Improvements in Battery Technology for the Exploration Program

Judith A. Jeevarajan, *Johnson Space Center*

The Exploration Systems Mission Directorate Program was started in Fiscal Year 2006 (FY06) to address the basic research and technology needs for the Exploration program. The work under this program titled "Energy Storage" was performed at Johnson Space Center (JSC) in collaboration with several other NASA centers, including Glenn Research Center, Marshall Space Flight Center, Jet Propulsion Laboratory, and Goddard Space Flight Center. The first year was geared toward increasing the performance of lithium primary, lithium-ion secondary, as well as fuel cell research. In FY06, the focus changed to develop the performance and safety of lithium-ion cells for use in future exploration missions. Under this new focus, collaborative work was carried out with university partners to improve the performance of cathode materials and test them independently. Cells were also purchased from industry based on safety improvements such as overdischarge tolerance and those with shutdown separators that activate at temperatures much lower than the thermal runaway temperatures of the cell. Small Business Innovative Research (SBIR) programs were also geared toward similar goals of meeting future exploration needs. Programs in this area included improvements in lithium primary cells of the carbon monofluoride ($LiCF_x$) chemistry that would operate over a wide temperature range and improvements in safety of lithium-ion cells with the use of the variable temperature shutdown separator.

Improvements in Lithium-ion cell performance with the use of new cathode materials were studied by collaborative work with Professor Manthiram and his team at The University of Texas at Austin (UT Austin). The cathode material synthesized was $xLi[Mn_{0.5-y}Ni_{0.5-y}Co_{2y}]O_2.(1-x)Li[Li_{1/3}Mn_{2/3}]O_2$. The material characteristics of the pristine as well as the Al_2O_3-modified cathodes were studied at UT Austin. The tests conducted indicated that the alumina modifications did not provide any additional increases in energy density (figure 1). Depending on the ratio of x and y in the cathode material, the energy density varies. Values between 138 mAh/g to 236 mAh/g for x=3/4 and y=1/3 and x=2/5 and y=1/12, respectively, were obtained. Independent testing of coin cells, manufactured by UT Austin, with their improved cathode material was conducted at JSC. Each coin cell underwent 25 cycles to determine its performance.

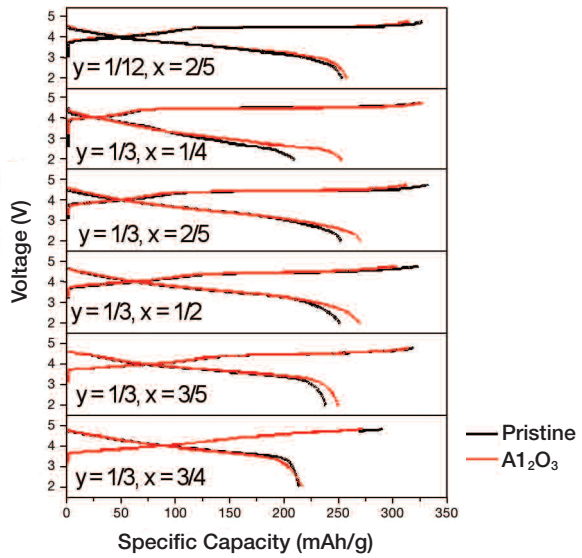

Fig. 1. Comparison of charge discharge profiles for the 12 samples studied (UT Austin data).

The LiTech (MER) 2.9 Ah lithium-ion cells were designed with an anode that was capable of tolerating overdischarge. The anode was made with a carbon-fiber current collector in the place of the conventional copper current collector. In the conventional cells, the copper current collector undergoes dissolution at low voltages, causing internal short circuits in the cells. With the use of the carbon-fiber current collector, the failures due to the dissolution of copper can be avoided. The LiTech cells were subjected to cycle life tests and safety tests that included overcharge, overdischarge, external short circuits, and simulated internal short circuits. The cycle life tests were performed using a C/3 rate of charge and discharge. The first 50 cycles were performed without a restraint on the cells, and the remaining 150 cycles were performed with a restraint. The capacity loss for the first 50 cycles was about 3.7%, and a 29% loss resulted at 140 cycles after the restraint was placed. The overcharge test was performed on fully charged cells with a 1C current to 12 V for a period of 6 hours. Inconsistent results were obtained with one cell displaying tolerance and the other cell rising in temperature above

200°C and charring completely. Overdischarge into reversal, external short circuits and simulated internal shorts on the cell resulted in a maximum temperature of about 30°C with the cells displaying tolerance to these conditions. However, the cells could not be charged or discharged after the tests. Theoretically, the cells should have displayed tolerance to overdischarge conditions with capability to recharge, but they did not display that behavior. Consultation with the cell manufacturer indicated that the results could be attributed to the use of impure electrolyte solvents.

