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Update on Performance Improvement of Sandia-Built $Li/(CF_x)_n$ and $LiFePO_4$ Cells

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Primary Lithium Batteries (Incl. Liquid Reserve)

Abstract

Because of the critical need for a lightweight, long-life power source, Sandia National Laboratories has initiated a program for improving the performance of $Li/(CF_x)_n$ cells. In-house capabilities have been developed for cell building and manufacturing in a manner that provides the flexibility to evaluate different formulations of electrolyte and cathode materials. In the last couple of years we have learned to coat $(CF_x)_n$ electrodes with uniform loading and to build 18650 cells with reproducible performance. Last year we demonstrated cathode electrodes coated on one side of the current collector with 1.8Ahr capacity. This year we have improved the loading to >2.5Ahr. We have also pulse tested cells as a function of temperature. $(CF_x)_n$ cells that are 90% fluorinated (x=0.9) showed better low temperature performance than cells with 100% fluorination, especially at sub-zero temperatures.

Additionally, we are also investigating $LiMPO_4$ materials as cathodes for Li-ion cells. Building upon the experience gained from $(CF_x)_n$, optimized $LiFePO_4$ electrodes were coated within a short time. These cells are being tested in an electrolyte with > 2 mS/cm conductivity near room temperature and which remains liquid even at -65°C. Cell performance in the new electrolyte at different temperatures will be described. Our cell building capabilities will be described in detail.

Keywords: Carbon-monofluoride; lithium iron phosphate; in-house facility for cell fabrication

Introduction

Two promising battery chemistries that have spurred interest in commercial, military, and space applications are carbon-monofluoride $(CF_x)_n$, a relatively old chemistry, and the olivine ($LiMPO_4$) based material, which is a relatively new chemistry. While $(CF_x)_n$ is a primary chemistry, $LiMPO_4$ is rechargeable. In our work we have studied this material and also a ~90% fluorinated material. The main compelling attributes of this material are the huge theoretical specific capacity (860 mAhrs/g) and energy density (~2200 Whrs/kg), the largest of the four well-known Li primary chemistries. In addition, CF_x exhibits very low self-discharge and a virtual absence of voltage delay. The $(CF_x)_n$ cells are also light weight. For example, a 3.6Ahr $Li/(CF_x)_n$ weighs only ~28g where as a 2.5Ahr Li-ion cell weighs ~40g. The US Army is interested in the $(CF_x)_n$ chemistry for this particular reason[1] among others.

Recently, the olivine-type materials, especially $LiFePO_4$, have generated wide-spread interest as cathode materials for Li-ion cells. $LiFePO_4$ was developed by Goodenough's research group at the

University of Texas in 1997[2]. This seminal work generated great interest in the material because, in addition to high specific energy, it is:

1. low cost,
2. thermally stable,
3. non-toxic and environmentally benign,
4. chemically stable and offers a flat operating voltage which is ~3 times the operating voltage of Ni-Cd cells

However, the technical barrier to commercialization was its very low intrinsic conductivity. In 2002 Chiang et al. at MIT[3] reported that they had successfully doped $LiFePO_4$ with appropriate cations to improve the conductivity, allowing development to move forward.

A Department of Energy technical report[4] on low-cost $LiFePO_4$ batteries observed that the cycling performance of $LiFePO_4$-based high-power lithium-ion cells was excellent and showed no degradation structurally or electrochemically.

Sandia National Laboratories has world-class facilities for building and testing lithium and lithium-ion batteries and we are interested in these chemistries for use in our internal applications. Our interest in studying these materials is not only to custom–build cells, but to develop these materials to our specifications, which requires improvements in the low temperature performance.

In this article we briefly mention the in-house facilities for fabricating electrodes and cells in detail. SNL's in-house facility includes equipment for: 1) electrode coating, 2) electrode slitting, 3) electrode winding, 4) cell grooving, 5) electrolyte filling, 6) cell crimping and more. We also have a 48-channel Maccor tester and several impedance units for electrochemical characterization. These facilities provide flexibility for cell fabrication techniques which in turn allows us to continually optimize cell performance. We will also describe the recent data obtained on $(CF_x)_n$ and $LiFePO_4$ cells.

