Electrochemical Impedance Spectroscopy to Compare Different Cells and Cell Aging Phenomena

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Abstract

Electrochemical Impedance Spectroscopy has been used extensively to document the impedance of Li-Ion cells. Primarily this technique has been used to characterize the impedance changes that occur inside the Li-Ion cell as the cell ages. Various cells have been tested to compare new cells with stored cells, new cells with cycled cells and new cells from different manufacturers. These results are presented to show the impedance variations that occur in $LiCoO_2$ cells. Testing has been performed at multiple voltages and temperatures to identify effects due to varying test conditions.

Introduction

A variety of 18650 cells were tested to determine the sensitivity of the EIS technique to changes in cell manufacturing. For this experiment Sony cells were purchased in January 1996 and January 2006 and Moli Energy Cells were purchased in December 2006. The 1996 Sony cells were either cycled under various test conditions described elsewhere[1] or stored in a refrigerator at approximately 4°C at 3.7V. This provides a baseline measurement with the new cells, a stored measurement comparison, a cycled measurement comparison, and a comparison with a different manufacturer. All cells had a $LiCoO_2$ cathode. The Sony cells had a hard carbon anode and the Moli Energy had a graphite anode. There were slight manufacturing changes in the Sony cell over the period 1996 to 2006 to increase the capacity from 1.1Ahr to 1.4Ahr. However, it is believed that the anode and cathode materials were unchanged.

Twenty-four 18650 cells from a single Sony lot were purchased in January 2006. Upon receipt of the cells, a baseline capacity and impedance as a function of voltage measurements were taken. The cells were then stored at room temperature, open circuit at 50% SOC until March 2007 when the testing was repeated at 10°C.

The cells from Moli Energy were purchased in December 2006 from a single lot. Upon receipt all 100 cells purchased had a baseline capacity measurement taken at 20°C. Eight (8) cells were then randomly chosen for further testing. These cells were stored for approximately one month following the baseline capacity measurements at 50% state of charge at room temperature (23°C) before beginning non-destructive testing.

Li-Ion 18650 cells manufactured by Sony were obtained in January 1996. After initial acceptance testing, the cells were then placed into ten groups of six and put into eight different test regimes. The test setup was designed to be able to measure for capacity loss mechanisms due to temperature, depth of discharge, and charge rate using a 2^3 factorial design. After the initial acceptance testing, completed in May 1997, the cells were held at open circuit while the test setups were prepared. Testing began in July 1997. The cells were tested under their respective test regimes until being removed from test between July 2002 and February 2003. The acceptance testing was repeated on the lots tested between June 2004 and January 2005. Following life testing, EIS measurements

were taken on the cells in February and March 2006. In general, the history of these cells consisted of acceptance testing followed by an open circuit stand at ambient temperatures for 6 months, cycle testing for five years and then another open circuit period at ambient temperature for 18 months. The acceptance tested was then repeated followed by another open circuit stand for 6 months and finally testing using the EIS technique presented here.

Experiment

The EIS measurement for results presented consisted of initially cycling the cells between 2.8V and 4.0V. Following a capacity cycle, the cells were held at 2.8V for 3 hours. The impedance measurement consisted of a current amplitude of 20mA at frequencies from 10kHz to 10mHz with a spacing of 10 points per decade. Following the impedance measurement the cell was charged in 0.3V increments to 4.0V at a C/10 rate and held at each voltage for 3 hours before repeating the impedance measurement. The C rate was determined independently for each cell type. Measurements were made with a Princeton Applied Research VMP2/Z. Throughout the progression of measurements taken the potentiostat became increasingly noisy making the low frequency results suspect for the 10ºC measurements on both the Sony and Moli Energy cells. The high frequency measurements correspond with the low impedance region and progress with decreasing frequency towards the high impedance tail.

