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Energy and Power Characteristics of Li-ion Cells

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Abstract

At Sandia National Laboratories we are evaluating the energy and power characteristics of commercially available Li-ion cells. Cells of several different sizes (20 Ah, 1.1 Ah, 0.750 Ah and ~0.5 Ah) and geometries (cylindrical and prismatic) from several manufacturers were studied. The cells were pulsed discharged at increasing currents (50 mA to 1000 mA) over a range of temperatures (+35°C to -40°C) and at different states of charge (4.1 V, open circuit voltage, fully charged, 3.6 V OCV partially discharged and 3.1 V OCV nearly discharged) and the voltage drop was recorded. The voltage drop was small at ambient and near ambient temperatures indicating that the total cell internal impedance was small under these conditions. However, at -40°C the voltage drop was significant due to an increase in the cell internal impedance. At a given temperature, the voltage drop increases with decreasing state-of-charge (SOC) or OCV. The cell impedance and other electrochemical properties as a function of temperature and SOC were also measured. The Ragone data indicate that the specific power and specific energy of Li-ion cells of different sizes are comparable and therefore scaling-up to ~20 Ah does not affect either the energy or the power.

Introduction

Ever since Sony Energytec, Inc.¹ introduced the first commercial lithium-ion cell in 1991, the lithium-ion rechargeable battery market has been increasing at an accelerating rate. The Sony cell is based on the rocking-chair lithium-intercalation concept and is composed of a lithiated carbon anode, a $Li_{1-x}CoO_2$ cathode and a nonaqueous electrolyte. Other manufacturers are now producing cells with variations of the same basic chemistry. These batteries can store 2-3 times

more energy per unit weight and volume than conventional technologies (lead-acid, nickel/cadmium). Because of the high energy (~100 Wh/kg; ~240 Wh/l), lithium-ion batteries are finding widespread use in a variety of devices including computers, cellular phones, power tools, implantable medical devices, etc., and are being proposed for use in military, space, and electric-vehicle applications, all of which have unique requirements. For example, computers and power tools may need short bursts of high power, whereas implantable devices (e.g. pacemakers) may require low power levels for a long period of time. When evaluating battery suitability for such unique applications, one needs to know a variety of battery characteristics, including the relationship between energy and power (Ragone plot), cell impedance as a function of temperature, pulse discharge capability as a function of both temperature and load, charge/discharge characteristics, and other electrochemical properties. However, no published data are available on the energy and power characteristics of Li-ion cells.

Large capacity (> 20 Ah) Li-ion cells are currently being tested and evaluated for military and space applications. To our knowledge, there are no published data available in the literature showing whether the power and energy per unit weight and volume of the large-capacity cells are comparable to those of the smaller-capacity cells. To fill this deficiency the study described in this paper was conducted to characterize the electrical performance of a wide range of commercial Li-ion cells of different sizes.

Experimental

Before welding tabs to the cells for electrical connections, both their weights and physical dimensions were measured. A Princeton Applied Research electrochemical impedance spectroscopy

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instrumentation and software (Model 273A potentiostat, FRA 1255 and M398 software) were used to collect impedance and pulse discharge data, and an Arbin battery cycler (Model BT2042) was used to cycle the smaller- capacity cells either galvanostatically or potentiostatically. A Maccor Series 2000 battery tester was used to cycle the large capacity cells. Cell temperatures during tests were controlled with a Tenney Jr. temperature chamber (benchtop model). The energy and power were computed from the discharge data as follows. To obtain energy, the voltage at each of the more than 2000 data points collected for every discharge curve is multiplied by the product of the discharge current and the time step before the voltage reading. These results are summed to give the total delivered discharge energy. For discharge power, the voltage is multiplied by the discharge current, and the results are summed over the number of points and averaged over the number of points calculated for the complete discharge curve. The Li-ion cells evaluated in this study along with the rated capacity and size are listed in Table-1. The rated capacity of the newest 18650 cylindrical cells has been increased to ~ 1500 mAh².

