Acquiring Impedance Spectra from Diode-Coupled Primary Batteries to Determine Health and State of Charge

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Acquiring Impedance Spectra from Diode-Coupled Primary Batteries to Determine Health and State of Charge

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Abstract—The U.S. Army uses BA5590 Lithium Sulfur Dioxide primary batteries for portable electronic systems. There remains a need, however, for technology that can rapidly assess these batteries and estimate their remaining state of health after being used without degrading them to determine if there is remaining useful life for additional missions. This allows the full range of charge to be consumed before the battery is recycled or disposed. Impedance spectroscopy measurements have been shown to be a useful diagnostic tool, but standard methods cannot be applied to the BA5590 batteries because of the up-front electronics. The BA5590 module is diode-coupled and a charge-neutral excitation signal would be half-wave rectified and completely corrupt the results. However, a rapid impedance spectrum measurement technique has been developed that can be used for the BA5590s based on the addition of a small discharge bias load superimposed on the sinusoidal excitation signal. The feasibility of this approach was initially simulated and then successfully applied to cell strings on four fresh BA5590 modules. The results clearly showed consistent and repeatable impedance spectra with no significant impact on the SOC as a result of the measurement. Details of this measurement technique and discussion of the preliminary results are presented.

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1. INTRODUCTION

The U.S. military relies on a wide variety of battery technologies for various applications ranging from fighter jets to radio communications. A common energy source that is used for communication and surveillance systems is the BA5590 Lithium Sulfur Dioxide primary battery. This battery module consists of two 12-V cell strings with each string consisting of five cells. The strings can be connected in series for a 24-V system, in parallel for a 12-V system, or

even used as two independent 12-V systems [1]. Although widely used, it has been difficult to find a low-cost solution for rapidly assessing the overall health and energy removed from the BA5590s after usage. As such, the reusability of a battery at the completion of a mission is generally unknown. Since military missions cannot risk battery failures, the conservative approach has typically been implemented where used BA5590s are prematurely recycled or discarded, resulting in significantly higher costs and unnecessary waste.

Electrochemical Impedance Spectroscopy (EIS) has been shown to be a useful diagnostic tool for assessing battery health and state of charge (SOC) [2-6]. Standard EIS measurements usually consist of sequentially sweeping through a given frequency range by injecting charge-neutral sinusoidal excitation signals into the battery (or other energy storage device) and capturing the response. Depending on system settings and the frequency range, the impedance measurement sweep could last somewhere between 10 minutes to an hour. Although this technique would be useful in assessing the health of a Lithium Sulfur Dioxide cell, or string of cells, it is not possible to implement on the BA5590 module due to the up-front control electronics, which includes fuse protection and diodes for charge feedback control [1]. The internal diode coupling, for example, in each cell string would rectify the charge-neutral excitation signal and corrupt the response. Thus, alternative impedance measurement techniques are required for successful health estimations of the BA5590 modules to assess their reusability and avoid premature discarding or recycling.

2. RAPID IMPEDANCE MEASUREMENTS TECHNIQUE

The Idaho National Laboratory, in collaboration with Montana Tech of the University of Montana, has developed novel approaches for acquiring impedance spectra using techniques that are significantly faster than standard EIS [7]. These techniques range from high resolution spectra (i.e., multiple data points within the impedance spectra) at the expense of measurement speed, or somewhat lower resolution spectra that can be achieved very rapidly. One technique that has been extensively validated is Harmonic Compensated Synchronous Detection (HCSD) [8]. Instead of a sequential measurement approach, HCSD uses a sumof-sines excitation signal that consists of frequencies separated by octave harmonics so as to eliminate the effects of crosstalk interference. With no crosstalk error, the duration of the excitation signal needs to be only one period of the lowest frequency. Thus, given a frequency range of 0.1 to 1638.4 Hz with 15 frequencies included within the sum-of-sines excitation signal (i.e., 0.1 Hz, 0.2 Hz, 0.4 Hz, 0.8 Hz, etc.), the measurement duration would only be ten seconds long. The overall battery response to the excitation signal is captured and then synchronously detected at each frequency of interest to determine the impedance spectrum.