Baseline Impedance Results

Initial results are presented for the Sony cells at 20ºC, results are presented for all voltages measured: 2.8V, 3.1V, 3.4V, 3.7V and 4.0V. These results are presented as a baseline measurement with which other measurements will be compared. Results are presented using a Nyquist format. It is clear that as the voltage of the cells increases the impedance decreases. The most significant impedance change occurs between 2.8V and 3.1V, after 3.1V the impedance changes are much smaller. For comparison with temperature, cell aging conditions, and cell manufacturers, results will only be presented at 2.8V and 4.0V. The frequency measurement at 10kHz corresponds with the impedance value at the bottom left of the chart and progresses to higher impedances as the probing frequency is lowered.

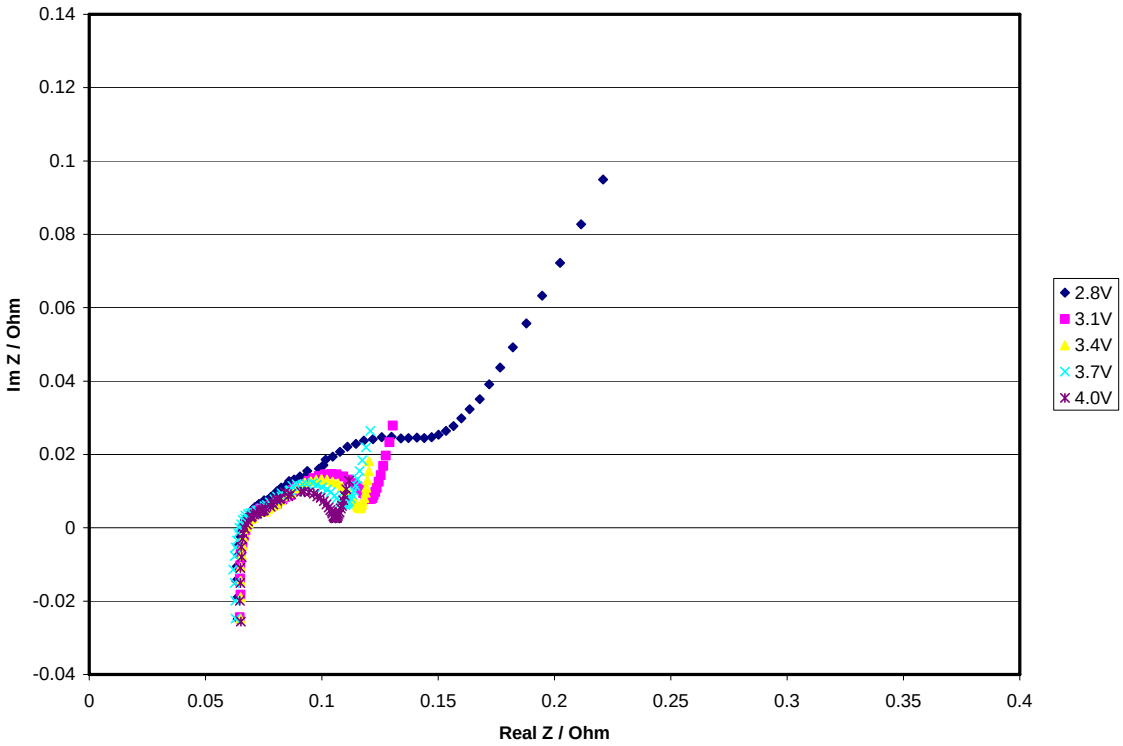

Figure 1. New Sony Cells at 2.8V, 20C

Temperature Comparison of Impedance Results

Sony Cells were measured at both 20ºC and 10ºC, fig 2. Test conditions were identical except for the temperature of the cells. At all voltages the increase in impedance at 10ºC compared with the 20ºC data is similar, approximately 1/3 increase in impedance. The overall shape of the curve is similar and the high frequency impedance is not observed to change. High frequency measurements are believed to probe cell design and structure. The fact that no noticeable change occurs at high frequency supports this theory as the cell structure and design are not expected to have a large temperature dependence. The mid-frequency is generally believed to probe the electrochemical reactions, which will have a moderate temperature dependence. The low-frequency measurements are believed to probe the rate limiting behaviors and diffusion in the cell which will have the largest temperature dependence. This temperature dependence as a function of frequency is observed in the measurements with the high impedances at low frequency showing the largest change in value.