Table 1. Li-ion cells investigated

Four different sizes: cylindrical 18650 and 17500 cylindrical: 89x64 mm and prismatic: 48.2x25.4 x 7.6 mm
 Manufacturers: A&T, Bluestar, Panasonic, Polystor, Sanyo, and Sony
 Cylindrical cells 18650: Polystor, Sanyo and Sony; 17500: A&T and Panasonic; 8964: Bluestar
 Prismatic: Sanyo

Rated capacity of the cells:

Prismatic: ~500 mAh
 Cylindrical 18650: >1000 mAh
 Cylindrical 17500: ~750 mAh
 Cylindrical Bluestar: ~20 Ah

Charge/Discharge Scheme of a Li-ion Cell

In Figure 1 are shown the schematics of charge and discharge reactions for a Li-ion cell. Lithiated carbon and cobalt oxide, are used in the example as anode and cathode, respectively. During discharge, Li⁺ leaves the anode and intercalates into the cathode matrix and during charge the reverse process occurs. Since metallic lithium is not involved in either of the processes, these cells

are potentially safer than rechargeable cells with metallic lithium as the anode because of dendrite formation.

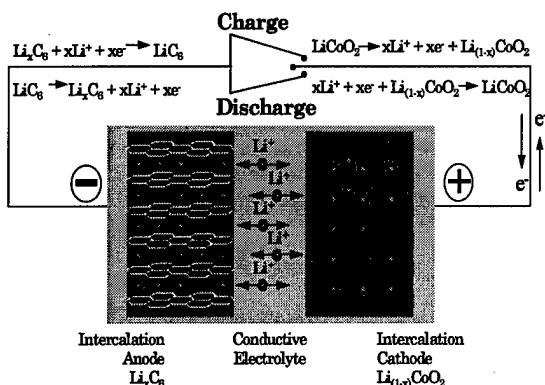


Figure 1: Schematic representation of a rocking-chair lithium-ion rechargeable battery

Results and Discussion

Impedance Measurement- In Figure 2, is shown the ohmic resistance of A & T and Panasonic Li-ion cells for the temperature range from +35°C to -40°C and for three state of charges (4.1, 3.6 and 3.1 V). The ohmic resistance is almost constant from 35°C to -20°C and increases at -40°C by 2 times for the Panasonic cells and by 1.5 times for the A&T cells. Further, the resistance is nearly constant with OCV. Similar results were obtained for the other cells.

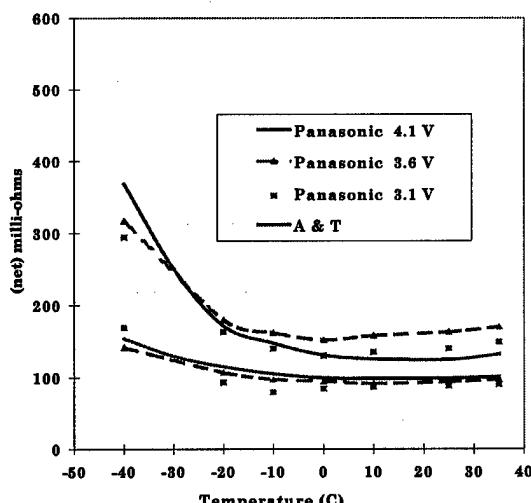


Figure 2: Ohmic resistance of Li-ion cells as a function of temperature and OCV.

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Pulse Discharge- The cells were pulsed at increasing currents (50 mA to 1000 mA) both as a function of temperature and OCV and the voltage drop was measured. In Figures 3 & 4 are given the voltage drop for different current pulses at 25°C and at -10°C respectively for A&T, Panasonic, Polystor and Sanyo cells.

