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Energy and Power 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 18650 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 ~500 mAh prismatic lithium-ion cells exhibit higher specific power and power density than the 18650 cells. Over the temperature range from 35°C to -20°C, the cell impedance is almost constant for both cell types. These cells show very little voltage drop for current pulses up to 1 A.

Keywords: Lithium-ion; Ragone data

1. Introduction

Ever since Sony Energytec, Inc. introduced a commercial lithium-ion cell in 1991, the lithium-ion rechargeable battery market has been burgeoning at an unprecedented 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 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 three times more energy per unit weight and volume than conventional systems (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 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 short communication describes measurements of some of the lithium-ion battery characteristics listed above. Lithium-ion cells of two different sizes (18650 and ~500 mAh prismatic) from two different manufacturers were electrochemically evaluated and their properties 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. 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).

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.

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 2 is shown in Figure 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. 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 and therefore 4.15 V was deemed more appropriate in that case.

Ragone plots for the three cells are shown in Figure 2. In Figure 2A is given the power density (W/l) vs. energy density (Wh/l) and in Figure 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 Figure 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 & 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 Figure 3. Overall, the cell impedance is very small for all three types. In Figure 4, 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. 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 the cell 1 should have a lower impedance than cell 2 (see Figure 2). The impedance data in Figure 4 show this trend. It is more 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, 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. Figure 4 shows that the variation in resistance among three samples of cell 1 is very small. Cells 2 & 3 also show a similar good reproducibility.

3.3 Operating Characteristics under Pulse Loads

New applications such as digital wireless communications need pulse power [2] so that more data can be packed into the available communication spectrum. We have evaluated the pulse performance characteristics of these batteries for 1 sec. current pulses ranging from 50 mA to 1000 mA as a function of temperature. Figure 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 Figure 4). 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 reproducibility of the results was very good and standard deviation in many cases approach 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 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, 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.

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 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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References

[1] *Batteries International, Issue* 31, April 1997, p12

[2] A. Anani, F. Eschbach, J. Howard, F. Malaspina, and V. Meadows, *Electrochimica Acta*, **40,** 2211(1995)

