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Electrochemical Characteristics of Lithium-Ion Cells

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Abstract

We describe below the electrochemical performance characteristics, including charge/discharge characteristics at different rates, of cylindrical 18650 (18 mm diameter, 65 mm high) and prismatic lithium-ion cells at ambient and sub-ambient temperatures. Ragone plots of power and energy data for these cells are compared and indicate that at room temperature the prismatic lithium-ion cells (~500 mAh) exhibit higher specific power and power density than the 18650 cells (~1100 mAh). The cell impedance was measured between 35°C and -40°C at three open circuit voltages: 4.1 v (fully-charged), 3.6 v (partially-discharged), and 3.1 v (almost completely discharged). Over the temperature range from 35°C to -20°C, the cell impedance is nearly constant for both cell types and increases by 2 to 3 times at -40°C. The impedance doesn't vary significantly with open circuit voltage (OCV). These cells show very little voltage drop at room temperature for current pulses up to 1 A. The charge/discharge characteristics of the cells are being studied at different rates as a function of temperature to compute the power, energy, and capacity outputs. This will not only broaden our database on lithium-ion cells, but will also allow us to evaluate the suitability of the cells as power sources for low-temperature applications. Other electrochemical characteristics of these cells including pulse response are being evaluated. Impedance measurements of the cells under load are planned to make meaningful correlations between the voltage drop and the current pulse amplitude.

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1. Introduction

A highly reliable rechargeable battery of high power and energy is critically needed for a variety of new and exciting technologies. In principle, a high voltage and high specific energy is achievable in a battery by using a low equivalent weight electropositive element. Because of its low equivalent weight (6.941) and high electrochemical standard potential (-3.038 V vs. the standard hydrogen electrode) lithium metal is an attractive material for high energy density batteries. The low equivalent weight results in a specific capacity of 3.8 Ah/g compared to other anode materials like lead (0.26 Ah/g) and the high electrochemical standard potential yields higher cell voltage (~4.1 V) compared to other batteries like Ni-MH (1.2 V).

The commercialization of lithium primary batteries was achieved fairly quickly in the 1960s and 1970s. However, the development of lithium rechargeable batteries was much slower because of the safety problem during cell failure caused by lithium dendrite¹ formation and aggravated by the reaction of high-area lithium powders formed by cycling. To overcome this problem, several possible alternatives to metallic lithium have been studied², but with very little success. However, a promising material based on carbon as an alternative to metallic lithium and lithium alloys has been proposed earlier³. This involves an innovative design, (called rocking-chair or shuttlecock) in which lithium ions shuttle between the anode and the cathode. In **Figure 1** is shown a schematic representation of a lithium-ion rechargeable battery under charge/discharge. During discharge lithium ions move from the anode into the cathode, and during charge lithium ions move from the cathode into the anode. The voltage of the lithiated anode is very close to that of metallic lithium (within +10 mV) and hence the cell voltage is not reduced by much. Because lithium ions shuttle between the anode and cathode, there is no deposition of metallic lithium on the anode surface in this design as in the case of lithium metal rechargeable batteries and lithium-ion batteries are therefore very safe.

The rocking-chair concept was incorporated and developed by Sony to produce the first so called lithium-ion cells for commercial applications⁴. Ever since Sony Energytec, Inc. introduced the first commercial lithium-ion cell in 1991, the lithium-ion battery market has been burgeoning at an unprecedented rate. For example, Sony announced plans to increase production of lithium-ion batteries to 15 million/month in the 1997 fiscal year, and as high as 30 million/month thereafter⁴. The Sony cell is composed of a lithiated carbon anode, a $\text{Li}_{1-x}\text{CoO}_2$

cathode and a nonaqueous electrolyte. Other manufacturers are producing cells with variations of the same basic chemistry.

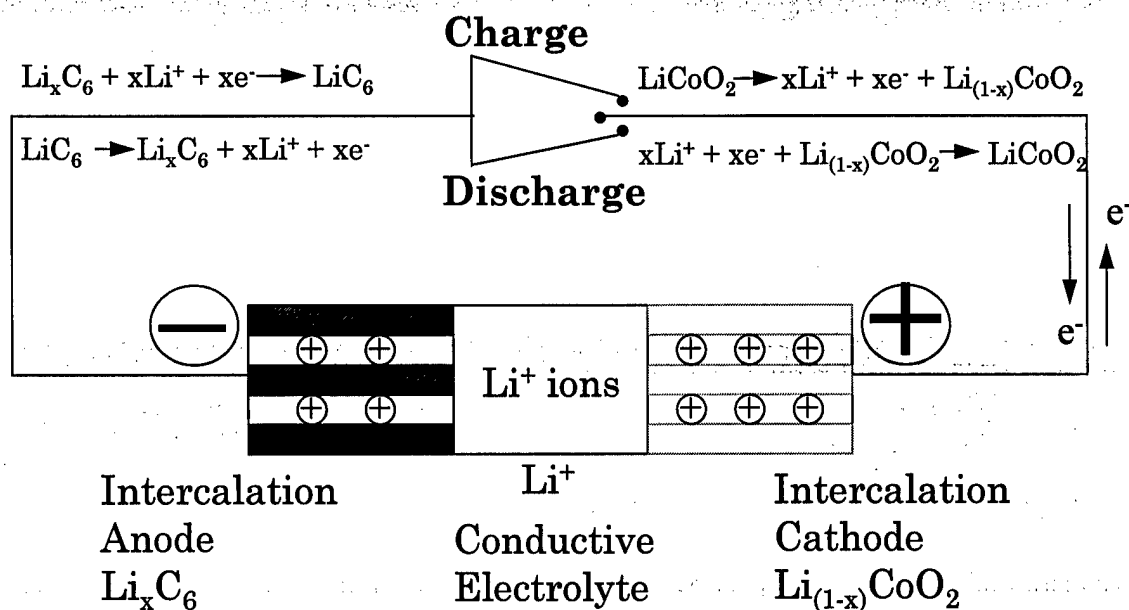


Figure 1. Schematic representation of a rocking-chair lithium-ion rechargeable battery.