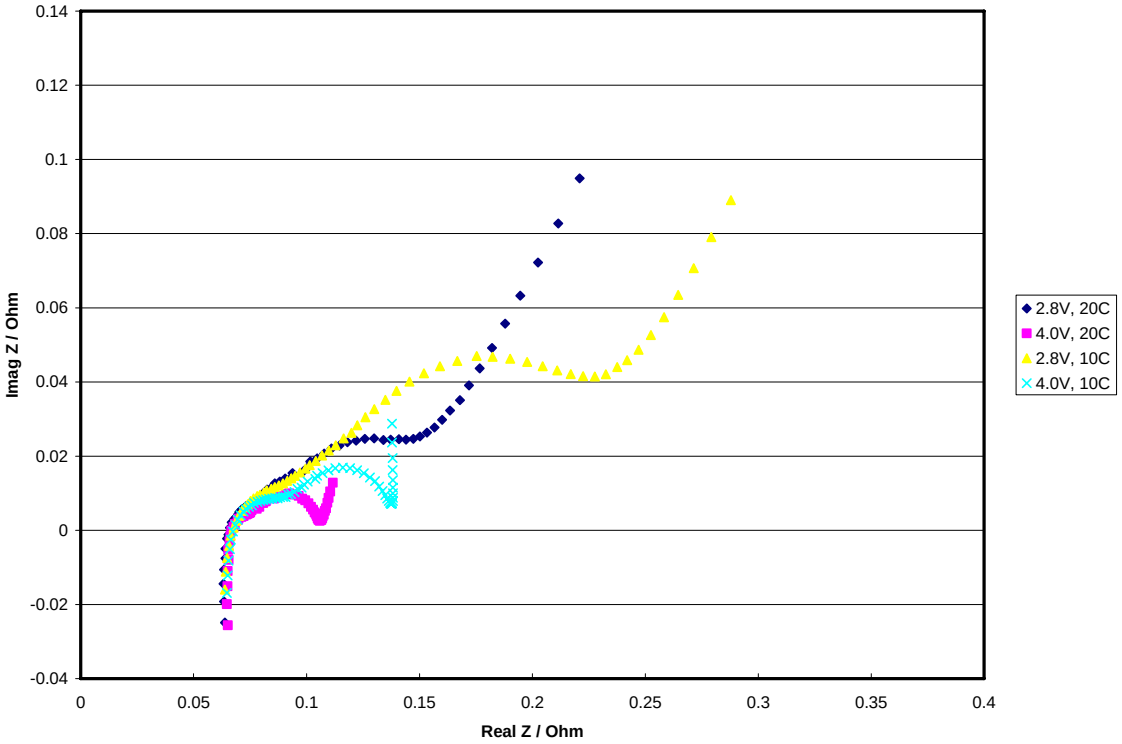

Figure 2. New Sony Cell Temperature Comparison at 10ºC and 20ºC

Stored Cell Comparison of Impedance Results

The stored cells show a significant increase in impedance over the new Sony cells, fig 3. The mid frequency semi circle is seen to grow extremely large and dominate the features of the scan. The low frequency diffusion tail is observed to begin at slightly lower frequencies compared with the new cells, likely due to the high impedance of the mid frequency semi circle. The high frequency region is not observed to change significantly. These measurements suggest a much longer time constant for the charge transfer reactions occurring in the cell. Diffusion comparison is difficult using the EIS technique due to the low frequencies required for the measurement. Note the change in scale for the Real Impedance when compared to the baseline measurements.

