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Energy and power characteristics of lithium-ion cells

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Abstract

We describe below the electrochemical performance characteristics of cylindrical (18 650) and prismatic ($48.26 \times 25.4 \times 7.62$) 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 ~500 mAh prismatic lithium-ion cells exhibit higher specific power and power density than the ~1100 mAh cylindrical cells. Over the temperature range from 35 to −20°C, the cell impedance is almost constant for both cell types. These cells at 100% state-of-charge (s.o.c.) show very little voltage drop for current pulses up to 1 A. © 1998 Elsevier Science S.A.

Keywords: Lithium–ion; Ragone data

1. Introduction

Since Sony Energytec introduced the first commercial lithium-ion cell in 1991, the lithium-ion rechargeable battery market has been increasing at an accelerated rate. For example, Sony has 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 thereafter [1]. The Sony cell is based on the rocking-chair Li-intercalation concept and is composed of a lithiated carbon anode, a $Li_{1-x}CoO_2$ cathode and a nonaqueous electrolyte. Other manufacturers are 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 (pacemaker), 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 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, and charge/discharge characteristics. A thorough and systematic investigation of energy vs. power characteristics is not currently available in the literature. This short communication describes measurements of some of the lithium-ion battery characteristics listed above. Lithium-ion cells of two different sizes (1100 mAh cylindrical and ~500 mAh prismatic) from two different manufacturers were electrochemically evaluated and their characteristics compared.

2. Experimental

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. PAR electrochemical impedance spectroscopy instrumentation and software (Model 273A potentiostat, FRA 1255 and M398 software) 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, NJ). The energy and power were computed from the discharge data as follows. Every discharge curve has over 2000 points,

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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

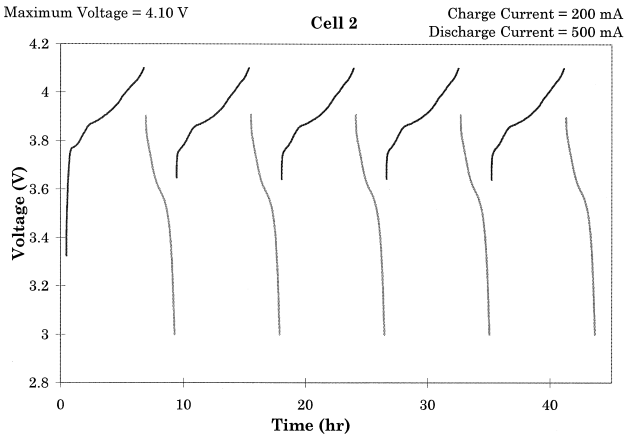
each point corresponding to a voltage. To obtain energy, each voltage is multiplied by the product of discharge current and the time before the voltage jumps to the next voltage. This procedure is repeated for each voltage, and the results are summed to give the total delivered discharge energy. For discharge power, the voltage is multiplied by the discharge current and the results are summed and averaged over the number of points.

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 volumes.

3.1. Electrical performance characteristics

The following electrical tests were done only at room temperature. Typical charge/discharge behavior of cell 2 is shown in Fig. 1. The cell was charged at 200 mA and discharged at 500 mA, and even after 80 cycles (not shown in the figure) 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. Similar results were found for cells 1 and 3. From the shapes of the discharge curves, it appears that cells 2 and 3 may have graphite anodes and cell 1 a coke anode. In all three cases, the discharge voltage cutoff used was 3.0 volts 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 effects on cycle life that might arise at higher voltages, the charge voltage limit was maintained at 4.1 V for these two cells. In contrast, cell 1 gave a lower capacity with a 4.1 V charge voltage cutoff,



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

Fig. 1. 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 number along with power and energy values.