Figure Captions

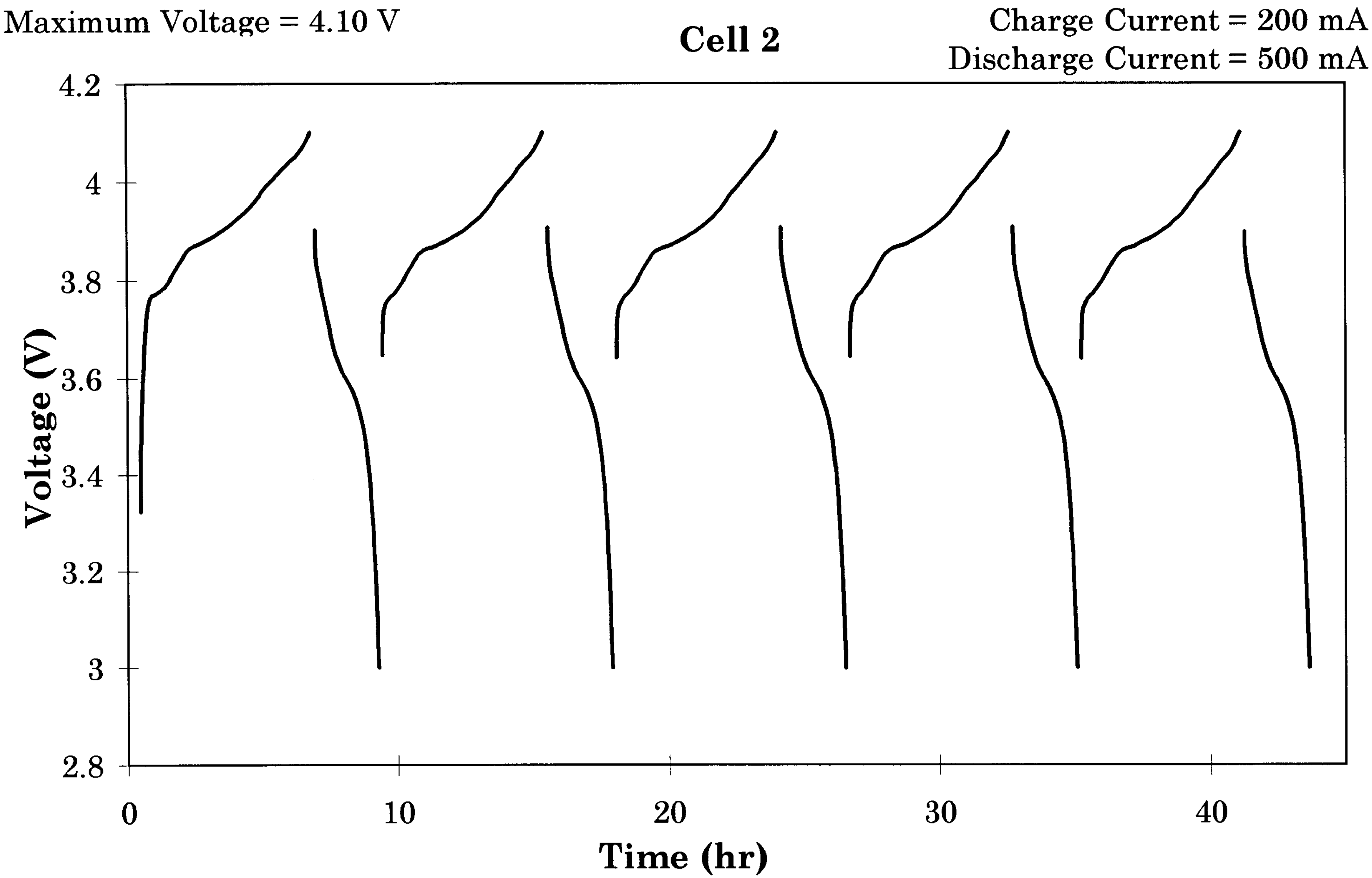
Figure 1. Charge/discharge characteristics of cell 2 at room temperature. Charge current = 200 mA, discharge current = 500 mA. The table shows the coulombic efficiency as a function of cycle # along with power and energy values.

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

Figure 3. NyQuist plots for the three cells. The impedance was measured at room temperature.

Figure 4. Cell resistance as a function of temperature.