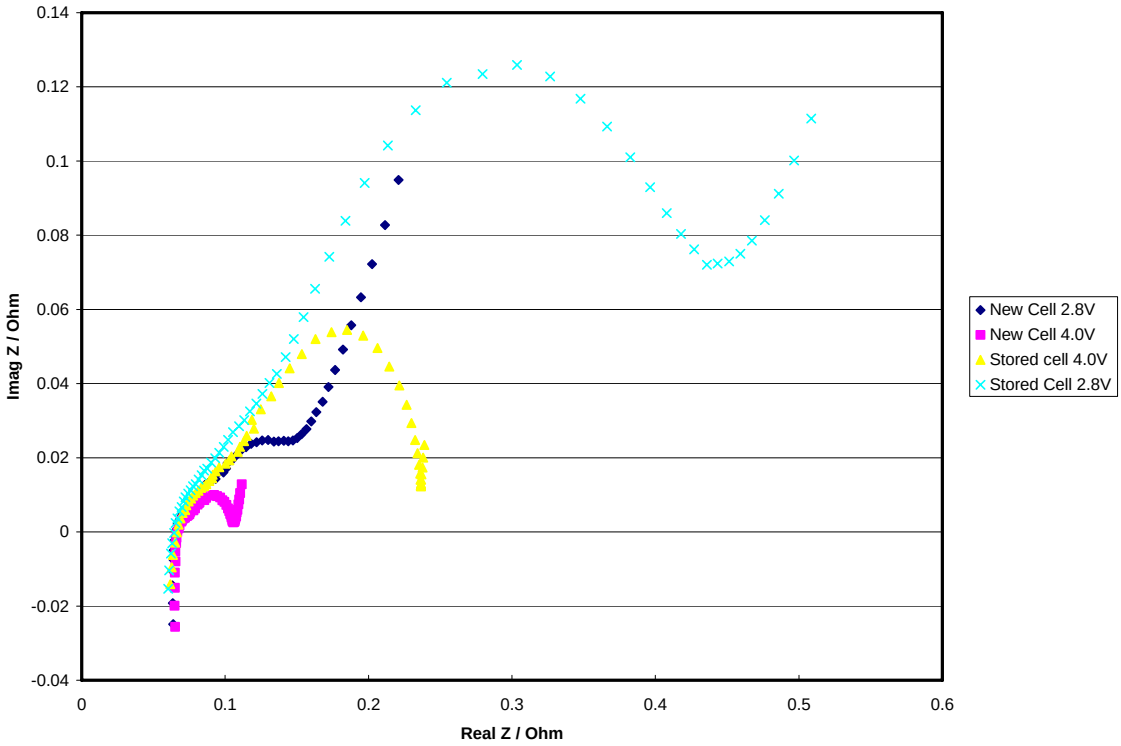

Figure 3. Comparison of New and Stored Sony Cells at 20ºC

Cycled Cell Comparison of Impedance Results

Cycled cell impedance growth varied considerably depending on the cycling conditions. The cycling conditions and impedance results are documented in a previous report[1]. One example cell from these cycling conditions is presented for comparison. This cell was cycled tested at 30C, 70%DOD with a 12 hour charge/discharge period for approximately 6 years and impedance results are presented, fig. 4. This cycling condition resulted in the median impedance growth, compared with all cycling conditions tested.