The Policell lithium-ion cells with a separator that shut down at 100°C were purchased and subjected to cycle life as well as safety tests. The shutdown characteristics at lower temperatures provide a margin between the electrical shutdown and thermal runaway that typically occurs above 130°C. The cycle life tests were carried out under charge and discharge of C/3 rates, and the best cells displayed a capacity loss of 13.3% over 200 cycles. The overcharge test was performed with a current of 1.4 A for 6 hours. The cells displayed tolerance to the overcharge reaching a maximum temperature of 52°C.

The Policell lithium-ion cells were tolerant to overdischarge into reversal, but under short circuit conditions, they displayed inconsistent behavior. One cell was completely charred with thermal runaway while the other did not display temperatures above 120°C. The cells exhibited shutdown behavior (drop in voltage) under the heat-to-vent test and did not go into a thermal runaway. Figure 2 shows the temperature rise in the cell that tracks the chamber temperature but does not go into a thermal runaway condition, indicating effective shutdown of the separator.

The Phase I SBIR project for the Exploration Systems Mission Directorate program was successfully completed with the demonstration of feasibility of performance of $LiCF_x$ cells at temperatures as low as –98°C. Low-temperature ionic liquids were synthesized by Covalent Associates; and in collaboration with Quallion, LLC, coin cells as well as AA-size cells were manufactured. Tests were performed at the lab scale as well as in coin cells at

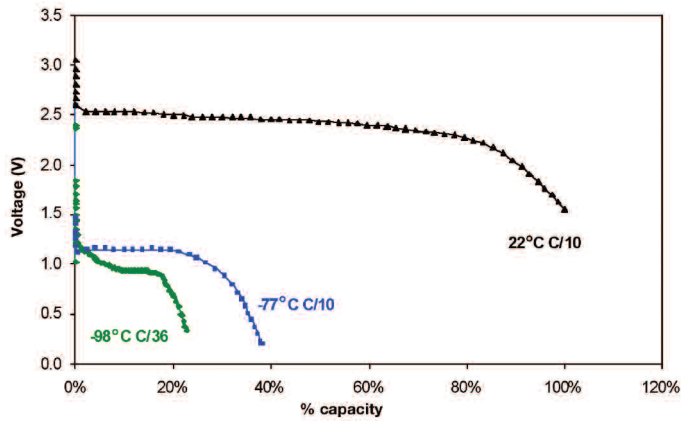

Fig. 2. Heat-to-vent Test for Policell Li-ion Cell showing Shut–down Characteristics.

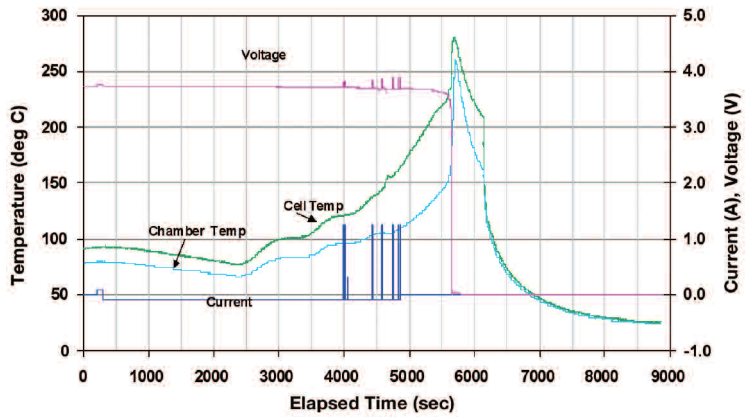

Fig. 3. Discharge Profiles for LiCFx Coin Cells at Different Temperatures.

temperatures as low as –98°C, and approximately 20% of the room temperature performance was obtained. At –40°C, approximately 40% of the room temperature performance was obtained (figure 3). In AA-size cells, 38% of room temperature performance was obtained at –70°C and above 98% was obtained at +60°C. The tests proved that performance over a wide temperature range was achievable with the ionic liquids in a $LiCF_x$ primary cell.

I would like to acknowledge Geminesse Dorsey, Jennifer Rivers, Mike Salinas, Laura Baldwin, and Tony Chu of the Energy Systems Test Area for their dedicated work on the test programs. Active participation in the collaborative research by all the NASA centers and UT Austin, and by the test services and cell vendors such as Mobile Power Solutions, Quallion, LLC, Covalent Associates, Policell Technologies, and LiTech/MER Corp. is greatly appreciated. Research efforts in improving the performance and safety of lithium primary and lithium-ion cells were fruitful due to this active collaboration and contribution from all the team members.