Figure 1 shows a comparison between a standard EIS measurement and an HCSD measurement for a commercially available lithium-ion cell. The EIS data covered a frequency range of 10 kHz to 10 mHz and took approximately 10 minutes to complete. The HCSD data covered a frequency range of 1638.4 Hz to 10 mHz and was captured within 10 seconds; the filter on the prototype hardware was limited to 2 kHz. The high frequency tail on the left side of the spectrum at frequencies greater than 398 Hz typically captures equipment artifacts [6] and is not shown in this figure. The point at which the high-frequency tail crosses the real axis is the ohmic resistance (R_0) , which includes the effects from the electrolyte, electrodes, tabs, etc. The semicircle in the mid-frequency region identifies the effective charge transfer resistance (R_{CT}) , which is primarily influenced by the kinetic reactions at the electrodes due to an imposed constant voltage or current signal. The low-frequency tail on the right is known as the Warburg impedance that is caused by the diffusion of ions [9]. The semicircle trough, identified at 0.316 Hz, is the measured transition point between the mid-frequency charge transfer resistance and the low-frequency Warburg tail. These data identify changes in the bulk behavior of the electrochemical processes as the cell is aging (or varying in SOC) and can provide valuable insight into battery degradation mechanisms.



Figure 1. Comparison between EIS and HCSD measurements for a commercially-available lithium-ion cell.

As shown in Figure 1, the EIS and HCSD measurements are similar in the mid-frequency charge transfer resistance. Previous studies have demonstrated that the observed growth in HCSD measurements as a function of cell age successfully correspond to standard EIS measurements [8]. Additionally, it has been shown that the spectra change as a function of SOC and could therefore be used as a means of gauging battery health [10]. Another advantage of the rapid impedance measurement techniques is that the prototype hardware is portable and includes the capability of acquiring measurements under load conditions [11]; under load measurements would include superimposing a sum-of-sines excitation signal on a battery that is under discharge or charge. HCSD measurements under load conditions have been successfully captured and analyzed during previous validation testing efforts of lithium-ion cells [12].

3. EXPERIMENTAL

Test Setup

The challenge of measuring impedance spectra on BA5590 battery modules is that the diode will half-wave rectify the charge-neutral excitation signal (I_{SOS}) and corrupt any measurement attempts. By using the prototype hardware, however, it is possible to forward bias the diodes by modifying the input excitation signal with the addition of a small bias current (I_{bias}) to the sum-of-sines; thus, the input signal is no longer charge neutral but under a discharge load. Since the rapid impedance measurements require only 10 seconds or less at a very low current, the addition of a small discharge bias should not adversely affect the overall SOC of the BA5590 as a result of the measurement.

Although this eliminates the errors introduced with the input excitation signal, the captured voltage response will still be corrupted by the additional voltage drop across the diode. This can be addressed, however, with a minor modification to the prototype hardware, as shown in Figure 2. A matching diode (*CompDiode*) is put into the current path of the battery and a differential amplifier senses its voltage drop during the measurement. That measured voltage is input to the control hardware preamplifier system and subtracted from the captured response to eliminate interference from the diode when detecting the battery impedance spectra. Note, however, that this compensation approach requires matching diodes for the best results.



Figure 2. Concept for diode-coupled primary batteries.

Simulations

To verify this impedance measurement approach for diodecoupled batteries, an equivalent test cell circuit was designed as shown in Figure 3 and simulated using the various component values provided in Table 1. This test cell circuit model provides an impedance spectrum that is comparable to battery performance and has been used for the development of the hardware and control software of the prototype rapid impedance measurement techniques [8, 11]. The various parameter values identified in Table 1 are intended to simulate a broad range of impedance growth that may be observed from a battery as it is aged from a fresh condition to end-of-life. Circuit analysis of Figure 3 yields Equation (1), where V_{in} is the test cell voltage, I_{in} is the sumof-sines current plus the bias current, and Z_I is defined in Equation (2).

