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Rapid Impedance Spectrum Measurements for Onboard State-of-Health Applications

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Rapid Impedance Spectrum Measurement for Onboard State-of-Health Applications

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Abstract: *Rapid impedance measurements can provide a useful online tool for improved state-of-health estimation. A validation study has been initiated at the Idaho National Laboratory for a rapid impedance technique known as Harmonic Compensated Synchronous Detection. This technique enables capturing the impedance spectra over a broad frequency range within about ten seconds. Commercially available lithium-ion cells are being calendar-life aged at 50°C with reference performance tests at 30°C every 32.5 days to gauge degradation The cells have completed the first set of reference performance tests and preliminary results are presented. The spectra change as a function of temperature and depth-of-discharge condition, as expected. The data indicate that the rapid impedance measurement technique is a benign measurement tool that can be successfully used to gauge changes in the corresponding pulse resistance.*

Keywords: rapid impedance measurements; state-of-health assessment; lithium-ion.

Introduction

Batteries and other energy storage devices are critical enabling technologies for several industries, including military, space, automotive, telecommunications, and consumer electronics. Increased power and energy demands are placed on battery technologies for applications ranging from soldiers on combat missions to extended all-electric range of plug-in hybrid electric vehicle technologies. These battery systems must also last longer and operate efficiently over a broad range of temperature conditions. In the automotive industry, for example, the battery life target is 15 years [1] and it will generally spend most of that useful life under idle conditions (e.g., parked overnight in a garage or parked at the job site) with periodic drive cycles as the owner commutes between home and work. Military combat missions may subject a battery to severe environments ranging between -40 and +50°C [2].

Developing an industry standard for the state-of-health (SOH) of energy storage devices remains a challenge. Existing management systems tend to focus on passive measurement techniques, where the battery voltage and current are periodically recorded as a function of time and temperature. From these data, estimations of state-of-charge (SOC) or available capacity are calculated based on look-up tables and coulomb counting techniques [3-6]. While these data can be very useful in assessing the health of a battery, it provides an incomplete picture since changes in resistance and available power capability cannot be estimated from passive measurements.

AC impedance is a good diagnostic tool that has been shown to strongly correlate with changes in both resistance and available power capability [7]. However, it has not generally been considered useful as an onboard sensor. The equipment is typically delicate, expensive, and requires a laboratory environment to operate. Furthermore, the measurements are generally sequential, ranging between 10 minutes to an hour depending on the system settings, which results in a test duration that is too lengthy for onboard applications. Rapid impedance measurement techniques have since been developed for onboard diagnostic assessment of changes in resistance and power capability [8]. When combined with passive measurements, a more complete estimate of battery state-of-health can be determined.

Background

Harmonic Compensated Synchronous Detection (HCSD) is a technique that enables rapid impedance spectrum measurements based on an input sum-of-sines excitation signal over a broad frequency range. The sum-of-sines contains frequencies that are separated by harmonics so as to eliminate the crosstalk interference between signals when detecting the impedance [8]. The measurement duration is only one period of the lowest frequency, so a frequency sweep from approximately 2 kHz to 0.1 Hz requires only 10 seconds to complete. The frequencies within the excitation signal that are greater than the fundamental will include multiple periods to fill the ten-second measurement window (e.g., the first harmonic frequency of 0.2 Hz would have two periods within the sum-of-sines, a frequency of 0.4 Hz would have four periods, etc.).

To validate the accuracy of the HCSD technique, several test cells were constructed using the schematic shown in Figure 1 [8-9]. The test cells were then subjected to standard AC impedance measurements (acquired in ten minutes) followed by ten-second HCSD measurements over a frequency range of 1638.4 Hz to 0.1 Hz with octave harmonic separation. The AC impedance measurements consisted of applying a constant voltage load (V_L) of 20 mV and capturing the current response. For the HCSD measurement, the load current (I_L) consisted of a 0.5A (RMS) sum-of-sines excitation signal and the load voltage response was captured.