These batteries can store three 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 very specific and different sets of unique performance requirements. For example, computers and power tools may need short bursts of high power, whereas implantable devices may require low current (power) 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 energy/power relationship (Ragone plot), cell impedance as a function of temperature, pulse discharge capability as a function of both temperature and load, and charge/discharge characteristics. A thorough and systematic investigation of all these characteristics is not, to our knowledge, currently available in the literature. This paper describes measurements of some of the lithium-ion battery characteristics listed above. Lithium-ion cells of two different designs and capacities

(cylindrical, ~1100 mAh and prismatic, ~500 mAh) from two different manufacturers have been electrochemically evaluated and their properties are compared.

2. Experimental

Two types of cells were investigated in this study. Cell 1 and Cell 2 are cylindrical (18 mm dia. and 65 mm high) and cell 3 is prismatic (48.26 mm long, 25.4 mm wide and 7.62 mm thick). Before welding tabs to the cells for electrical connections, both their weights and physical dimensions were measured. These weights and the computed cell volumes are listed in Table 1. A Princeton Applied Research impedance unit (Model 398, Princeton, New Jersey) was used to collect impedance and pulse discharge data, and an Arbin battery cycler (Model BT2042, College Station, Texas) was used to cycle the cells either galvanostatically (charge/discharge currents) or potentiostatically. Cell temperatures during tests were controlled with a Tenney Jr. temperature chamber (benchtop model, Union, New Jersey). For pulse measurements a Princeton Applied Research 273A potentiostat in conjunction with a Tektronix Oscilloscope (Model # THS 720) was used. The pulse data stored in the oscilloscope were then transferred to a computer using the "Wavestar" program version 1-0-3 for further analysis.

3. Results and Discussion

In Table 1, the type and number of cells used in this study are given along with their respective weights and calculated volumes.

Table-1 Lithium-Ion Cell Types and Physical Dimensions

| Cell Type | Number Tested | Weight (g) | Volume (l) |
|---------------------------------------|---------------|------------|------------|
| Cylindrical, Manufacturer A, (cell 1) | 5 | 40.14 | 0.0171 |
| Cylindrical, Manufacturer B, (cell 2) | 1 | 46.46 | 0.0202 |
| Prismatic, Manufacturer B, (cell 3) | 2 | 20.03 | 0.0093 |

3.1 Charge/Discharge Characteristics

The charge/discharge studies were done only at room temperature. Typical charge/discharge behavior of cell types 1, 2 and 3 are shown in Figures 2, 3 and 4, respectively. The cells were charged at 50- 200 mA and discharged at 100-500 mA, and even after 80 cycles (not shown in the Figures) the capacity remains practically constant. A coulombic efficiency (charge out/charge in) of ~1 was calculated. This, along with a constant cell capacity with cycling, indicates that lithium ions cycle reversibly between the anode and cathode without any apparent

parasitic side reactions. Charge/discharge studies at subambient temperatures will be initiated in future experiments.

In all three cases, the discharge voltage cutoff used was 3.0 V and the charge voltage cutoff was 4.15 V (cell 1) or 4.10 V (cells 2 and 3). For cells 2 and 3, the charge/discharge results were identical even if the charge voltage cutoff was increased from 4.1 V to 4.15 V. In order to minimize possible detrimental effects on cycle life that might arise at higher voltages, the charge voltage limit was maintained at 4.1 V for these two cell types. In contrast, cell 1 gave a lower capacity with a 4.1 V charge voltage cutoff and therefore 4.15 V was deemed more appropriate in that case.

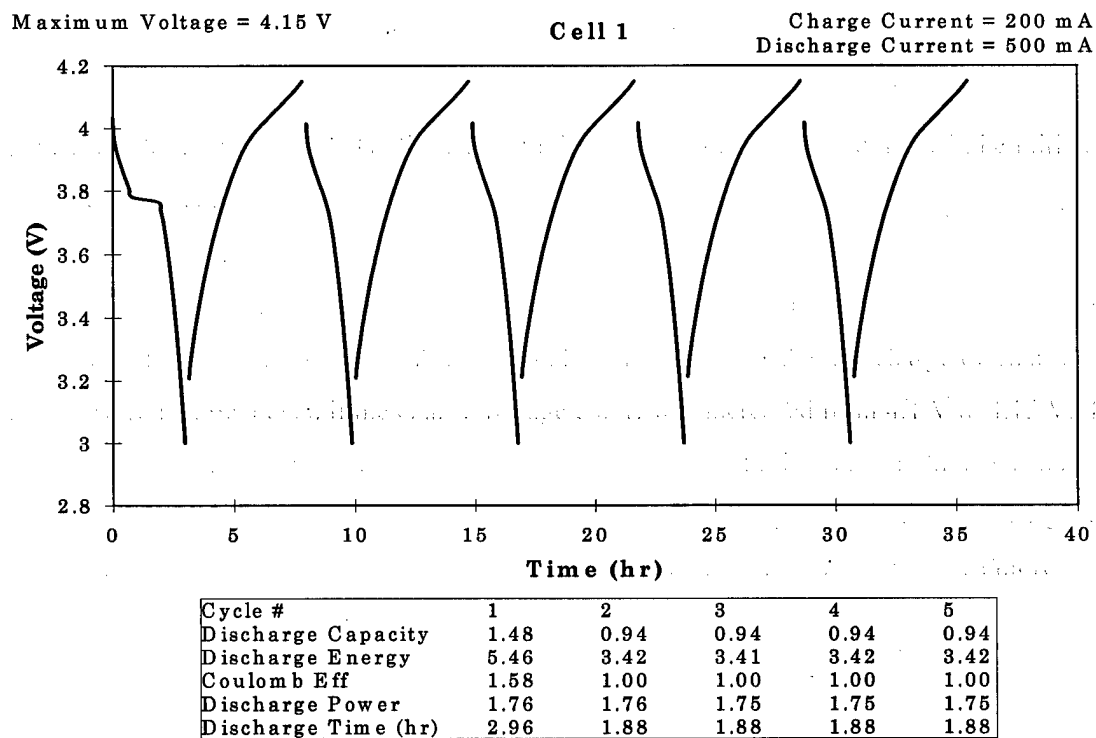
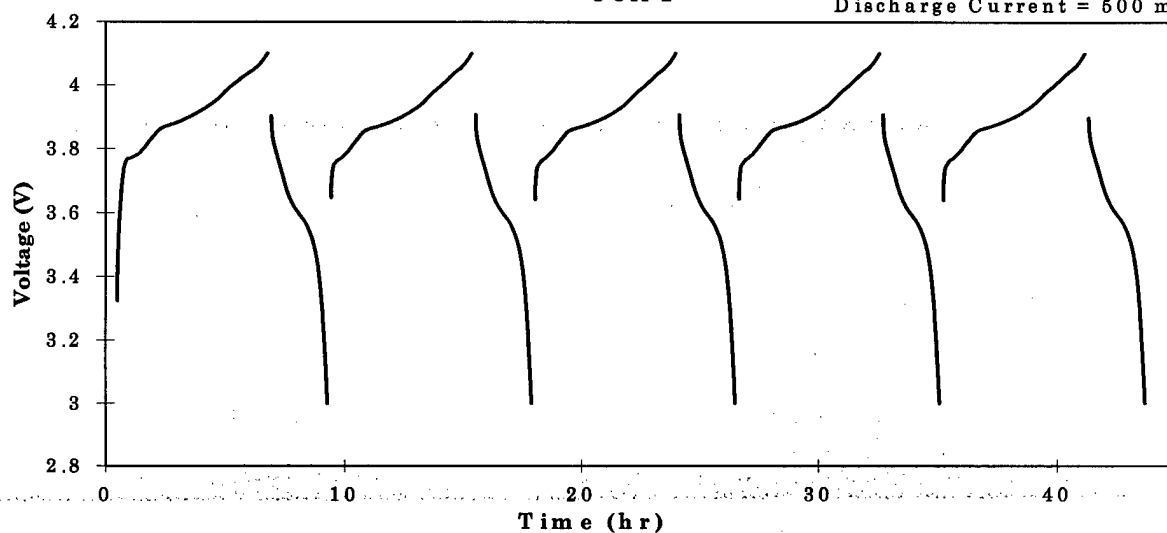


