SAND99-1076C

Low Temperature Electrical Performance Characteristics of Li-Ion Cells

RECEIVED JUN 09 1999 OSTI

Ganesan Nagasubramanian
1521 Lithium Battery R & D
Sandia National Laboratories
Albuquerque, NM 87185. (pH)505/844-1684, email: gnagasu@sandia.gov

ABSTRACT

Advanced rechargeable lithium-ion batteries are presently being developed and commercialized worldwide for use in consumer electronics, military and space applications. The motivation behind these efforts involves, among other things, a favorable combination of energy and power density. For some of the applications the power sources may need to perform at a reasonable rate at subambient temperatures. Given the nature of the lithium-ion cell chemistry the low temperature performance of the cells may not be very good. At Sandia National Laboratories, we have used different electrochemical techniques such as impedance and charge/discharge at ambient and subambient temperatures to probe the various electrochemical processes that are occurring in Li-ion cells. The purpose of this study is to identify the component that reduces the cell performance at subambient temperatures. We carried out 3-electrode impedance measurements on the cells which allowed us to measure the anode and cathode impedances separately. Our impedance data suggests that while the variation in the electrolyte resistance between room temperature and -20°C is negligible, the cathode electrolyte interfacial resistance increases substantially in the same temperature span. We believe that the slow interfacial charge transfer kinetics at the cathode electrolyte may be responsible for the increase in cell impedance and poor cell performance.

INTRODUCTION

Approximately nine years ago, Sony Energytec Inc. introduced the first lithium-ion cell into the marketplace. Shortly thereafter, virtually every consumer battery company embarked on development activity aimed at production of this cell. Li-ion cells have a favorable combination of energy and power [1]. Because of this, Li-ion is rapidly taking over the high-performance rechargeable battery market supplanting NiCd and NiMH batteries that cannot meet the energy needs of today's portable electronic products for consumer application. Further, Li-ion is being actively considered for Space and Aerospace applications. For example, to power Rovers and Landers in Mars Exploration missions, NASA is considering Li-ion cells. In recent years, the need for power sources for a variety of applications including computers, medical, power tools, consumer electronics, space and military, is increasing rapidly. The power sources need not only to support many new and additional features in the devices but also need to perform over a wider temperature regime. A thorough and complete understanding of the battery from the point of view of performance, especially at subambient temperatures, is very important for a successful use in these applications.

EXPERIMENTAL

18650 and 17500 Lithium-ion cells of three different manufacturers evaluated. Before welding tabs to the cells for electrical connections, both their weights and physical dimensions were measured. Average values for weights and computed cell volumes are given in **Table 1** along with the cell type, capacity, manufacturer, and the number of cells tested. Initially, the cells were charged and discharged at room temperature (for at least 5 cycles) at a very low rate (~C/20) as "break-in" cycles. The discharge capacities given in **Table 1** represent the average of 5 cycles per cell and are also averaged over the number of cells tested for that type. The nominal (rated) cell capacity is slightly higher than the measured discharge capacity. The cells were charged and discharged at different currents ranging from 20 mA to 1.0 A using an Arbin battery cycler (model BT2042, College

Station, Texas). The charge/discharge measurements were also carried out at different temperatures and cell temperatures during tests were controlled with a Tenney Jr. temperature chamber (benchtop model, Union, New Jersey). For cell impedance measurement, a Princeton Applied Research (PAR) potentiostat (model 273A) in conjunction with a 1255 Solatron Oscillator (Model 378) was used. The impedance of the Li-ion cells was measured from 65 kHz to 0.1 Hz as a function of temperature for three different OCVs (open circuit voltages). For current pulse measurement, a PAR potentiostat/galvanostat (model 273A) was used and the voltage response was captured with a Tektronix Oscilloscope (model THS 720). The pulse data stored in the oscilloscope were transferred to a computer using a "Wavestar" program (version 1-0-3) for data processing and plotting.

Table 1 Physical characteristics and Capacities of Lithium-ion cell types

Manufacturer	Cell type and Dimensions (mm)	Rated cell capacity (mAh)	Measured discharge capacity (mAh) at C/20	Weight (g)	Volume (l)	Number of cells Tested
A&T	Cylindrical (17500)	800	750	25.98	0.0106	3
Moli	Cylindrical (18650)	1400	1380	41.08	.0168	5
Panasonic	Cylindrical (17500)	780	751	24.13	0.0090	3