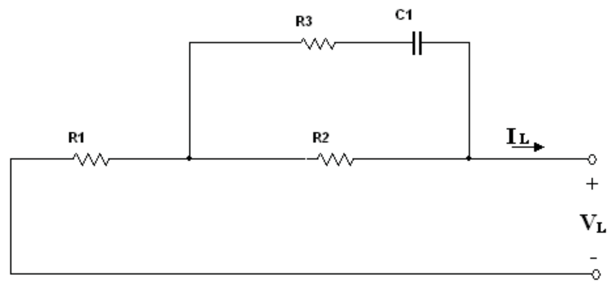

Figure 1. Test Cell Equivalent Circuit.

Figure 2 shows the AC impedance and HCSD measurements for a test cell having the component values shown in Table 1. Both measurements yield the same impedance spectrum, which demonstrates the accuracy of the rapid technique. The HCSD approach does have fewer data points due to the strategic frequency spread. The lower resolution in the HCSD, spectra, however, does not reduce the definition of the semicircle arc. At high frequencies, the capacitor essentially behaves as a short circuit and the impedance should be approximately 23.6 mΩ. The measured value, however, is closer to 24.8 mΩ and the increased amount may be coming from a combination of shunt tolerances and the presence of additional contact resistances during the measurements. At very low frequencies, the capacitor is essentially open, and the impedance should be about 30 mΩ. The measured value, as shown in Figure 2, is approximately 30.3 mΩ. Similar results were also observed with other test cells.

Experimental

Validation studies using the HCSD technique are presently underway at the Idaho National Laboratory using commercially-available lithium-ion cells having a rated capacity of 1.2 Ah and a voltage range of 4.2 to 2.7 V. The cells are undergoing calendar-life testing at an elevated temperature of 50°C. The test matrix consists of three different groups with each group having three cells. One group of cells (Group A) is undergoing a pulse-per-day test followed by a clamp at the voltage corresponding to 60% SOC. The pulse-per-day test consists of ten-second discharge and charge pulses with a forty-second rest in between. The second group of cells (Group B) is also voltage clamped at 60% SOC, but is given a ten-second HCSD measurement once every 24 hours instead of a pulse test. The third group (Group C) is simply clamped at the target voltage with no periodic interruptions for measurements. Every 32.5 days, the calendar-life test on all cells is interrupted for reference performance tests (RPTs) at 30°C. The RPTs are used to gauge the rate of cell degradation as a function of cell age. Included in the RPT is a ten-second HCSD measurement between full charge and full discharge in 10% depth-of-discharge (DOD) increments.

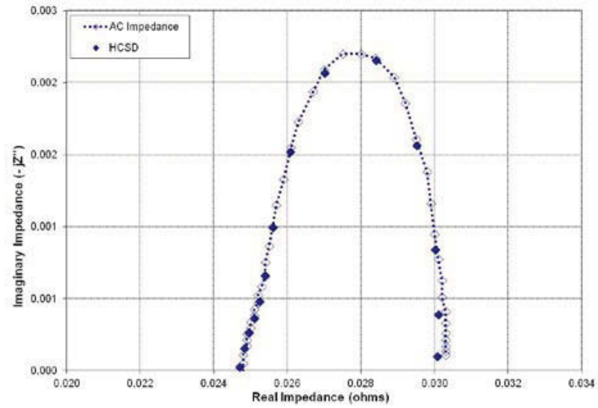

Figure 2. Impedance Spectra for a Test Cell Equivalent Circuit.

Table 1. Component Values for Test Cell Circuit

Component	Value
R_1	15 mΩ
R_2	15 mΩ
R_3	20 mΩ
C_1	9 F

To date, the cells have completed the first set of calendar-life aging and the first RPT. The second set of calendar-life aging is presently underway. Testing is being conducted on a Maccor series 4000 with a voltage and current range of 10 V and 12.5 A, respectively. The cells are placed in a Tenny Jr. temperature chamber capable of maintaining the ambient temperature to within ±3°C. The HCSD measurements are performed with a first generation prototype hardware system with a maximum voltage capability of 5-V [7]. Newer hardware prototypes are presently being designed for 50-V systems.