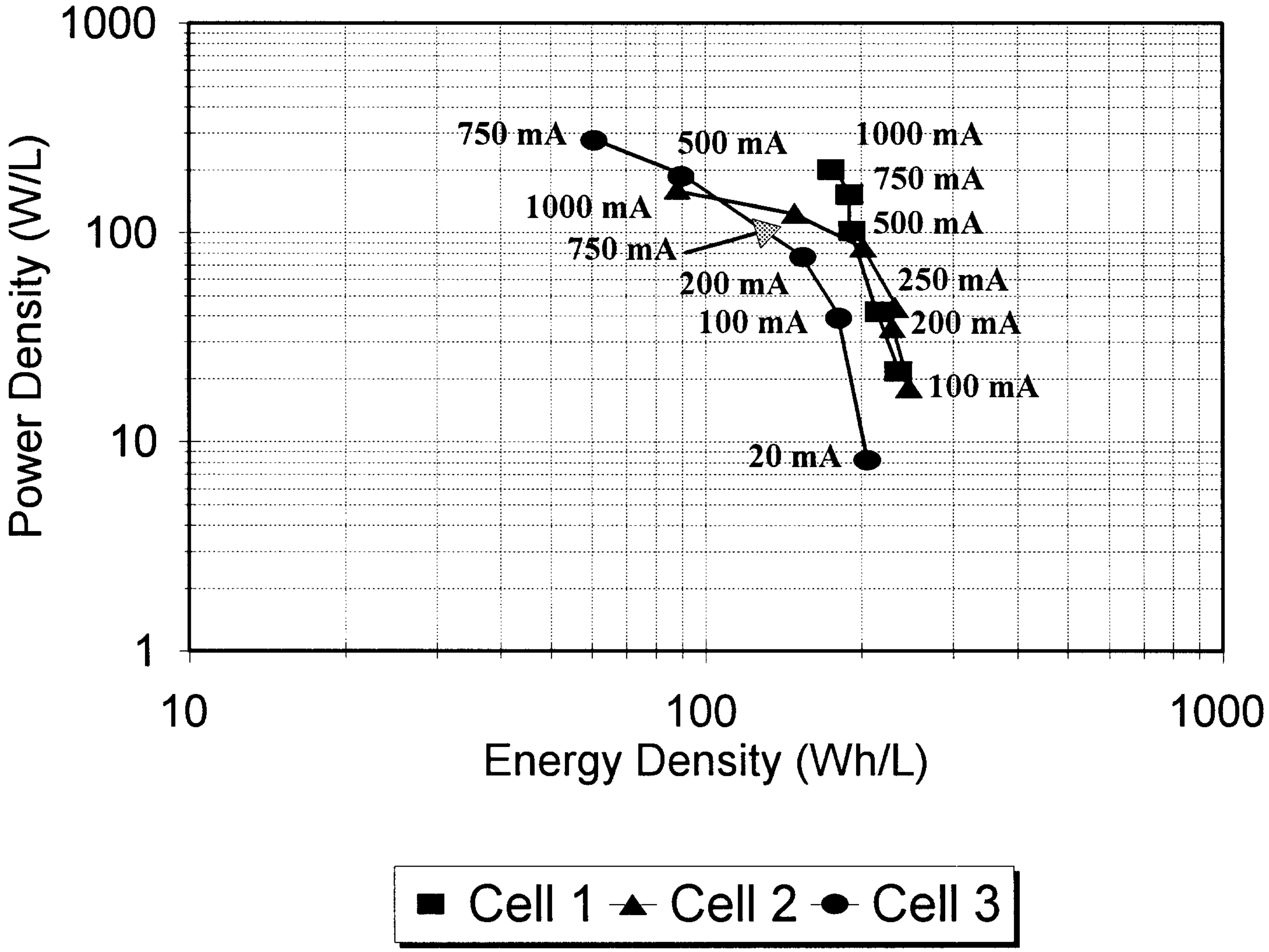
Figure 5. Cell voltage drop at room temperature as a function of current pulse amplitude. Pulse duration = 1 sec., all cells had accumulated 80 - 100 cycles.