RESULTS AND DISCUSSION

A typical NyQuist plot (real vs. imaginary impedance) for a fully charged (OCV = 4.1 V) A&T and Panasonic cells at -40°C is shown in **Figure 1**. It has an inductive tail in the frequency regime 65 kHz – 2.7 kHz and then a small hump followed by a larger hump. The inductive tail has been observed by others for Li-MoS_2 cells **[2]**, and in that case has been attributed to the jellyroll and/or porous electrode designs. The inductive tail in the case of these cells could also be due to a similar design feature. The first smaller impedance hump in **Figure 1** appears to be due to both the cathode and anode electrolyte interfaces and the second loop mainly to the cathode electrolyte interface based on our three electrode measurements. The ohmic cell resistance (high frequency x-axis intercept), which includes electrolyte resistance and other resistances such as electrode bulk resistance, separator resistance, etc., in series with it, is small (~ 0.08 Ω). However, the overall cell impedance including ohmic resistance, cathode electrolyte R_{ct}, (chrage transfer resistance) and anode electrolyte R_{ct} is higher (several Ohms). It is clear from **Figure 1** that the contribution to the cell impedance from the electrode electrolyte interface is nontrivial. The implication of this observation is that there is room to improve the power output of the cell further by optimizing the anode and cathode electrolyte interfaces to reduce the interfacial resistance. Similar impedance behavior was observed for the Moli cells.

We carried out three electrode studies (a lithium reference electrode was introduced into a open cell) and studied the impedances of the individual electrodes (anode and cathode). In **Figure 2** is given the total cell impedance and the cell impedances of the cathode and anode at -20°C in the form of NyQuist plots. The plots indicate that the cathode electrolyte interface is more resistive than the anode electrolyte interface. In **Figure 3** is given a typical charge discharge curve for the A&T cell. The cell was charged at 50 mA to 4.1 V and discharged at 100 mA to 3.0 V. The Faradaic efficiency (charge in/charge out) is close to one indicating the absence of parasitic side reaction. Similar behavior was observed for the Moli and Panasonic cells.

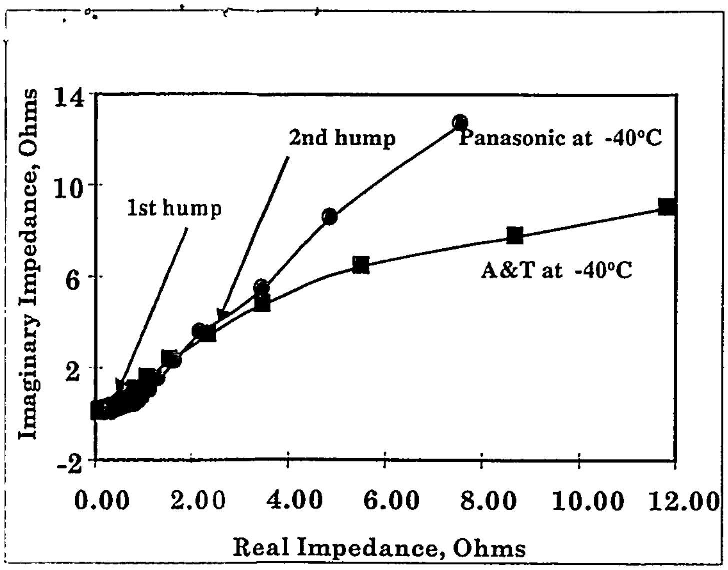

Figure 1. NyQuist plots for Panasonic and A&T Cells at -40C

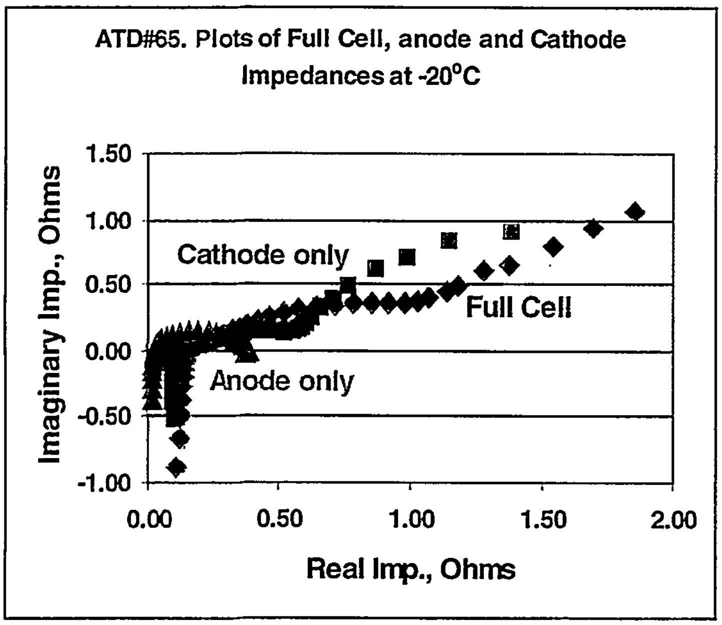

Figure 2. Plots of Full cell, anode and cathode impedances for a Sony Cell at -20C.