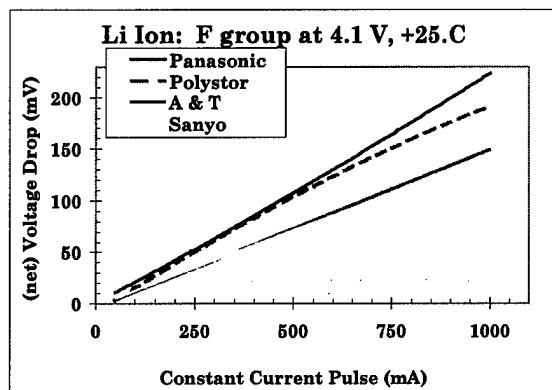


Figure 3: Voltage drop vs. pulse current at room temperature.

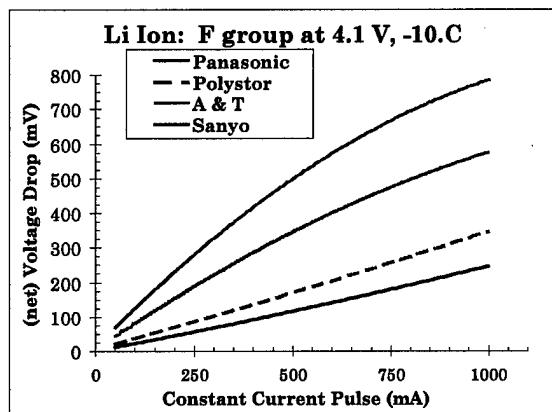


Figure 4: Voltage drop vs. pulse current at -10°C.

The voltage drop at both temperatures increases with increasing current pulse. At 25°C the voltage drop increases nearly linearly for all the four cells. However, at -10°C only Sanyo and Polystor show a linear increase, while for A&T and Panasonic the increase in voltage drop is nonlinear. This suggests that the influence of the interfacial charge transfer resistance (R_{ct}) is nontrivial. The voltage drop is higher at -10°C than at 25°C although the resistance data shown in Figure 2 doesn't indicate this behavior. Additional data on the impedance

behavior are being collected to elucidate this effect.

Charge/Discharge Characteristics- The charge /discharge characteristics of the cells were measured for increasing currents from 20 mA to 1 A for the smaller capacity cells and from 2 A to 20 A for the large capacity Bluestar cells. In Figures 5, 6 and 7 are shown the charge discharge curves for A&T cells at room temperature and for Bluestar cells at room temperature and at 0°C respectively. The A&T cells were charged at 50 mA and discharged at 100 mA. The Bluestar cells were charged at 2 A and discharged at 2 or 4 A. The charge and discharge curves are symmetrical, which indicates that the coulombic efficiency (charge in/charge out) is equal to one.

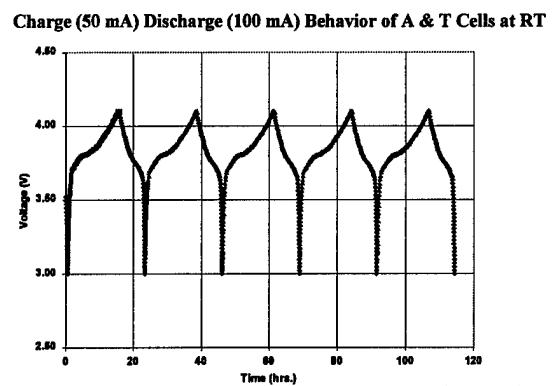


Figure 5: Charge/Discharge curves for A&T cells at room temperature. Charge and discharge currents are shown above.