Figure 2. Charge/discharge characteristics of cell 1 at room temperature. Charge current = 200 mA, discharge current = 500 mA. The table shows the coulombic efficiency as a function of cycle # along with power and energy values.

Maximum Voltage = 4.10 V

Cell 2

Charge Current = 200 mA
Discharge Current = 500 mA



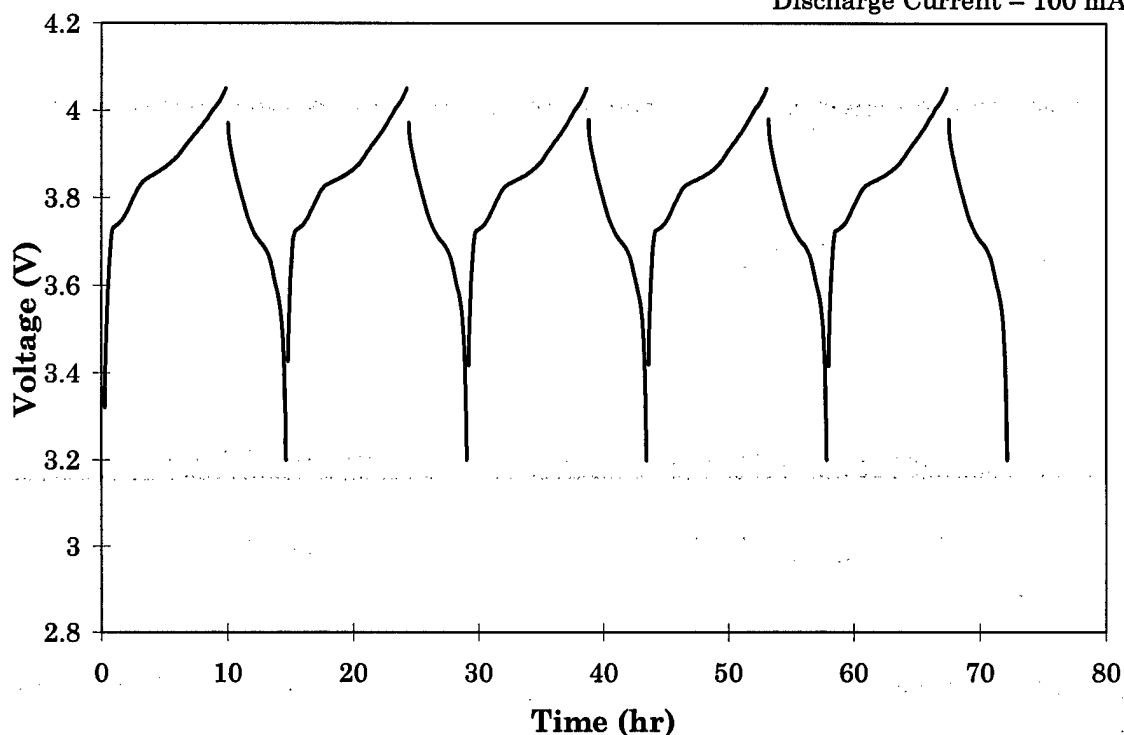
| Cycle # | 1 | 2 | 3 | 4 | 5 |
|--------------------|------|------|------|------|------|
| Discharge Capacity | 1.21 | 1.18 | 1.18 | 1.18 | 1.18 |
| Discharge Energy | 4.30 | 4.22 | 4.21 | 4.21 | 4.22 |
| Coulomb Eff | 0.96 | 1.00 | 1.00 | 1.00 | 1.00 |
| Discharge Power | 1.73 | 1.73 | 1.73 | 1.73 | 1.72 |
| Discharge Time | 2.35 | 2.36 | 2.36 | 2.36 | 2.36 |

Figure 3. Charge/discharge characteristics of cell 2 at room temperature. Charge current = 200 mA, discharge current = 500 mA. The table shows the coulombic efficiency as a function of cycle # along with power and energy values.