Table 1. Equivalent circuit test cell component values.

Cell	R1	R2	R3	С
TC2	$15 \mathrm{m}\Omega$	$15 \mathrm{m}\Omega$	$10 \mathrm{m}\Omega$	18F
TC4	$33 \mathrm{m}\Omega$	$33 \mathrm{m}\Omega$	$33 \mathrm{m}\Omega$	18F
TC6	$50 \mathrm{m}\Omega$	$50 \mathrm{m}\Omega$	$40 \mathrm{m}\Omega$	22F
TC8	$10 \text{m}\Omega$	$5 \mathrm{m}\Omega$	$5 \mathrm{m} \Omega$	21F



Figure 3. Circuit Diagram of a test cell.

$$V_{in} = I_{in} \left(R_1 + Z_1 \right)$$
 (1)

$$Z_{1} = \frac{R_{2}R_{3}}{R_{2} + R_{3}} \left(\frac{S + \frac{1}{C_{1}R_{2}}}{S + \frac{1}{C_{1}(R_{2} + R_{3})}} \right)$$
(2)

Using the relationships defined in Equation (3), the cell input voltage can be re-expressed in Laplace notation as shown in Equation (4). To solve this equation recursively, the method of Roberts [13], as defined by Equation (5), can be used if the sample time step, Δt , is selected such that it is much less than ω_1^{-1} and ω_2^{-1} . The final solution for the equivalent circuit in Figure 3 is then given by Equation (6), where x(n) is the recursive variable.

$$R_{EQ} = \frac{R_2 R_3}{R_2 + R_3}$$

$$\omega_1 = \frac{1}{C_1 R_2}$$

$$\omega_2 = \frac{1}{C_1 (R_2 + R_3)}$$
(3)

$$V_{in} = I_{in} \left(R_1 + R_{EQ} \right) + \underbrace{I_{in} R_{EQ} \left(\frac{\omega_1 - \omega_2}{S + \omega_2} \right)}_{X(S)}$$
(4)

$$S \to \frac{d}{dt}, \frac{dx}{dt} \approx \frac{x(n+1) - x(n)}{\Delta t}$$
 (5)

$$x(n+1) = I_{in}(n) (\omega_1 - \omega_2) R_{EQ} \Delta t + x(n) (1 - \omega_2 \Delta t)$$
(6)

$$V_{in} = I_{in}(n) \left(R_1 + R_{EQ} \right) + x(n)$$

To model the addition of an internal diode coupling for this equivalent circuit model, an ideal diode equation [14] is assumed. The simplified form of the resulting voltage $V_D(n)$ is given by Equation (7), where $I_{in}(n)$ is the sampled sum-of-sines excitation plus the discharge bias current, V_T is the diode thermal voltage (i.e., 26 mV), and I_s is the diode reverse saturation current (i.e., 1 nA).

$$V_D(n) = V_T ln \left(\frac{I_{in}(n)}{I_s} \right)$$
(7)

For the compensation diode (*CompDiode* in Figure 2), the voltage, $V_{CD}(n)$, was modeled the same way as shown in Equation (8). Since errors can be observed if the compensation diode is not perfectly matched with the internal diode coupling, the model in Equation (8) also includes an arbitrary mismatch of 5% to observe the resulting effects on the impedance spectra measurements.

$$V_D(n) = V_T ln \left(\frac{I_{in}(n)}{I_s} \right)$$
(8)