Experimental

Recipe for making slurry for the cathode and Electrode Coating are described in reference 5.

Anode

For 18650 cells, thin lithium electrodes with copper cladding (Furukawa, Japan) were employed as the anode. The copper was 8-10 microns thick with a 20-micron Li film vapor deposited on each side. The Cu cladding was necessary to withstand the tension applied while winding the cell. A nickel tab was normally cold-welded to the anode before winding.

Cell Winding

Jelly rolls were made on the semi-automatic Micro Tech winder. Typically we used a 54-mm wide anode, 50-mm wide cathode, and 58-mm wide Celgard (North Carolina, USA) 2325 separator for the 18650 cells. Since the anode is on the outside of the roll it is longer than the cathode by about 4-5 cm. The Micro Tech winder can take almost any electrode length.

Cell Grooving

The anode tab was spot-welded to the bottom of the 18650 can through central mandrel hole and the can was grooved just above the roll to prevent the roll from sliding out of the can. The cell grooving was accomplished using the 18650 Cell Groover. After grooving, the header (consisting of a burst disc, polypropylene-type cup, Ni washer as replacement for the PTC current controlling device) was attached to the cathode tab using the Amtech ultrasonic welder.

Cell Filling and Crimping

After attaching the header, the cells were transferred to an argon atmosphere glove box for electrolyte filling and crimping. Cells took approximately 3.2 ml of electrolyte. After filling, the cells were crimped and the open circuit voltage was measured to insure against shorting. Before testing for capacity or impedance, the cells were kept at 40°C overnight to allow for soaking of the electrolyte into the cathode bulk.

Results and Discussion

Improved Cell Capacity

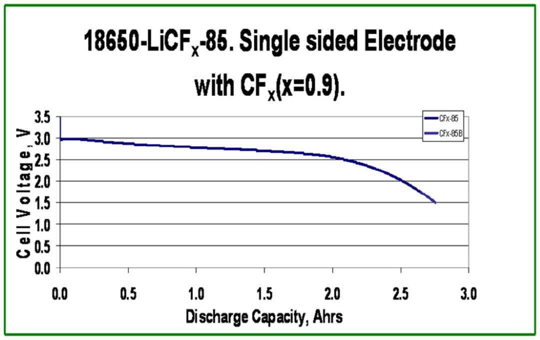

Figure 1. Enhanced Capacity from 1.8 Ahrs to 2.7 Ahrs

By optimizing processing parameters we were able to increase the delivered capacity of 18650- cells. Figure 1 shows the cell voltage vs. discharge capacity for a cell that had $(CF_x)_n$ electrode coated on one side of the current collector. The delivered capacity is ~2.7Ahr, nearly ~1Ahr greater capacity than that achieved in our laboratory a year ago. Our objectives were to increase cell capacity and improve low temperature performance; therefore, power and rate capability were not addressed.

Temperature Performance

We also tested $(CF_x)_n$ cathodes (x=1.0 and 0.9) in 18650 cells for pulse performance while cycling oven temperature between -40 and 72°C. The temperature profile will be described at the meeting. At each temperature the oven stayed for 4 hrs before moving to the next. The test duration was 48 hrs. The pulse duration was kept very short- 4 mS every 10 sec, and the total capacity removed during the 48 hour test was ~ 276µAhr. In order to determine the capacity at which the cell failed, a constant current (CC) discharge was performed after the first pulse testing and removed a predetermined amount of capacity. The cells were pulse tested again while cycling the oven temperature. After the 2nd pulse testing, a predetermined amount of capacity was removed from the cell again and the pulse testing was resumed. This procedure was repeated several times until the cell reached 1.5V cutoff voltage. Figures 2 & 3 show the voltage response of the cells for the last pulse measurement during which the cells failed. Both cells failed at -40°C. The capacity drained at 25°C after the test is also shown in the figures.