Maximum Voltage = 4.10 V

Cell 3

Charge Current = 50 mA
Discharge Current = 100 mA



| Cycle # | 1 | 2 | 3 | 4 | 5 |
|---------------------|------|------|------|------|------|
| Discharge Capacity | 0.47 | 0.47 | 0.46 | 0.46 | 0.46 |
| Discharge Energy | 1.74 | 1.73 | 1.72 | 1.72 | 1.72 |
| Coulomb Eff | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| Discharge Power | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 |
| Discharge Time (hr) | 4.60 | 4.64 | 4.62 | 4.62 | 4.61 |

Figure 4. Charge/discharge characteristics of cell 3 at room temperature. Charge current = 50 mA, discharge current = 100 mA. The table shows the coulombic efficiency as a function of cycle # along with power and energy values.

Ragone plots for the three cells are shown in **Figure 5**. Ragone plots relating power/density to achievable energy/density have been used for many years as an empirical basis for comparative performance evaluation of various battery systems since being first announced in 1968 by Ragone⁵. In Figure 5A is given the specific power (W/kg) vs. Specific energy (Wh/kg) and in Figure 5B is given the power density (W/l) vs. energy density (Wh/l). 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 discharge currents are indicated on the Figure and vary from 20

mA at the low end to 1000 mA at the high (1000 mA was the upper limit for the Arbin tester). Two salient features emerge from the data in Figure 5A:

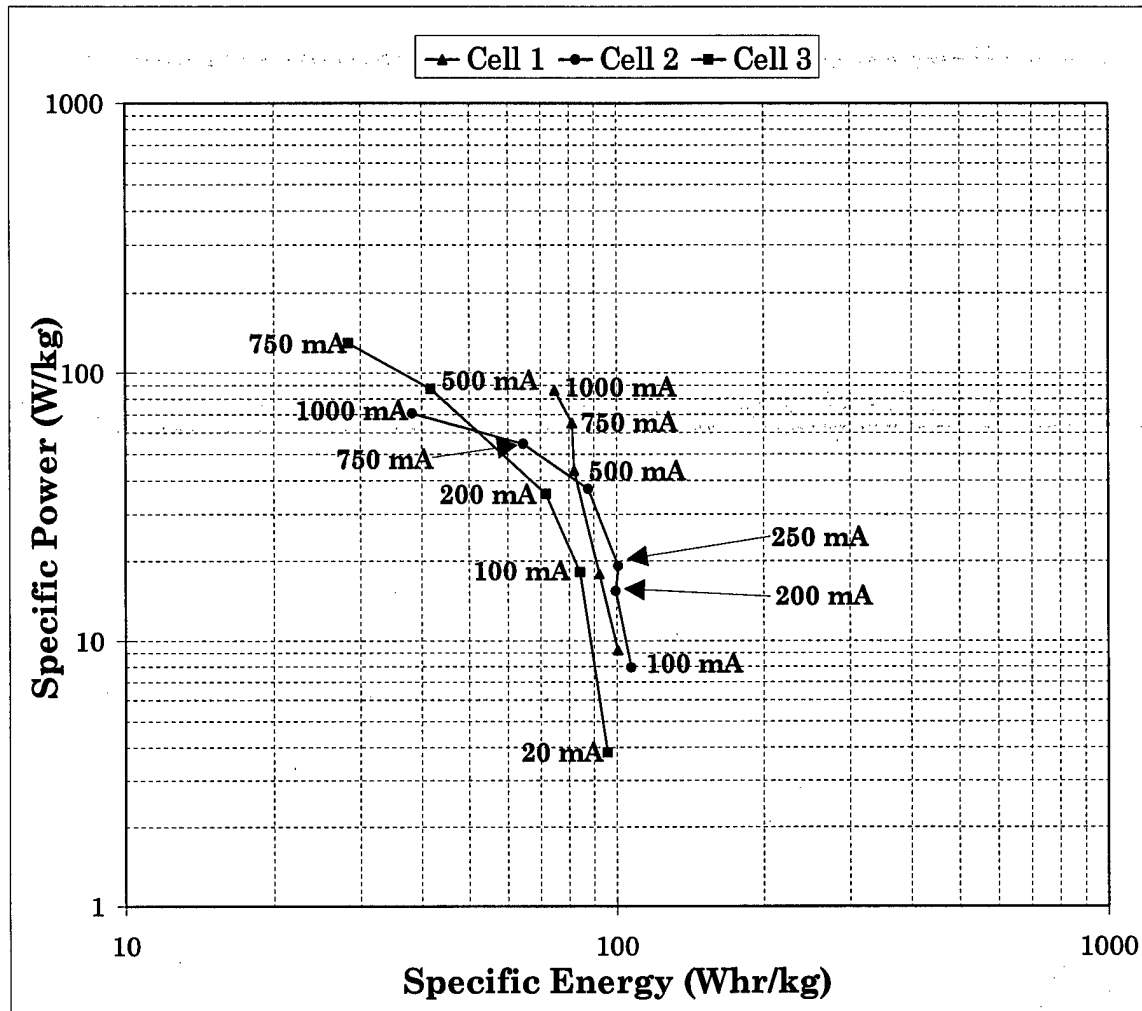


Figure 5A. Ragone plots for the three cell types. The discharge currents are indicated on the Figure.

- 1) The prismatic cell (cell 3) exhibits higher specific power and lower specific energy than the two cylindrical cells at discharge currents between 100 mA and 750 mA.
- 2) Although the specific energy for cylindrical cell 2 is marginally higher than that for cell 1 at discharge currents between 100 mA and 500 mA, at discharge currents of 750 mA and higher cylindrical cell 1 gives more specific power and energy.

The observations are essentially the same for the power and energy density (Figure 5B). These results indicate that the prismatic cell may possibly have thinner electrodes, resulting in a lower capacity (as reflected by the energy density) than the cylindrical cells. Apparently, the two

cylindrical cells (cells 1 & 2) have essentially the same internal design. The better performance of cell 1 at higher discharge currents might be related to lower cell impedance. To verify if the cell impedance controls the power output, the cell impedance was computed from a-c impedance measurements and correlated with the power delivered.