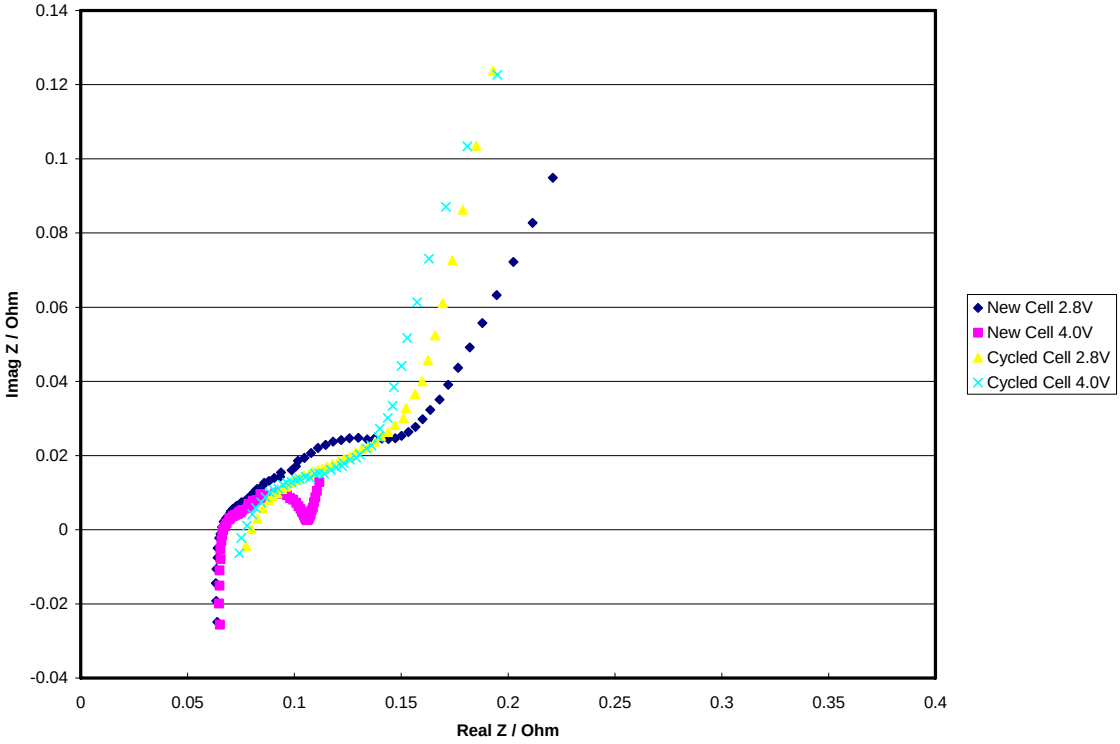

Figure 4. Comparison of New and Cycled Sony Cells at 20ºC

Cell Aging Comparison of Impedance Results

The comparison with a new cell, a stored cell and a cycled cell provides very interesting results. For clarity the results are presented in two graphs, fig 5 shows the comparison at 2.8V while fig 6 shows the comparison at 4.0V. There is very little change in the cycled cell impedance between 2.8V and 4.0V. This is significantly different from both the new cells and the stored cells. The high frequency impedance has shifted slightly higher, although it remains consistent at all voltages and temperatures. The mid frequency semi-circle has almost entirely disappeared. It is likely that this is due to a rate limiting barrier in the cell masking the processes contributing to this impedance. This barrier, or new impedance, in the cell is then observed to dominate at all voltages explaining the similarity observed between 2.8V and 4.0V.