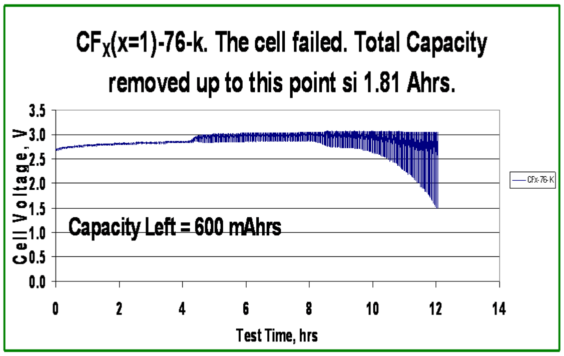

Figure 2. Cell Voltage vs. time at different temperatures.

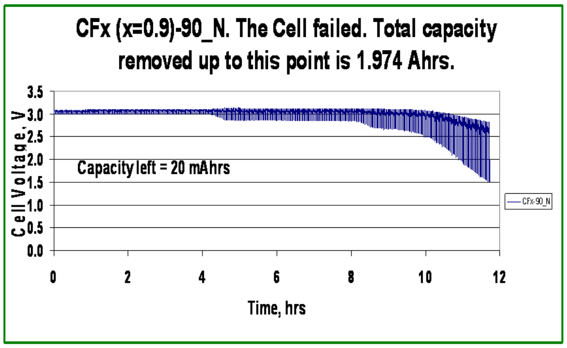

Figure 3. Voltage response at different temperatures

Figure 2 shows the performance of the CF$_x$ cathode with x =1.0 after removing 1.8 Ahrs capacity. The remaining capacity as determined by the CC discharge is 0.6 Ahrs. Although the total cell capacity for this cell was 2.4 Ahrs the cell failed after removing 1.8 Ahrs. Figure 3 shows a similar plot for the cathode with x=0.9. This cell failed after removing ~2 Ahrs and the remaining capacity was only 0.02 Ahrs. Remember that this cell contains the 90% fluorinated cathode and so the theoretical capacity is lower than that for the first cell. Despite the lower capacity this cell performed better than the fully fluorinated material in terms of delivered capacity. This observation clearly indicates that performance of the cathode with higher capacity doesn't necessarily translate to better performance at lower temperatures. Our data show that the cell with x=1 only delivered ~ 75% of the capacity while the other gave ~ 99% of the capacity before failing.

Performance of $LiFePO_4$

$LiFePO_4$ electrodes were fabricated and tested for performance in cells using metallic lithium as the anode.

Coin Cell Performance:

Several coin cells were tested for capacity and rate capability. The cells exhibited highly reversible Li^+ insertion/de-insertion. The discharge current for the first 3 cycles is 0.1mA and that for the last two cycles is 0.2mA.

Figure 4 shows plots of average capacity at the two discharge currents. Cell- to- cell reproducibility was good which suggests that the cathode loading is uniform across the length of the electrode.

We also measured impedance of the 18650 cells. The NyQuist plot shows the typical inductive tail followed by two semicircles in the high frequency region; this feature that has been reported by us[5] and others before.

The ohmic resistance at ~0.348 ohms is about 5 times higher than normally observed for this chemistry. This means that the resistance of the cell especially that of the cathode needs improvement.

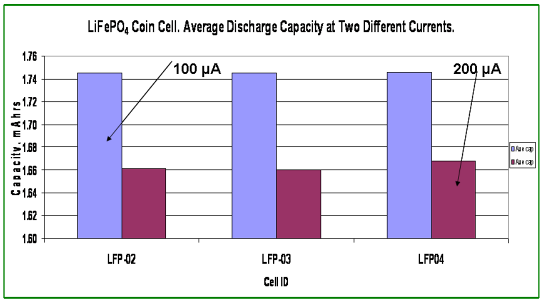

Figure 4. Cell to Cell Variation in Performance is Negligible

Summary

The capacity of 18650-cells with single sided $(CF_x)_n$ electrodes has been improved to >2.5 Ahrs. The delivered capacity at low temperature of the $(CF_x)_n$ with x=0.9 was higher than that with x=1.0 cathode. We also prepared $LiFePO_4$ electrodes with uniform coating and built into coin and 18650 cells. The performance of this cathode in coin cells was found to be very reproducible. We are currently testing 18650 cells and the performance data will be reported at the meeting. The impedance of Sandia built 18650 $LiFePO_4$ cells is higher than the commercial cells.

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