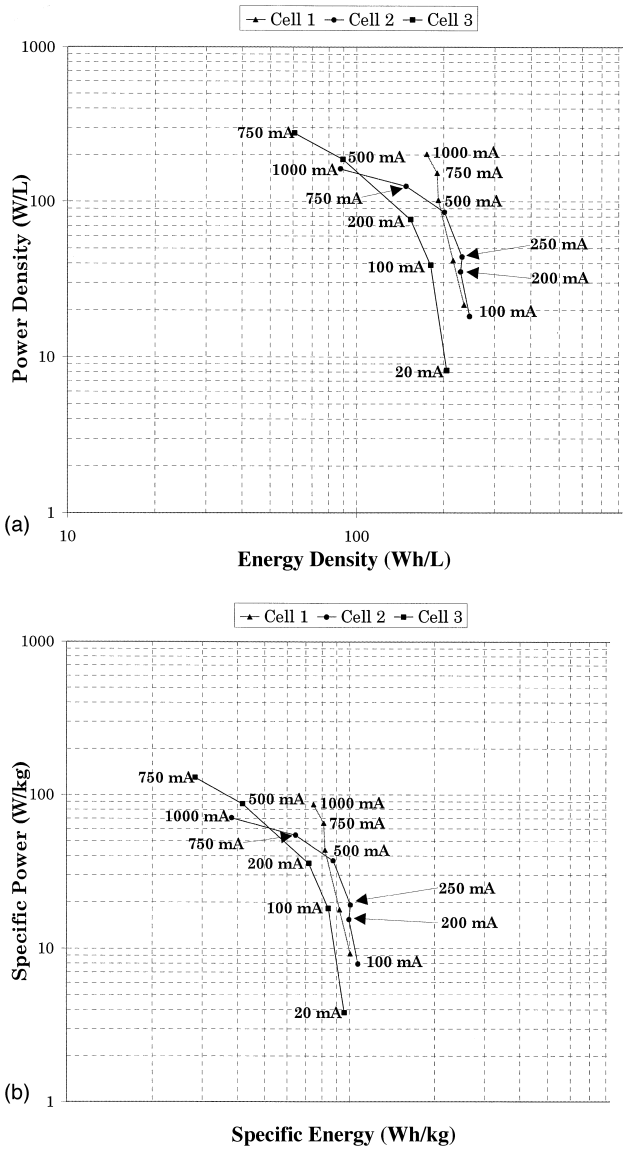


Fig. 2. Ragone plots for the three cells. The discharge currents are indicated in the figure.

and therefore 4.15 V was deemed more appropriate in that case.

Ragone plots for the three cells are shown in Fig. 2. In Fig. 2a is given the power density (W/l) versus energy density (Wh/l) and in Fig. 2b is given the specific power (W/kg) vs. specific energy (Wh/kg). 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 discharge currents are indicated on the figure and vary from 20 mA at the low end to 1000 mA at the high end. Two salient features emerge from the data in Fig. 2a.

(1) The prismatic cell (cell 3) exhibits higher power density and lower energy density than the two cylindrical cells at discharge currents between 100 mA and 750 mA.

(2) Although the energy density 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 power and energy density.

The observations are essentially the same for the specific power and energy. 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 and 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 the a.c. impedance measurements and correlated with the power delivered.

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 Fig. 3. All the three cells show an inductive behavior. This type of behavior has been observed earlier for Li/MoS_2 batteries [2]. Although there is no physical analog that corresponds to the inductive behavior in a chemical system, the inductive behavior is generally attributed to the porous electrode and/or to the jelly-roll design. Overall, the cell impedance is very small for all three types. In Fig. 4, the high-frequency *x*-intercept, which corresponds to the resistance of the electrolyte and any other series resistance such as bulk electrode resistance, is plotted as a function of temperature. The resistance of each cell is almost constant over the temperature range studied and 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 cell 1 should have a lower impedance than cell 2 (see Fig. 2). The impedance data in Fig. 4 show this trend. It is more difficult to compare the

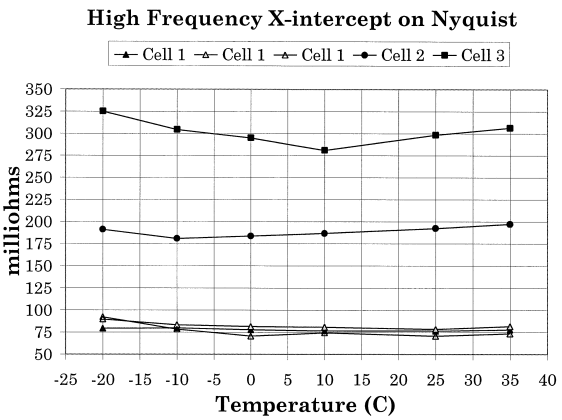


Fig. 4. Cell resistance as a function of temperature.