Results

Figure 3 shows the HCSD impedance measurements at each 10% DOD increment for a representative cell at beginning of life (i.e., RPT0). The spectra do not show any significant changes at the ohmic resistance (i.e., the point at which the spectra cross the real axis [10]). However, the effective charge transfer resistance in the mid-frequency region, as estimated by the width of the semicircle arc [10], increases with increasing DOD. The increased impedance may be due to a loss of lithium inventory as the cell is being discharged. This implies that the changes in HCSD spectra could be useful in rapidly gauging the battery SOC condition. The low-frequency Warburg tail on the right side of the spectra does not seem affected by the DOD condition, but the angle of the tail changes somewhere between 30 and 40% DOD. The cause of this is still under investigation, but some of it may be attributable to a transient effect at lower frequencies which has also been previously observed [8].

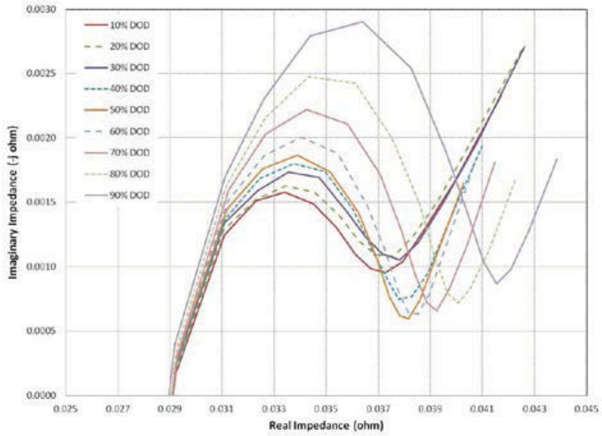

Figure 3. HCSD Measurements at each 10% DOD Increment.

Figure 4 shows the HCSD impedance spectra measured at 30°C at both RPT0 and RPT1 for a representative cell at 40% DOD (this roughly corresponds to 60% SOC, which is the calendar-life aging condition). The ohmic resistance shows a small increase, which is consistent with previous studies [8], but the majority of the impedance increase occurs in the effective charge transfer resistance, as expected. The mid-frequency region shows growth in both the real and imaginary components as a result of the first 32.5 days of calendar-aging at 50°C. The Warburg tail appears to be unaffected by aging and essentially retains the same angle.

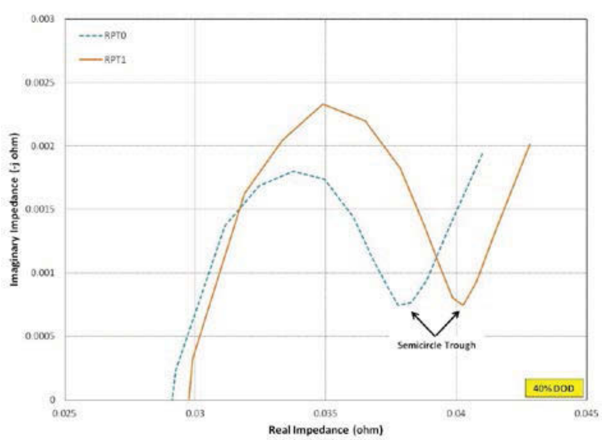

Figure 4. HCSD Measurements at 40% DOD for a Representative Cell at RPT0 and RPT1.

Table 2 shows the average percent-increase between RPT0 and RPT1 in the effective charge transfer resistance. The resistance was estimated based on the real value at the semicircle trough, which is the transition point between the semicircle and Warburg tail, as indicated in Figure 4. All three groups show similar degradation in the impedance for each given DOD condition. The differences between each group are generally within one or two standard deviations of each other. These data indicate that periodic HCSD measurements (Group B) are benign tests that do not significantly impact cell degradation.