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

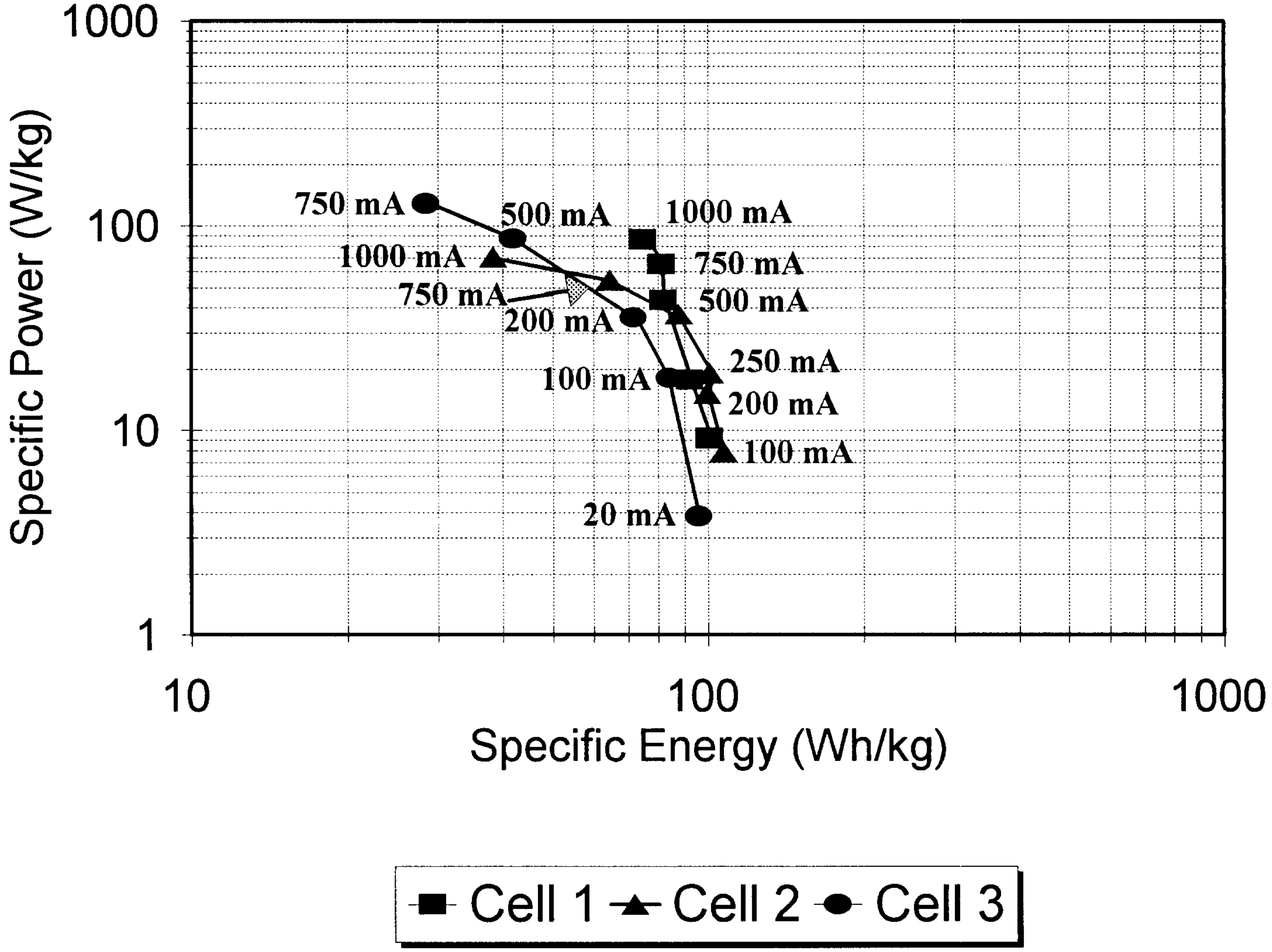
Fig. 1

Fig. 2 A



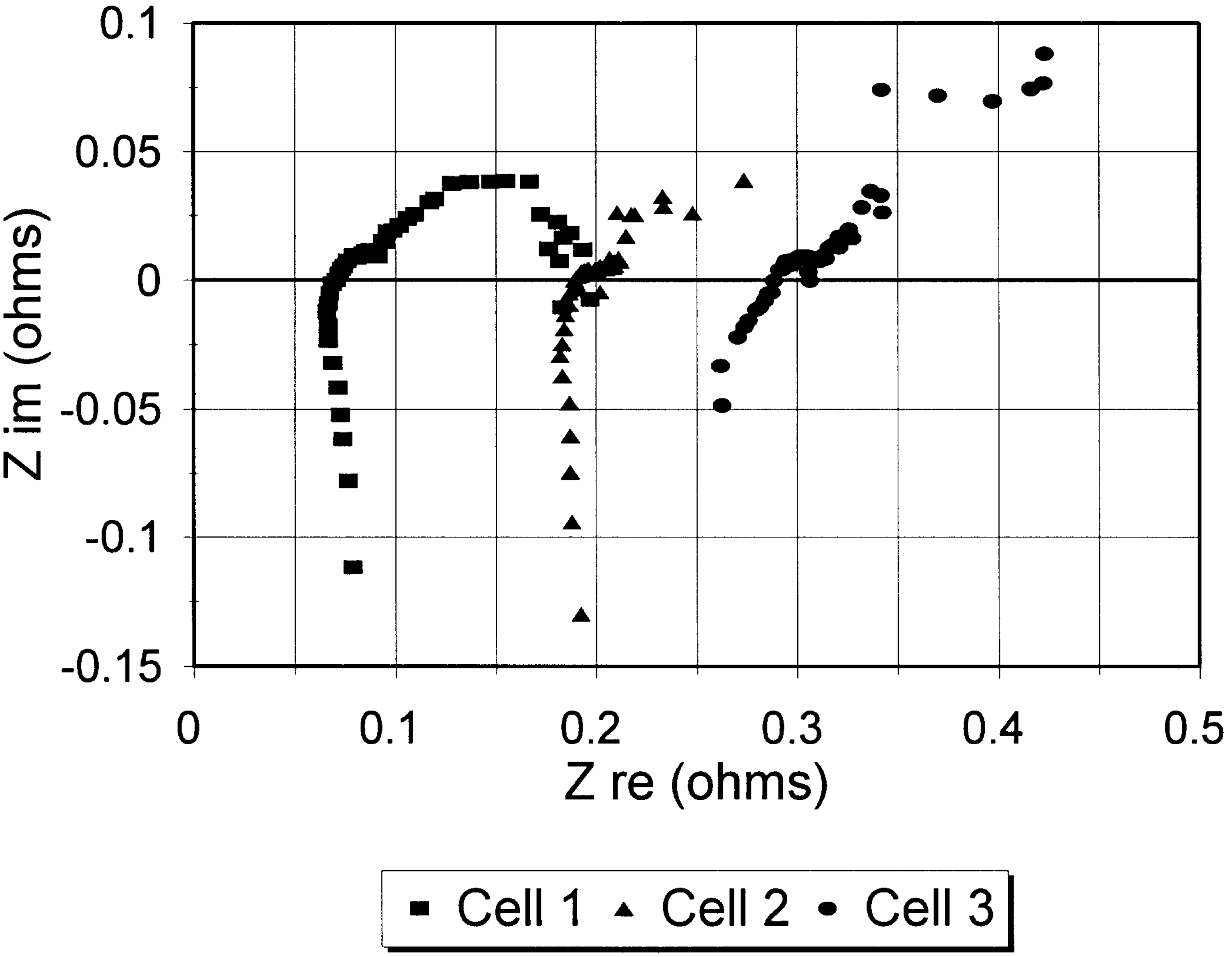
1000
100
10
1
Power Density (W/L)
10
100
1000
Energy Density (Wh/L)
750 mA
500 mA
1000 mA
750 mA
500 mA
1000 mA
750 mA
200 mA
250 mA
100 mA
200 mA
100 mA
20 mA
■ Cell 1 ▲ Cell 2 ● Cell 3