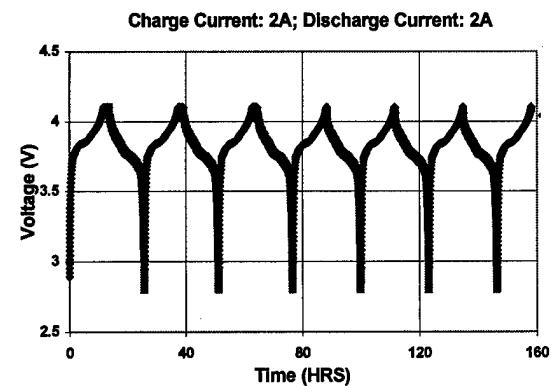


Figure 6: Charge/Discharge curves for Bluestar cells at room temperature. Charge and discharge currents are shown above.

Charge (2A) Discharge (4A) Behavior of Bluestar Cells at 0°C

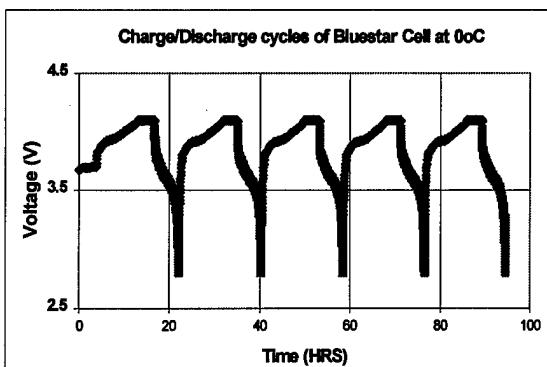


Figure 7: Charge/Discharge curves for Bluestar cells at 0°C. Charge and discharge currents 2A and 4A, respectively.

Such a high coulombic efficiency indicates the absence of parasitic side reactions and that Li^+ intercalation and deintercalation in the cathode and anode are the only Faradaic reactions that are occurring in the cell.

Power and energy were computed from the discharge curve as described in the experimental section. These were then normalized to unit weight and volume of the cell and are plotted as Ragone data.

Ragone Data- Ragone plots relating power/density to achievable energy/density have been used for many years as an empirical basis for comparative performance evaluations of various battery systems since being first announced in 1968 by Ragone³. In figure 8 is shown the specific power vs. specific energy for the different cells tested including Bluestar, A&T and Panasonic and others. Each data point represents the average of 5 discharge tests per cell and is also averaged over the number of cells tested for that type (see Table 1). The reproducibility of the results was very good and standard deviations are within 1%.

The plot indicates that the performance of the Bluestar cell is comparable to that of the A&T and Panasonic cells. This suggests that the scaling up from ~1 Ah to 20 Ah doesn't reduce either the specific power or the specific energy.

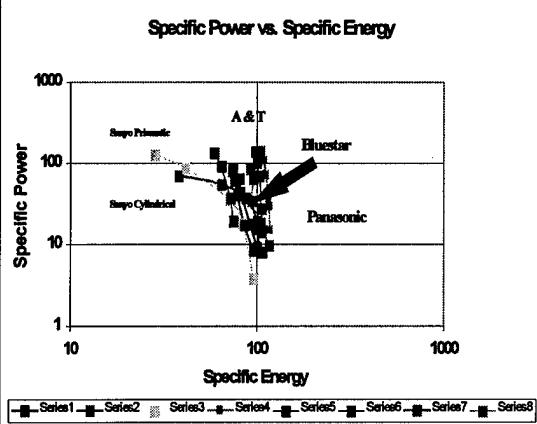


Figure 8: Specific Power vs. Specific Energy for different cells.

Conclusions

Electrochemical properties of several Li-ion cell types ranging in capacity from 0.5 Ah to 20.0 Ah have been studied. The cell Ohmic resistance is nearly constant between 35°C and -20°C and at -40°C increases by ~2 times. These cells can be pulsed at very high currents (up to 1 A) at ambient and subambient temperatures down to -10°C. Also, these cells possess a favorable combination of energy and power. The A & T and Panasonic cells show little reduction in energy at powers up to ~140 W/kg. The specific energy and specific power of 20 Ah cell are comparable to that of the smaller capacity cells indicating that scaling-up doesn't affect the energy and power characteristics.

Acknowledgment

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