Table 2. Real Impedance Growth at the Semicircle Trough

Group	A Pulse/Day	B HCSD/Day	C V-Clamp
10% DOD	5.40%	5.44%	5.18%
20% DOD	5.43%	5.70%	5.29%
30% DOD	5.31%	5.77%	6.16%
40% DOD	6.53%	6.62%	5.77%
50% DOD	5.87%	6.33%	6.09%
60% DOD	5.96%	6.16%	5.88%
70% DOD	4.46%	5.79%	4.58%
80% DOD	4.09%	5.18%	4.09%
90% DOD	3.18%	3.99%	3.37%

Figure 5 shows the discharge pulse resistance growth during the first set of calendar-life aging at 50°C for a representative cell; the corresponding regen resistances are similar. As expected, the resistance grows as a function of test time while exposed to the elevated test temperature. The initial resistance was 39.8 mΩ and it increased to 42.9 mΩ after 32.5 days. Figure 6 shows a subset of the HCSD measurements that were taken once every 24 hours during the first set of calendar-life aging for a representative cell. With the increased test temperature, the size of the mid-frequency arc is reduced, as expected. Since the frequency range of the measurement remained the same (1638.4 Hz to 0.1 Hz), more of the Warburg tail is captured in these spectra. Nevertheless, the majority of the impedance growth occurred in the effective charge transfer resistance as a function of test time while the ohmic resistance and Warburg tail remain relatively unaffected.

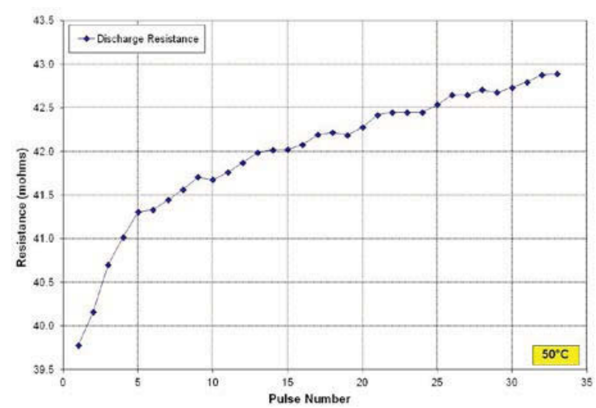

Figure 5. Discharge Resistance Growth for a Representative Cell During Calendar-Life Aging at 50°C.

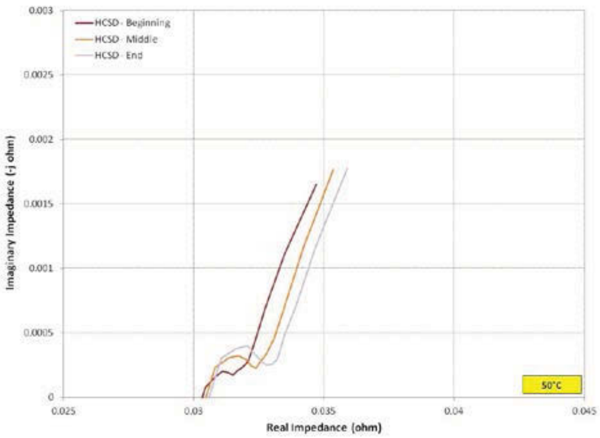

Figure 6. Some HCSD Measurements Performed During Calendar-Life Aging at 50°C for a Representative Cell.

Figure 7 shows the average growth in HCSD impedance, estimated from the semicircle trough, at 50°C (Group B) as a function of the corresponding average discharge pulse resistance determined from Group A. The linear regression fit shows a strong correlation with a goodness-to-fit coefficient of r^2=0.960. These results imply that changes in pulse resistance, whether large or small (as shown in Figure 5) can be successfully captured by changes in the HCSD impedance spectra at elevated temperatures (Figure 6).