Fig. 2 B



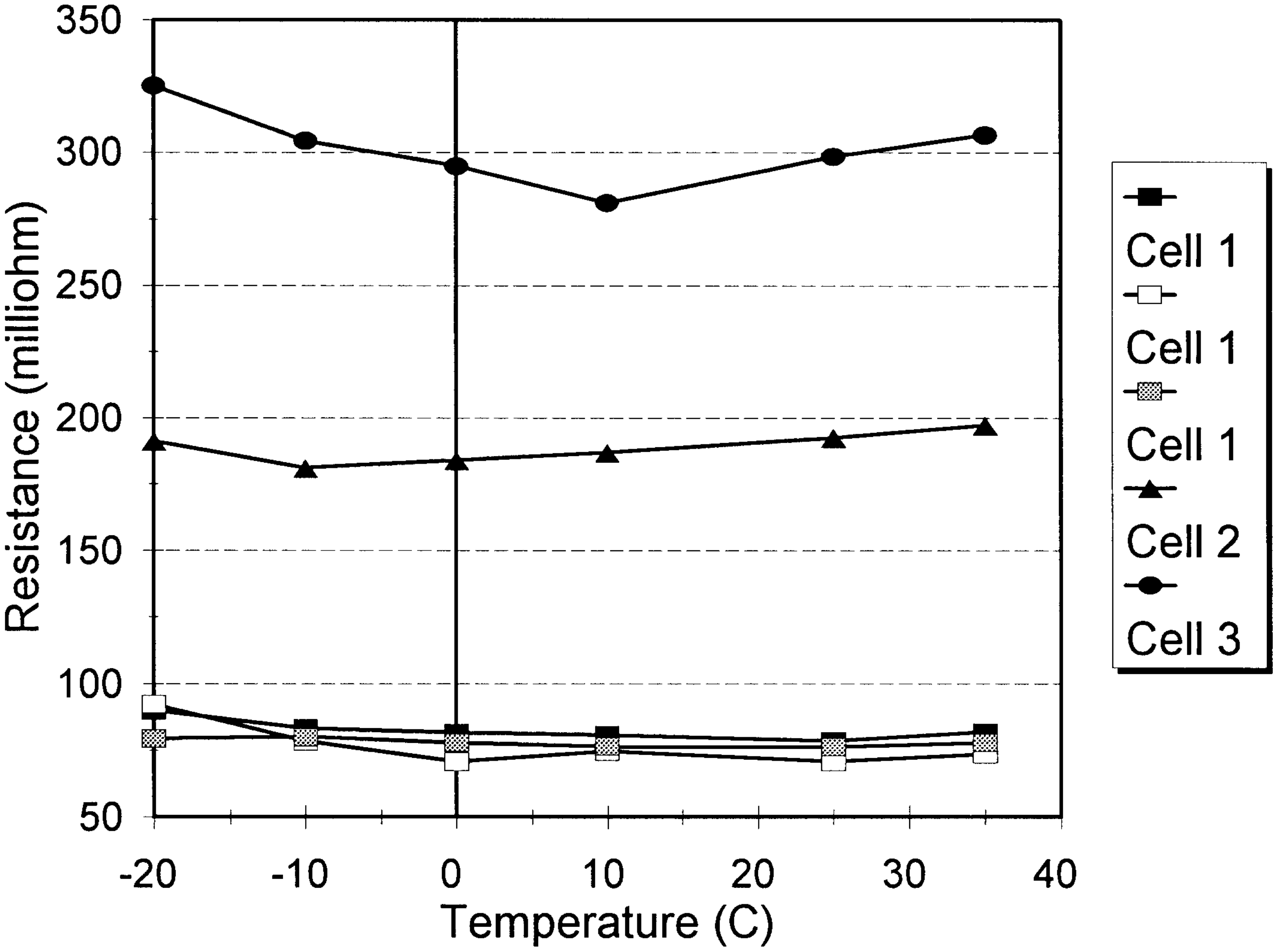
1000
100
10
1
Specific Power (W/kg)
10
100
1000
Specific Energy (Wh/kg)
750 mA
500 mA
1000 mA
750 mA
200 mA
100 mA
20 mA
1000 mA
750 mA
500 mA
250 mA
200 mA
100 mA
Cell 1
Cell 2
Cell 3