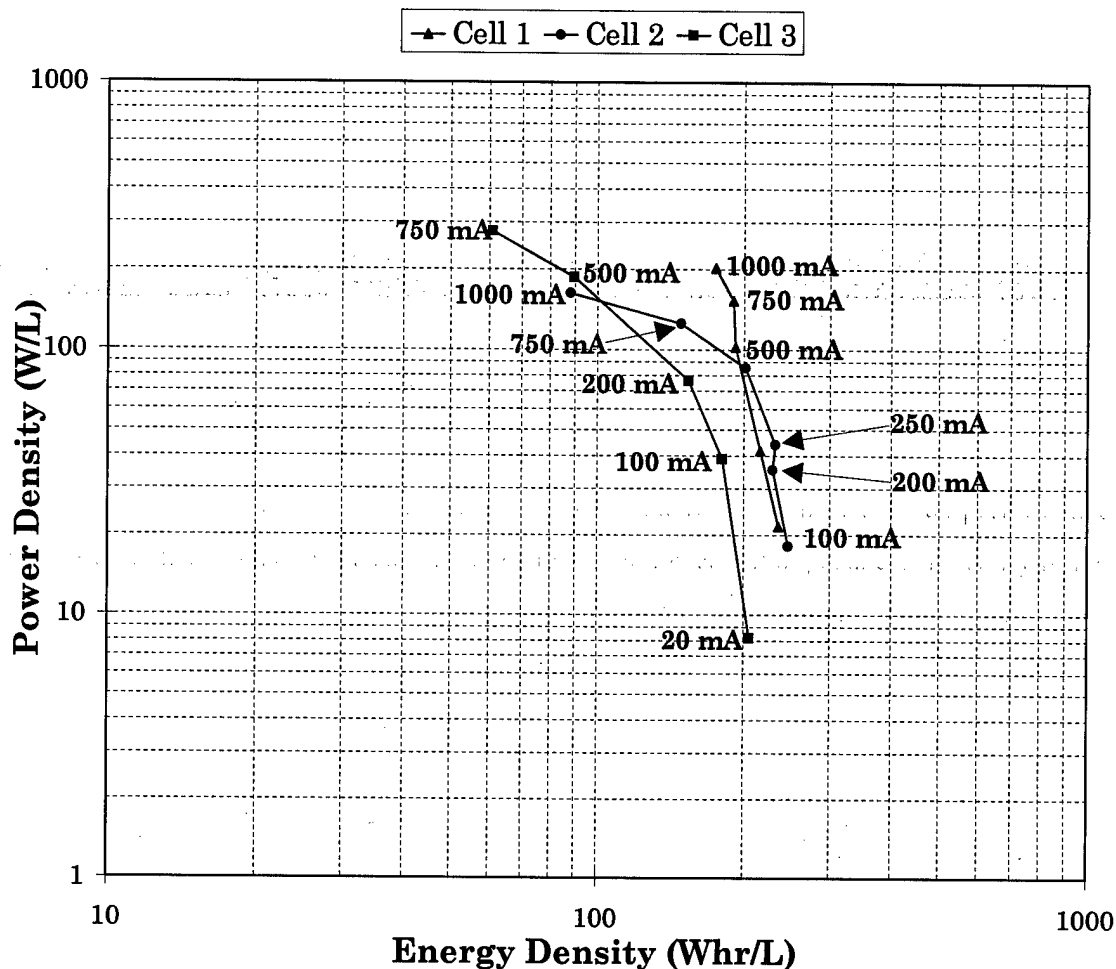


Figure 5B. Ragone plots for the three cell types. The discharge currents are indicated on the Figure.

3.2 Impedance Measurements

The impedance of the cells was measured in the frequency regime 65 kHz to 0.1 Hz at various temperatures between 35°C and -20°C. The peak-to-peak amplitude of the applied a-c signal was 1.5 mV. Typical Nyquist plots for the three cell types at room temperature are given in

Figure 6. Note the high frequency inductive behavior for the three cells. A similar observation has been made earlier for jelly-roll Li-MoS₂ cells⁶. Overall, the cell impedance is very small for all three types. In **Figure 7**, the high frequency x-intercept, which corresponds to the resistance of the electrolyte and any other series resistances such as bulk electrode resistance, is plotted as a function of temperature (35°C to -40°C) and at three open circuit voltages: 4.1 V (fully charged), 3.6 V (partially discharged), and 3.1 V (nearly fully discharged). The resistance of each cell is almost constant from 35°C to -20°C and increases by 2 to 3 times at -40°C. The cell resistance decreases in the following order: cell 3 > cell 2 > cell 1. If the internal impedance primarily governs a cell's power performance, then the cell 1 should yield more power density than cell 2 (see Figure 5B) and this is certainly observed at higher currents. It is difficult to compare the power performance of the prismatic cell (cell 3) based on cell impedance to that of the cylindrical cells due to the different cell designs. The measured power density is higher for the prismatic cell than the cylindrical cells, and the cell impedance is also higher. This is not unexpected since the prismatic cell is much smaller in size than either of the two cylindrical cells and therefore most likely contains a lower electrode area. Unfortunately, the actual electrode area is not known for any of the three cells. A more meaningful comparison of the power performance of the two types of cells could be made if the impedances of the cells under load were available. We are in the process of making impedance measurements while the cell is under load and a quantitative correlation between the delivered power and these impedance measurements will be published in a future paper. To check for any cell-to-cell variation in impedance, cell impedance data were collected on several samples of each cell. Figure 7 shows that the variation in resistance among three samples of cell 1 is very small. Cells 2 & 3 also show a similar good reproducibility.