Simulation parameters were generally chosen to match anticipated conditions during actual cell testing and verification. The sum-of-sines excitation current signal was set to 62.5 mA RMS with a bias discharge current of 300 mA (i.e., a 300 mA constant current discharge with a superimposed sum-of-sines signal). The frequency range for the simulation differed from actual cell testing to adequately cover various semicircle sizes in the impedance spectra. For simulations, the frequency range is 0.0125 to 51.2 Hz, which results in an 80 second measurement duration for one period of the lowest frequency. The sum-of-sines excitation signal is shown in Figure 4. The bias current clearly forces the sum-of-sines to remain negative (i.e., discharge) at all times during the measurement and this ensures that the diodes are always forward biased. The sampling frequency of the captured voltage response was set to 40 kHz, which corresponds to the capability of the data acquisition system of the prototype hardware system. The resulting time step, Δt , is significantly smaller than any of the time constants from the test cell equivalent circuits in Table 1, so there were not any aliasing errors during the sampling. The simulated time record of the voltage response, $V_{TR}(n)$, with diode compensation is given by Equation (9) and this response signal can then be processed with the HCSD algorithms to generate the impedance spectrum.



Figure 4. Sum-of-sines and bias current time plot.

$$V_{TR}(n) = V_{in}(n) + V_D(n) - V_{CD}(n)$$
(9)

Cell Testing

The purpose of the physical cell testing was to determine the usefulness and repeatability of this impedance measurement technique with a preliminary scoping study using fresh BA5590 batteries. The first step was to verify the accuracy of this approach using a well-understood, commercially available lithium-ion cell chemistry that has been previously characterized and tested against standard impedance measurement techniques [7, 8, 10, and 12]. This high-power cell consisted of a graphite anode and a layered oxide cathode with Nickel, Manganese, and Cobalt [8]. A cell was initially subjected to an impedance spectrum measurement under normal conditions (i.e., no-load) over a frequency range of 0.1 to 1638.4 Hz. This corresponded to a ten second measurement using an excitation current level of 62.5 mA (RMS). The cell was then manually diode-coupled and the impedance measurement was repeated using the

same frequency range and excitation current level with the addition of a 300 mA discharge bias current (i.e., under load). The compensation diode was a model number 5820SM schottky, which is the same one used in the Army BA5590 modules.

Following lithium-ion cell verification, initial measurements were performed on four fresh BA5590 batteries using the same frequency range and excitation signal (i.e., 62.5 mA RMS sum-of-sines with a 300 mA bias discharge current). The modules were at a fully charged condition for this scoping study. The two individual cell strings within the modules were measured independently and each cell string was subjected to a total of four different measurements to determine overall repeatability and consistency of the resulting spectra. For each module, the first string of the five cells was measured back-to-back (labeled as "Run 1" and "Run 2"), followed by back-to-back measurements of the second string. Once all four module measurements were completed, the sequence was repeated (labeled as "Run 3" and "Run 4"). As with the lithium-ion cell chemistry, the frequency range for this scoping study was also 0.1 to 1638.4 Hz.

4. **Results**

Simulations

Figure 5 shows the simulated impedance spectra for the four test cell equivalent circuit models shown in Table 1. The ideal response, shown with the green "o" symbol, was calculated using standard frequency analysis techniques [8]. The simulated response, shown with the blue "*" symbol, was determined based on the recursive solution described in Equation (6) above. In all of the simulations, the HCSD response is offset from the ideal response because of the deliberate mismatch of the diode voltages in Equation (8). The diode mismatch causes an interference spectrum that corrupts the simulated response signal. Since the same mismatch was used on all simulation cases, the interference spectra are constant. The observed shift from the ideal in the test cell response, however, varies due to different sizes in the impedance spectrum. The low impedance spectra from test cells TC2 and TC8 show larger shifts whereas the higher impedance spectra from test cells TC4 and TC6 show a smaller shift.

Despite the impedance spectra offset, the size of the semicircle is similar in both height and width for each of the test cell simulation results. To illustrate, the impedance measurement of TC8 was repeated assuming a perfectly matched diode coupling. Figure 6 shows the resulting impedance spectra and that the HCSD response now perfectly overlays the theoretical response despite the significant shift observed in Figure 5(d). These data indicate that a diode mismatch mostly impacts ohmic resistance but does not significantly affect charge transfer resistance and that observed changes in R_{CT} can still be used to effectively gauge degradation in cells as a function of aging or changing SOC.