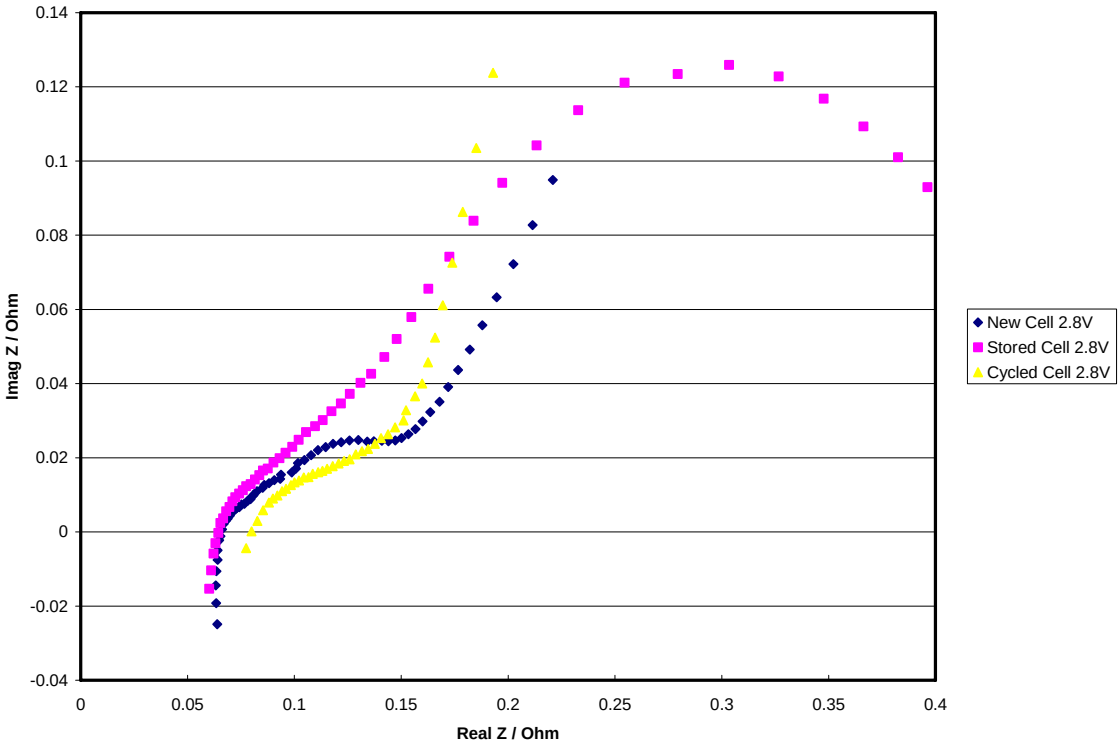

Figure 5. Comparison of New Cell, Stored Cell and Cycled Cell at 20ºC, 2.8V

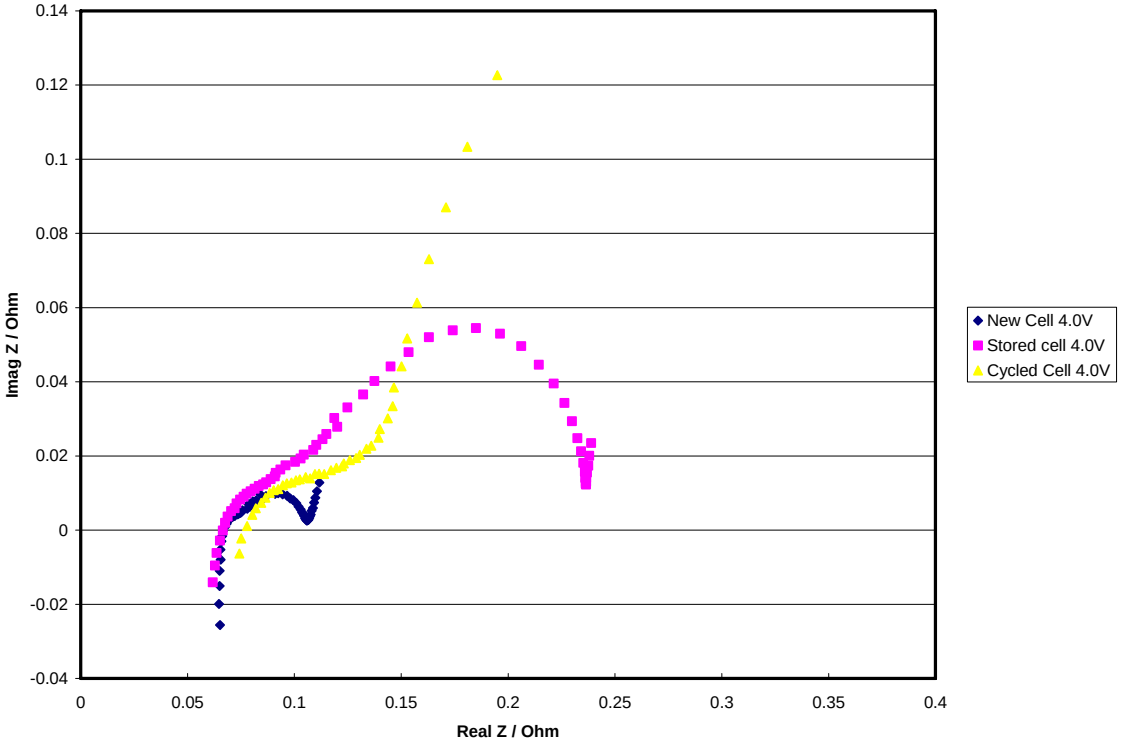

Figure 6. Comparison of New Cell, Stored Cell and Cycled Cell at 20ºC, 4.0V

Moli Energy Cell Comparison with Baseline Impedance Results

Moli Energy Cells were also manufactured with a $LiCoO_2$ cathode. However, the anode material was graphite, compared to the hard carbon in the Sony cell. The cells may also have different electrolytes and internal structures due to different design and manufacturing practices. Results are presented comparing the Sony and the Moli Energy cells, fig 7. The Moli cell was rated at 2.2Ahr while the Sony cell was rated at 1.4Ahr. The Moli cell displays significantly higher impedance at low voltages. This suggests that the impedance in this region is due to the anode material in the cell. A comparison at high voltages is shown in fig 8. The Sony cell exhibits a more pronounced double semi-circle than the Moli cell and slightly lower impedance. The high and low frequency tails are also slightly different in both length and slope. A number of factors likely contribute to the differences observed in the cells. This provides a basis for expecting that this technique may be used to identify material and manufacturing changes in Li-Ion cells. A more controlled study varying cell parameters would be required in order to identify how sensitive this technique is.