Li Ion Cells: Nyquist Plot at +25.C

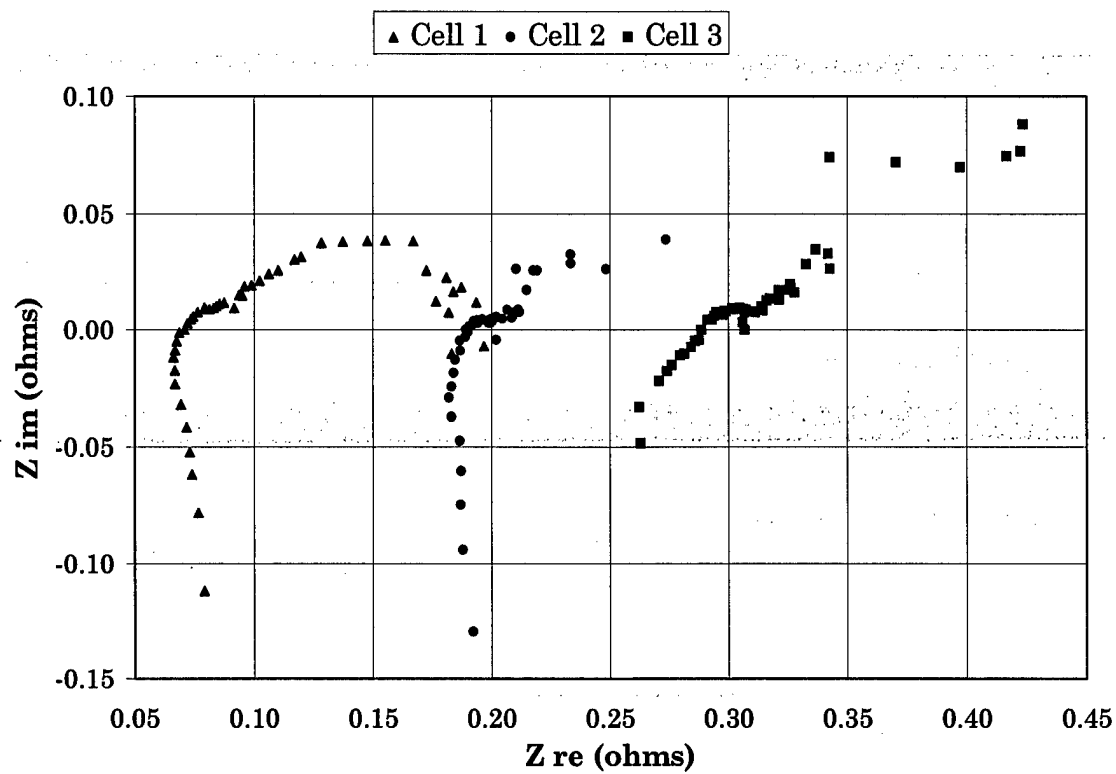


Figure 6. Nyquist plots for the three cell types. The impedance was measured at room temperature.

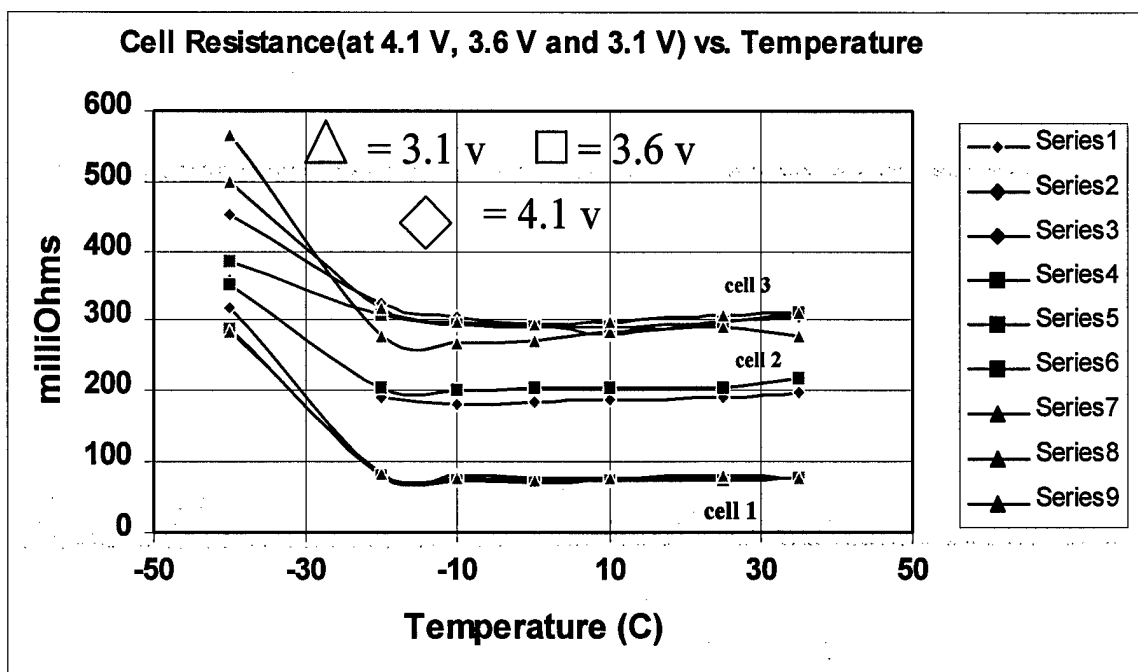


Figure 7. Cell resistance as a function of temperature and OCV

3.3 Operating Characteristics under Pulse Loads

New applications such as digital wireless communications need pulse power⁷ so that more data can be packed into the available communication spectrum. We have evaluated the pulse performance characteristics of these batteries for 1 s current pulses ranging from 50 mA to 1000 mA as a function of temperature. Figure 8A shows the voltage drops of these cells at room temperature while Figures 8B and 8C show the voltage drops of these cells at 10°C and -20°C respectively. The voltage drops for all three cells correlate with the cell resistance. For cell 2 and cell 3 the voltage drop is nearly linear with current at room temperature, indicating a constant resistance that corresponds to the internal resistance of the cell (see Figure 7). This suggests that the interfacial charge transfer resistance is low and doesn't vary with current load. Cell 1 shows a smaller voltage drop than cell 2 or cell 3, which corresponds to its lower cell resistance, and its voltage drop is not as linear with current. This nonlinearity may be related to known differences in the anode materials used by the two manufacturers. In Table 2 is summarized the voltage drops at 10°C and -20°C along with that for 25°C for different current pulses. Each data point represents the average of 6 pulses per cell and is also averaged over the number of cells tested for that type. The number of cells tested for each type are the same as given in Table-1. At 10°C and -20°C the highest pulse amplitudes tested were 500 mA and 250 mA, respectively. The cells may be capable of operating at higher currents, but we wanted to avoid any possibility of damage

at this stage of the testing. We plan to characterize the cells at higher currents and will report the results in a future paper. The voltage drops at 10°C and -20°C are also linear with current pulse amplitude, once again indicating that the contribution of the interfacial resistance to the internal cell impedance is negligible. The pulse data suggest that the lithium-ion cells can be pulsed at very high currents without significantly affecting the cell performance.