Fig. 3



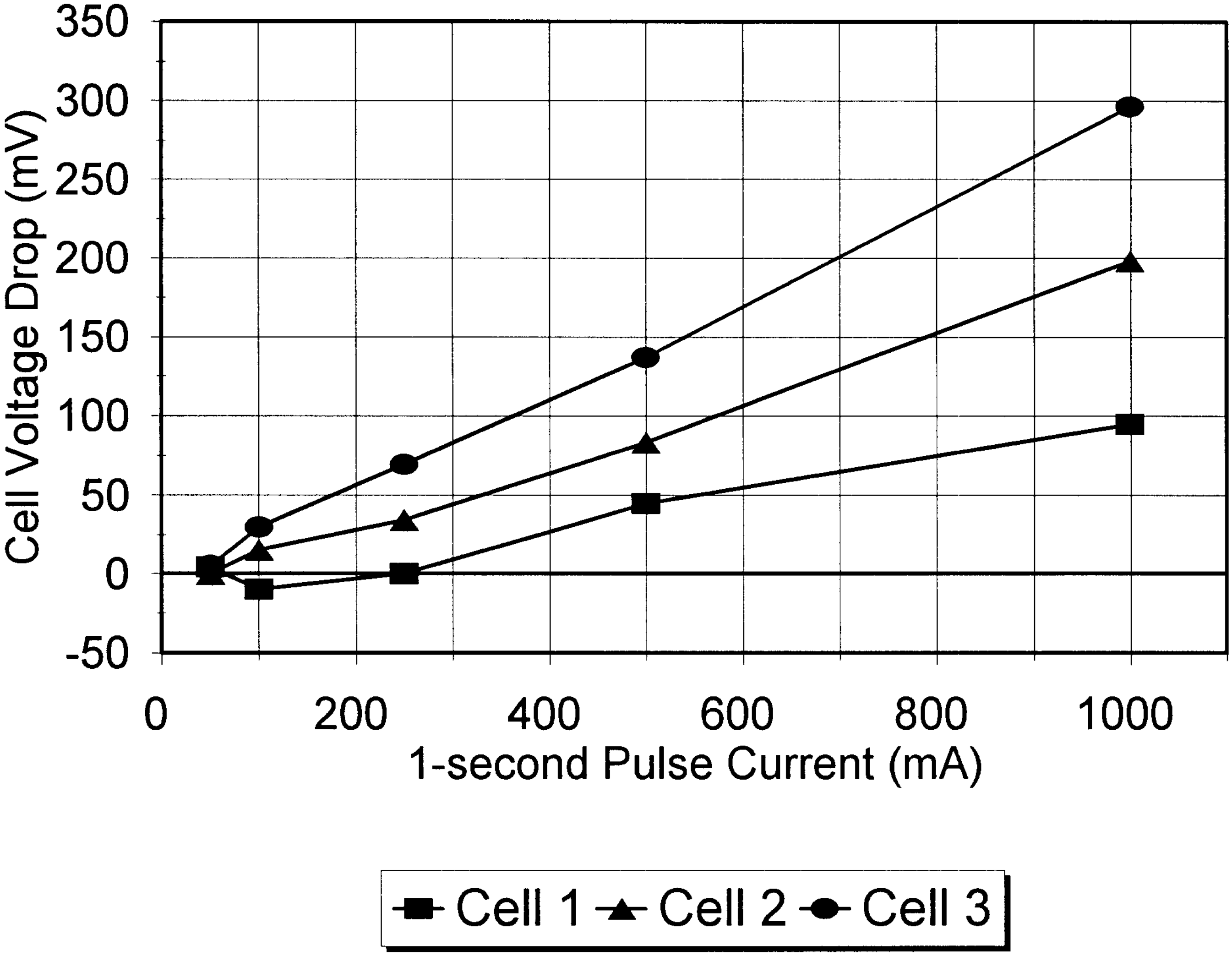
0.1
0.05
0
-0.05
-0.1
-0.15
Z im (ohms)
0
0.1
0.2
0.3
0.4
0.5
Z re (ohms)
■ Cell 1
▲ Cell 2
● Cell 3

Fig. 4



350
300
250
200
150
100
50
Resistance (milliohm)
-20
-10
0
10
20
30
40
Temperature (C)
■ Cell 1
□ Cell 1
▨ Cell 1
▲ Cell 2
● Cell 3

Fig. 5



350
300
250
200
150
100
50
0
-50
Cell Voltage Drop (mV)
0
200
400
600
800
1000
1-second Pulse Current (mA)
Cell 1
Cell 2
Cell 3