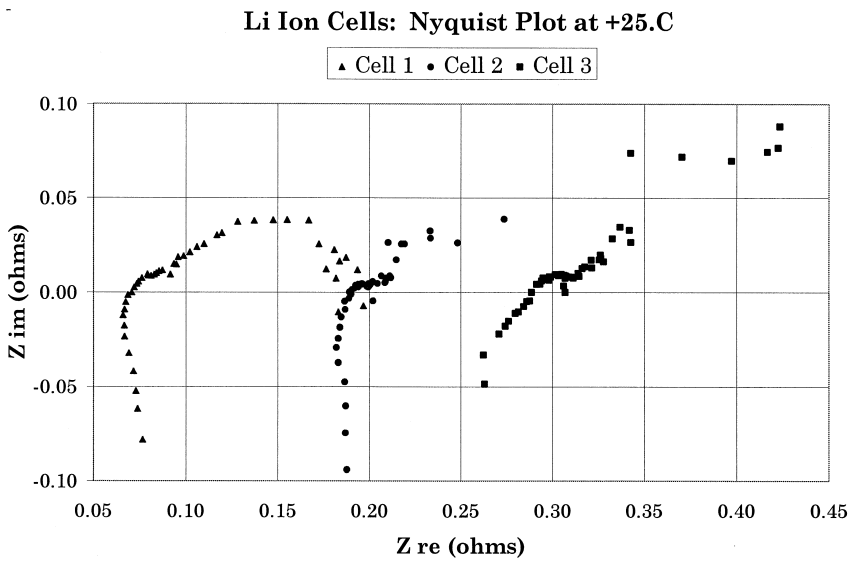


Fig. 3. Nyquist plots for the three cells. The impedance was measured at room temperature.

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, although 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 performances 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. Fig. 4 shows that the variation in resistance among three samples of cell 1 is very small. Cells 2 and 3 also show a similar good reproducibility.

3.3. Operating characteristics under pulse loads

New applications such as digital wireless communications need pulse power [3] 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. Fig. 5 shows the voltage drops of these cells at room temperature. The voltage drops for all three correlate with the cell resistance. For cell 2 and cell 3, the voltage drop is nearly linear with current, indicating a constant resistance that corresponds to the internal resistance of the cell (see Fig. 4). This suggests that the interfacial charge transfer resistance is low and does not 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, the voltage drops are summarized for 10°C, −20°C, and 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 reproducibility of the results was very good and standard deviation in many cases approaches zero. 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

Table 2
Voltage drop (mV) as a function of temperature for different 1-s 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	~6	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						

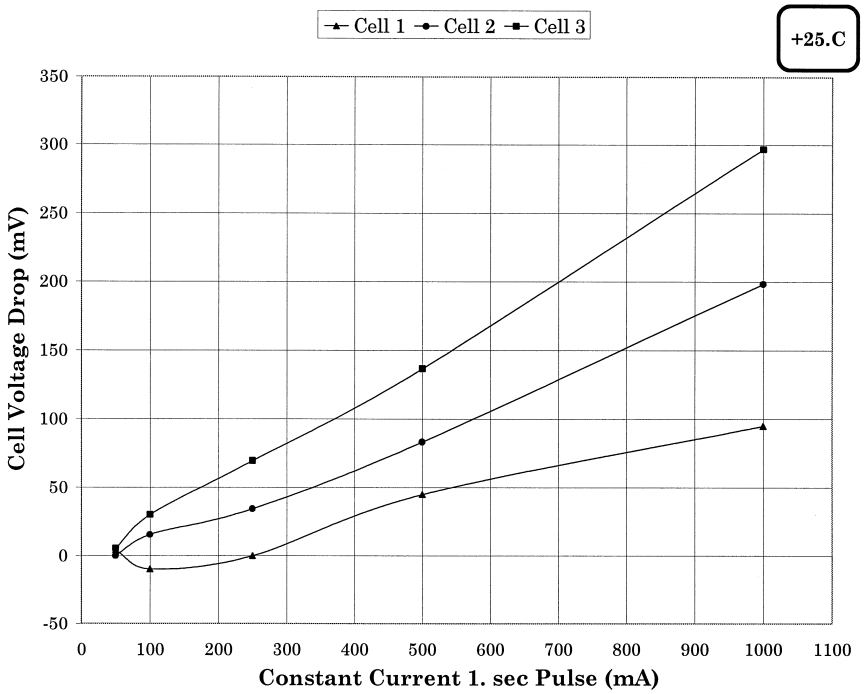


Fig. 5. Cell voltage drop at room temperature as a function of current pulse amplitude. Pulse duration = 1 s, all cells had accumulated 80–100 cycles.

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 full paper. The voltage drops at 10°C and −20°C are also linear with current pulse amplitude, again indicating that the contribution of the interfacial resistance to the internal cell impedance is negligible. The pulse data suggest that at 100% s.o.c., the lithium ion cells can be pulsed at very high currents without significantly affecting the cell performance.

4. Conclusions

Electrochemical performance characteristics have been measured for cylindrical lithium–ion cells from two manufacturers and prismatic lithium–ion cell from one of the 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, the cylindrical cell with the lower impedance displayed a higher energy density than the other. 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 A. 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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