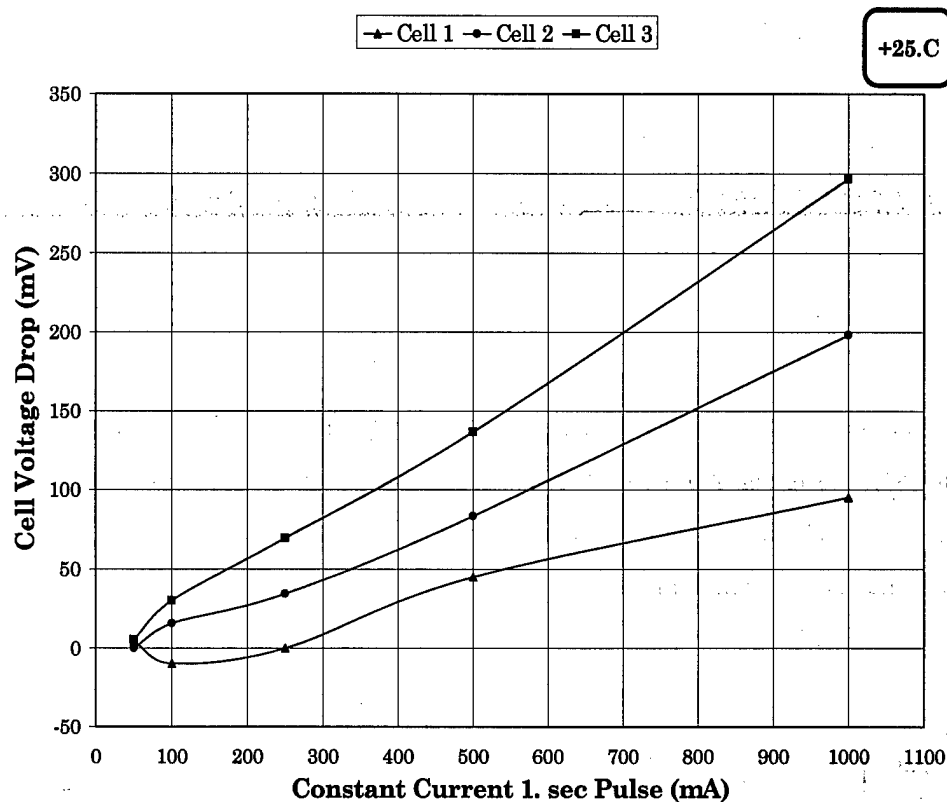


Figure 8A. Cell voltage drop at room temperature as a function of current pulse amplitude. Pulse duration = 1 sec., all cells had accumulated 80 - 100 cycles.

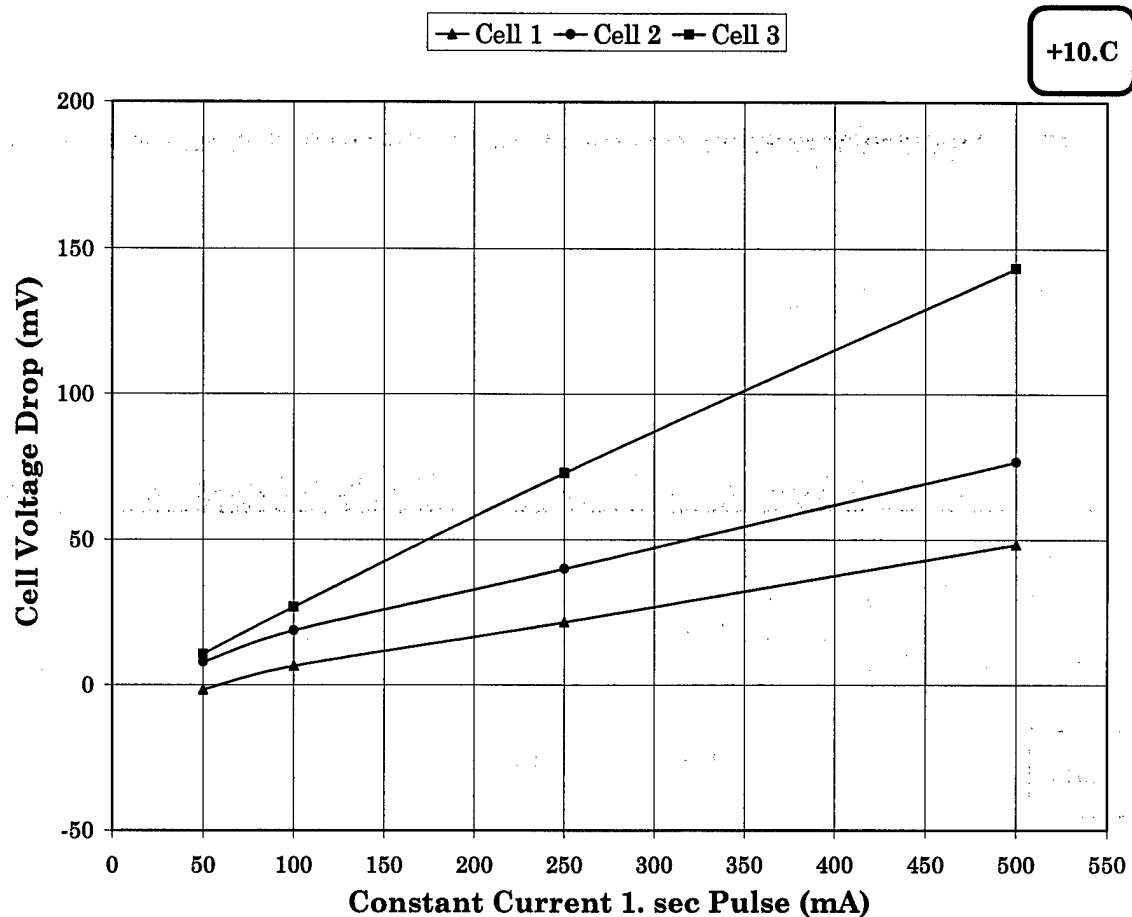


Figure 8B. Cell voltage drop at 10°C as a function of current pulse amplitude.