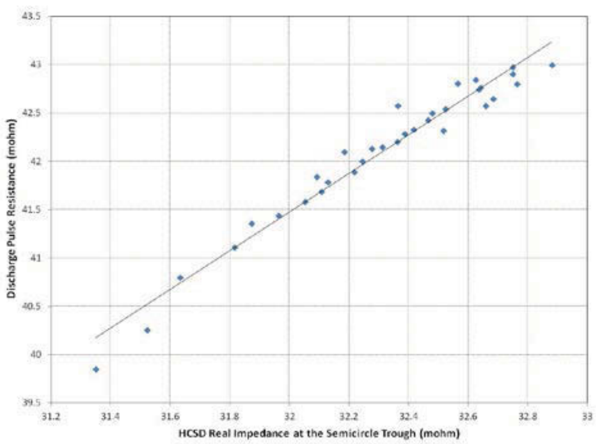

Figure 7. Average Correlation between HCSD and Pulse Resistance during Calendar-Life Aging at 50°C.

Summary

The Idaho National Laboratory has initiated a set of validation tests for a rapid impedance measurement technique known as HCSD. The HCSD technique has been shown to yield comparable spectra to standard AC impedance measurements and could be used as an onboard diagnostic tool. Lithium-ion cells are being calendar-life aged at 50°C with periodic interruptions for reference performance tests at 30°C. Preliminary results indicate that the HCSD technique is a consistent and repeatable measurement that can accurately assess changes in pulse resistance during aging. Furthermore, the reference performance tests indicate that the cells subjected to HCSDs during calendar-life show a similar degradation compared to the cells with no periodic measurements. Additional RPTs will determine if these observed trends remain the same as the cells continue to degrade.

Acknowledgements

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References

1. *Battery Test Manual for Plug-In Hybrid Electric Vehicles, DOE/ID-11070.* 2003.
2. Naval Air Warfare Center Aircraft Division. *Performance Specification--Batteries, Storage, Aircraft: General Specifications For; MIL-PRF-8565K.* 2001.
3. M. Sternad, M. Cifrain, D. Watzenig, G. Brasseur, and M. Winter. *Condition monitoring of lithium-ion batteries for electric and hybrid electric vehicles.* 2009, Elektrotech. Informationstechnik, Vol. 126 (5), pp. 186-193.
4. W.D. Kurle, S.B. Johnson, R.W. Nordness, S.L. Firman, D.M. Gustavson, P.Y. Choi. *Smart Battery With Maintenance and Testing Functions. U.S. Patent 6,072,299* June 6, 2000.
5. C.R. Gould, C.M. Bingham, D.A. Stone, and P. Bentley. *New Battery Model and State-of-Health Determination Through Subspace Parameter Estimation and State-Observer Techniques.* 2009, IEEE Trans. Veh. Technol., Vol. 58 (8), pp. 3905-3916.
6. T. Okoshi, K. Yamada, T. Hirasawa and A. Emori. *Battery condition monitoring (BCM) technologies about lead-acid batteries.* 2006, J. Power Sources, Vol. 158, pp. 874-878.
7. J.P. Christophersen, D.F. Glenn, C.G. Motloch, R.B. Wright, C.D. Ho, V.S. Battaglia. *Electrochemical Impedance Spectroscopy Testing on the Advanced Technology Development Program Lithium-Ion Cells.* 2002, IEEE Trans. Veh. Technol., Vol. 56 (3), pp. 1851-1855.
8. Christophersen, J., Morrison, J., Morrison, W. and Motloch, C., "Rapid Impedance Spectrum Measurements for State-of-Health Assessment of Energy Storage Devices," *SAE Int. J. Passeng. Cars - Electron. Electr. Syst.* 5(1):2012
9. *Advanced Technology Development Program for Lithium-Ion Batteries: Gen 2 Performance Evaluation Final Report*, INL/EXT-05-00913, Jul. 2006.
10. *Handbook of Batteries*. David L. Linden, ed., and Thomas B. Reddy, ed., 3rd ed., New York: McGraw Hill, 2002.