Figure 5. Nyquist plots of all the Test Cells.



Figure 6. Test Cell #8 simulation with perfect diode match.

Cell Testing

Figure 7 shows impedance spectra for an aged lithium-ion cell under: (a) a no-load condition; and (b) a diode-coupling condition under load (the coupling in this case was based on two reasonably well-matched diodes). The figures were captured from MATLAB control software, but the raw data were unfortunately lost. Nevertheless, these data demonstrate that ohmic resistance is the same for both measurements (approximately 30 m Ω), as expected for well-matched diodes in this case. Likewise, the midfrequency charge transfer resistance is similar, with a maximum height of approximately 90 m Ω on the imaginary axis and a semicircle trough at about 60 m Ω on the real axis. The spectra differ at the low-frequency Warburg tail since the diode-coupled measurement was captured under a load condition. This deviation in the low-frequency tail has been observed previously [12], but it clearly does not impact the critical mid-frequency semicircle region. Thus, these results demonstrate that it is possible to capture spectra from a diode-coupled battery under load conditions and acquire results that are highly comparable with a standard measurement under no-load conditions.

Following lithium-ion cell verification, impedance measurements were performed on four fresh BA5590 modules at full charge. The impedance of each cell string (i.e., "Side 1" and "Side 2") was measured back-to-back on each module (i.e., "Run 1" and "Run 2" on "Side 1," followed by "Run 1" and "Run 2" on "Side 2"). This sequence was then repeated (i.e., "Run 3" and "Run 4"). The cell string voltage was also recorded prior to each measurement. Figures 8 through 11 show the resulting spectra for all measurement runs on both cell strings for the four modules, respectively. The spectra in all cases are both consistent and repeatable and demonstrate the feasibility of this measurement approach. The semicircle arcs are generally similar in both height and width for all measurements, which is to be expected since they were all performed at roughly the same full charge condition.

The ohmic resistances are not easily identifiable in these spectra since the semicircle arc is not fully completed at 1638.4 Hz; this indicates that higher frequencies are required to capture the full arc. However, as mentioned above, the filter in the prototype hardware for rapid impedance measurements is limited to 2 kHz and modifications would be required to achieve higher frequencies. Nevertheless, the combination of both the ohmic and charge transfer resistances (i.e., the point at which the semicircle arc crosses the real axis on the right hand side) can be clearly identified on all spectra measurements. The behavior of the Warburg tail is similar to the observed effects from the lithium-ion cell in Figure 7. There also appears to be a relationship between the angle of the tail and the voltage. The tail generally tends to drop lower as the measured voltage is reduced. This effect will need to be investigated further, especially as measurements are performed at lower SOCs.



Figure 7. Lithium-ion cell impedance measurements under (a) no-load conditions and (b) load conditions with diode compensation.

Figure 12 shows the measured voltage immediately prior to each impedance measurement. The cell voltages generally dropped between the back-to-back measurements (i.e., between "Run 1" and "Run 2," as well as between "Run 3" and "Run 4"), which is expected since the excitation current includes a small discharge load. However, the cells also generally show a small voltage recovery between "Run 2" and "Run 3" when a longer rest period was included. These data indicate that the addition of a discharge bias current does not significantly impact the SOC condition of the BA5590 module since the measurement is only ten seconds long.









Figure 9. Impedance spectra for Module 2 on (a) Side 1 and (b) Side 2.





Figure 10. Impedance spectra for Module 3 on (a) Side 1 and (b) Side 2.







Figure 11. Impedance spectra for Module 4 on (a) Side 1 and (b) Side 2.



Figure 12. Measured voltage prior to each impedance measurement.

Figure 13 shows the measured combination of both the ohmic and charge transfer resistances calculated from the spectra (i.e., the point at which the spectra cross the real axis). The real impedance in all cases is relatively similar and ranges between 3.2 and 2.6 Ω with an average of 2.9 Ω . Since all of these measurements were performed at or near full charge, it is to be expected that the impedance values should be similar. Thus, the data indicate that this rapid impedance measurement approach can yield consistent and repeatable results for diode-coupled batteries such as the BA5590.



