C	-40°C to +85°C	-40°C to +85°C	-40°C to +85°C	-40°C to +85°C
Operating Temperatures (°C)	-40°C to +60°C	-40°C to +60°C	-40°C to +60°C	-40°C to +80°C	-40°C to +80°C
Capacity/Energy (Ah/Wh)	4.9Ah / 12.5Wh	4.9Ah / 12.5Wh	3.5Ah / 9Wh	1.4Ah / 3.7Wh	0.8Ah / 2.0Wh
Specific Energy (Wh/kg)	420	420	375	240	180
Energy Density (Wh/L)	680	680	615	540	490
Specific Power* (W/kg)	**1800**	**2400**	**3000**	**1700**	**1200**
Power Density* (W/L)	**2800**	**3800**	**4800**	**3800**	**3500**

In conclusion, EaglePicher has made great progress in developing a Li/CF_x-MnO_2 hybrid technology, which offers a combination of power and energy for military and space applications requiring high rate capability and long service life in an extended operating temperature range from -40 to 60°C. The hybrid chemistry pouch cells provide an opportunity to develop lightweight, compact, and versatile batteries to address industry needs and requirements.

Acknowledgements

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