Pulse duration = 1 sec., all cells had accumulated 80 - 100 cycles.

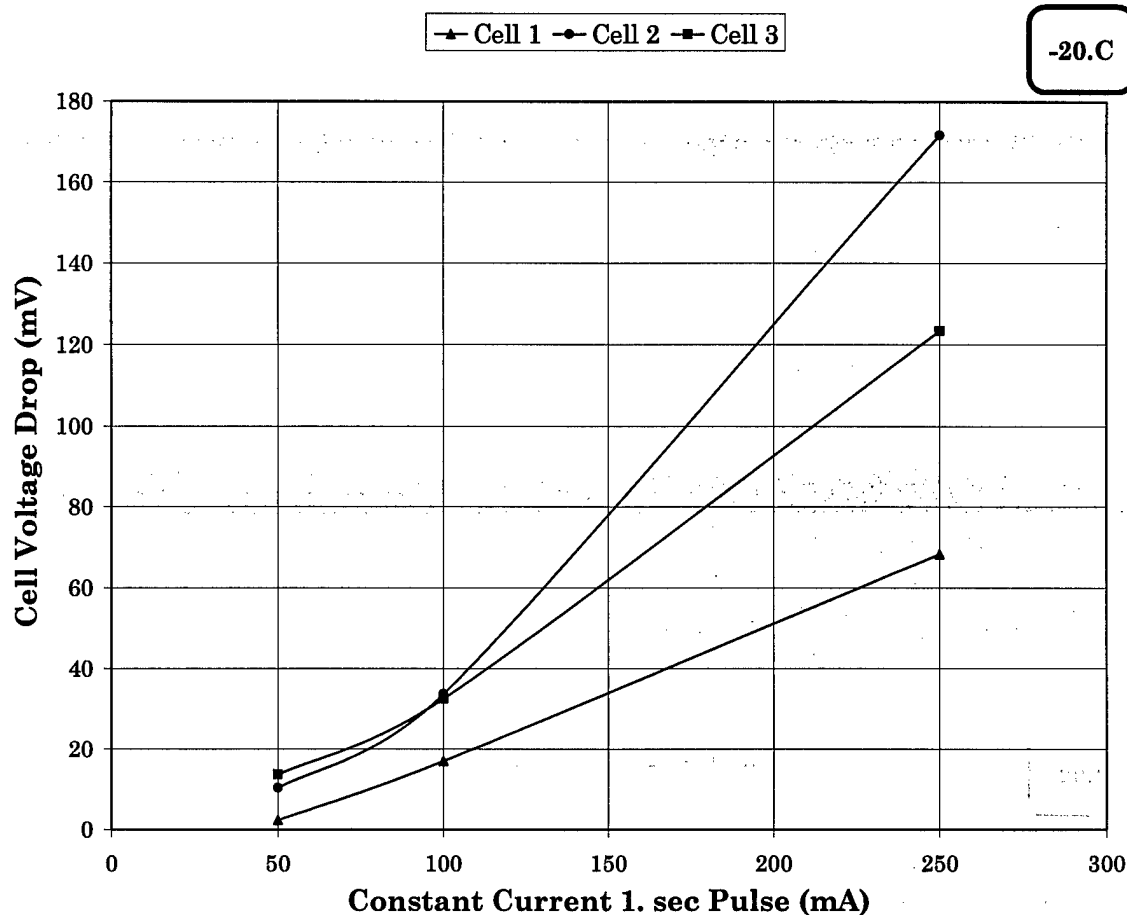


Figure 8C. Cell voltage drop at -20°C as a function of current pulse amplitude.

Pulse duration = 1 sec., all cells had accumulated 80 - 100 cycles.

Table 2 Voltage drop (mV) as a function of temperature for different 1 sec. current pulses

| Current Pulse, A | 25°C | | | 10°C | | | -20°C | | |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | cell 1 | cell 2 | cell 3 | cell 1 | cell 2 | cell 3 | cell 1 | cell 2 | cell 3 |
| 0.05 | 4.2 | 0 | 5.3 | 0 | 7.8 | 10.7 | 2.3 | 10.3 | 13.7 |
| 0.1 | ~0 | 15.7 | 30.2 | 6.5 | 18.7 | 26.8 | 17.0 | 33.7 | 32.5 |
| 0.25 | 0 | 34.5 | 69.5 | 21.7 | 40.0 | 72.8 | 68.3 | 172.0 | 123.0 |
| 0.5 | 45.0 | 83.3 | 136.7 | 48.3 | 76.7 | 143.0 | | | |
| 1.0 | 95.0 | 198.3 | 296.7 | | | | | | |

4. Summary

Electrochemical performance characteristics have been measured for cylindrical (18650) lithium-ion cells from two manufacturers and a ~ 500 mAh prismatic lithium-ion cell from one of the same manufacturers. The cells were found to have negligible capacity loss up to about 100 cycles and coulombic efficiencies during charge/discharge were very close to 1. Charge voltage cutoffs of 4.1 or 4.15 V gave maximum delivered capacities. Comparison of Ragone plots for the three cells studied showed that the prismatic cell exhibited higher specific power and power density, while the two cylindrical cells gave higher specific energy and energy density. At the higher discharge currents tested, one of the cylindrical cells displayed a better retention of high energy density than the other, and this correlates with a lower impedance for the better performing cell. In general, all of these cells showed low impedances at temperatures down to -20°C. Impedance measurements under load are planned to obtain a more meaningful comparison between the prismatic and cylindrical designs since the electrode areas are likely to differ significantly. Pulse performance characteristics of the cells were also measured as a function of temperature for current pulses ranging from 50 mA to 1 Amp. The voltage drop is nearly linear with current indicating that the contribution of the interfacial resistance to the total cell impedance is negligible. This also indicates a facile charge transfer at the electrode/electrolyte interface.

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