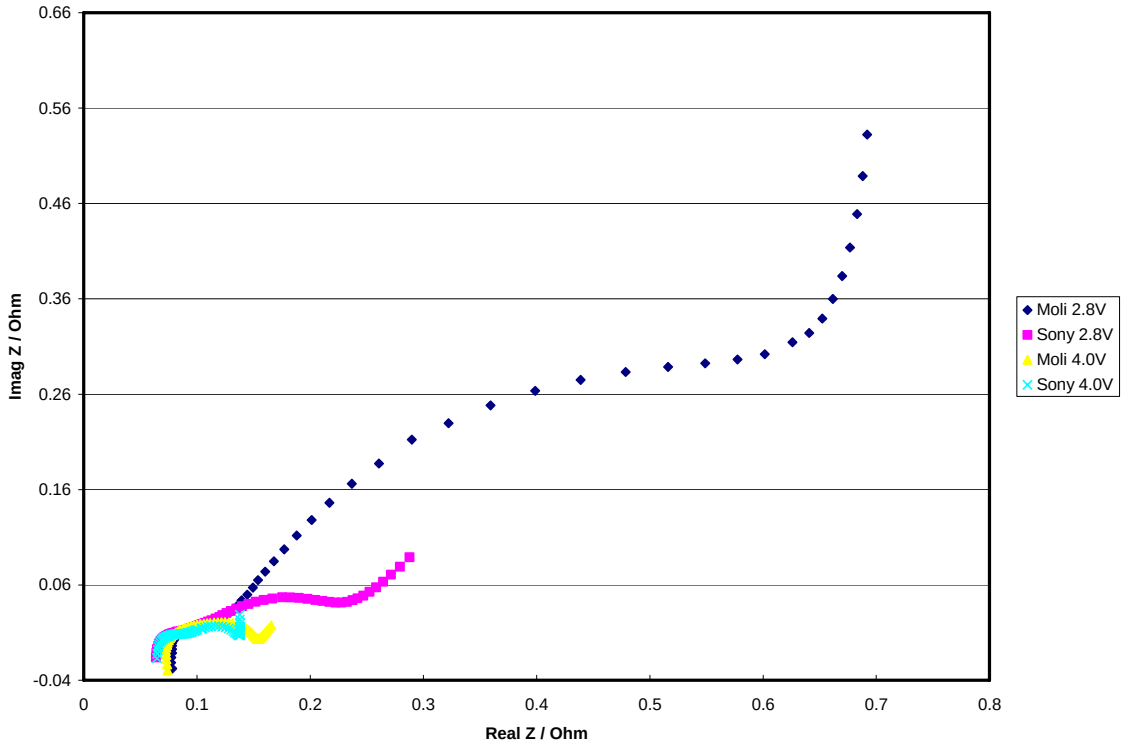

Figure 7. Comparison of Moli Energy Cells with Sony Cells at 10ºC

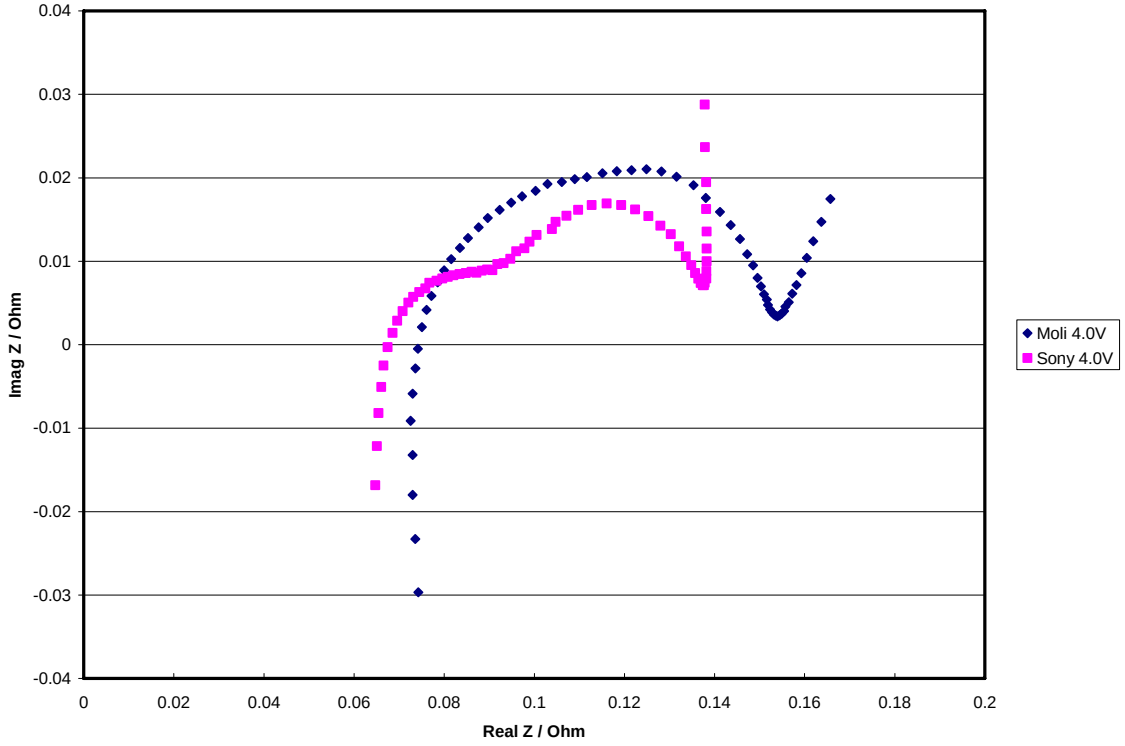

Figure 8. Comparison of High Voltage Impedance of Moli and Sony Cells at 10ºC

Conclusion

The EIS technique has been used to document changes occurring in cells. In a new Li-Ion cell the impedance is observed to increase significantly below 3.1V. This corresponds with the voltage dropping below the discharge plateau in these cells. Slight changes in impedance are also observed above 3.1V voltage. Cells that have been stored show much higher impedances at all voltages and temperatures, however the overall shape of the impedance scan remains similar. Cells that have been cycled show a change in impedance at low frequencies that is distinctly different from both the new cells and the stored cells. Cells from different manufacturers are shown to display significantly different impedance scans.

The EIS technique shows promise in identifying changes occurring in material and design of Li-Ion cells. Initial measurements demonstrate the differences observed as a function of cell temperature, voltage, aging conditions and manufacture. Comparison with a baseline measurement provides interesting results to aid in identifying degradation mechanisms in cells and what changes may have occurred in cell material or design. This method is particularly useful when coupled with other electrochemical techniques, to aid in identifying contributions of various materials and processes to the impedance observed.

Acknowledgements

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References

[1] J.S. Halpine, "AC Impedance to Measure Degradation Mechanisms", AIAA-2006-4111, proc. 4th IECEC, San Diego, CA, 2006