Delivered energy and power of the cells were computed from the discharge curves at different rates and the Ragone plots [3] {normalized energy and power for weight (specific power and energy) and volume (energy and power density)} are given in **Figures 4 and 5** for the cells at different temperatures. At room temperature, the cells perform very well. However, at lower temperatures,the performance is poor with practically no energy delivered at -40°C. Our three

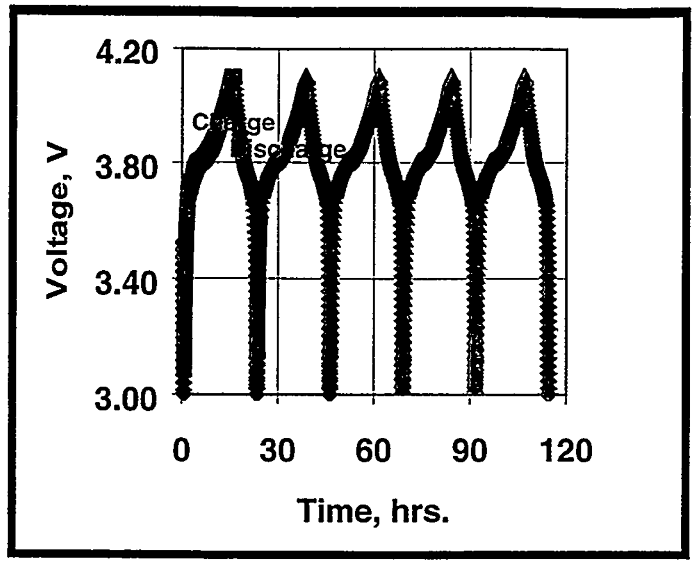

Figure 3. Charge (50 mA)/Discharge(100 mA) cycles for A&T Cell at Room Temperature.

electrode impedance data suggests that the cathode electrolyte interface may be responsible for the poor performance at lower temperatures.

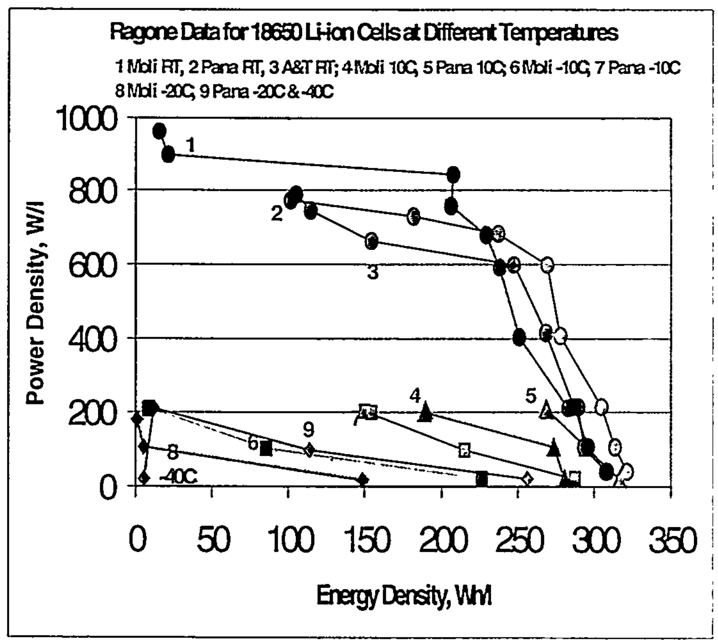

Figure 4. Power Density vs. Energy Density for the Cells.

CONCLUSION

We have studied the electrochemical performance characteristics of Li-ion cells from three manufacturers. At ambient temperature all the cells perform well. However, at subambient temperatures, the performance is very poor with almost no energy delivered at -40°C. The poor

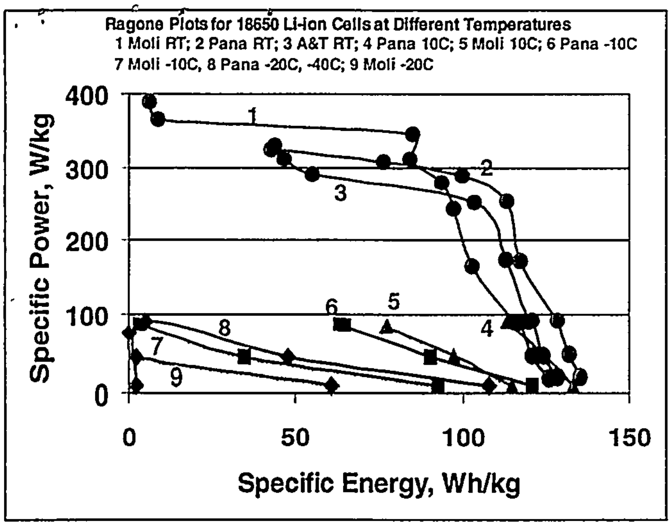

Figure 5. Specific Energy vs. Specific Power for the Cells.

performance is associated with the high impedance of the cathode electrolyte interface. The electrolyte resistance is constant between room temperature and -20°C.

ACKNOWLEDGMENT

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000. I am grateful to D. R. Bradley and H. L. Case for performing the electrochemical measurements.

REFERENCES

[1] G. Nagasubramanian, R. J. Jungst , J. Power Sources 72, 189-193(1998).

[2] F. C. Laman, M. W. Matsen, and J. A. R. Stiles, J. *Electrochemical Soc.,* **133,** 2441(1986).

[3] D. Ragone, in Proc. Soc. Automotive Engineers Conference, Detroit, MI., May (1968).