Figure 13. Measured combination of both the ohmic and charge transfer resistances calculated from the spectra.

5. SUMMARY AND CONCLUSIONS

The BA5590 module is a commonly used battery in military communications and surveillance systems in both training and combat missions. Although standard impedance spectroscopy measurements are a useful diagnostic tool for battery health assessment, the technique cannot be readily applied to the BA5590 since it contains up-front protection circuitry that would completely corrupt the measurement. The rapid impedance measurement technique, however, provides additional flexibility in capturing the spectra based on minor modifications to both the excitation signal and captured response. The excitation current signal is placed under a discharge load condition and the additional bias voltage due to the diode coupling is subtracted from the response signal using a matching diode that is placed in the current path. Preliminary results clearly indicated that these modifications enable consistent and repeatable impedance spectra on the BA5590 modules. The voltages prior to each measurement show that the SOC is not significantly affected by the addition of a small bias discharge current and the overall resistances calculated from the resulting combination of both the ohmic and charge transfer resistances were similar for all acquired results at or near a full charge condition. Thus, it is possible to obtain impedance spectra on diode-coupled batteries for state-ofhealth estimations and reusability assessments.

6. FUTURE WORK

This preliminary scoping study has clearly demonstrated the possibility of capturing impedance spectra on BA5590 modules. The measurements up to this point have only been performed at or near full charge conditions and additional studies are required to assess the change in spectra as a function of the state-of-charge. These data would enable the development of a battery health metric for the BA5590s that could yield an almost instantaneous assessment of used batteries to determine if they may be reissued on another mission or should be discarded or recycled. Other studies supporting this health assessment effort would include characterizing the spectra at various temperatures.

The prototype hardware should also be upgraded to allow for measurements greater than 2 kHz so as to fully capture the charge transfer resistance (i.e., the width of the semicircle arc). However, since it is anticipated that both the ohmic and charge transfer resistances will be affected by state-of-charge, it should still be possible to develop a battery health metric even if the hardware upgrades are not completed prior to future studies with the BA5590.

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Biographies



Jon P. Christophersen received a B.S. and M.S. in electrical engineering from the University of Idaho (Moscow, ID) in 1999 and 2005, respectively, and a Ph.D. from Montana State University (Bozeman, MT) in electrical engineering in May 2011. He has been

a research engineer with the Energy Storage and Transportation Systems Department at Idaho National Laboratory since February 2000. He has lead responsibility for all high-power-cell testing, analyses, and reporting under the U.S. Department of Energy's Applied Battery Research and Technology Life Verification Testing Programs, as well as various battery and ultracapacitor manufacturer deliverables as part of the U.S. Advanced Battery Consortium (USABC) Program. His research interests include battery life prognostics and state-of-health estimation. He received an R&D 100 Award in 2011 for the Impedance Measurement Box, which offers innovative breakthroughs on rapid impedance measurement techniques for onboard monitoring of energy storage devices. He has authored or co-authored over 15 peer-reviewed journal publications; holds 2 patents, with several additional patents pending; and has presented numerous conference proceedings papers and presentations related to energy storage testing, modeling, and prognostics.



John L. Morrison has been teaching Electrical Engineering courses and advising graduate students for Montana Tech of the University of Montana since 2001. He had taken early retirement from the Idaho National Environmental and

Engineering Laboratory (INEEL) in the early summer of 2001. He holds a Ph. D. in Electrical Engineering from the University of Idaho (1992) and an M.S. and B.S. in Electrical Engineering from the University of Connecticut (1967, 1968). He previously taught Electrical Engineering courses for the University of Idaho branch in Idaho Falls. He served as a Visiting Professor at Idaho State University in Pocatello, Idaho, for a 3-year appointment (1997–2000). He received an R&D 100 Award in 2011 for the Impedance Measurement Box, which offers innovative breakthroughs on rapid impedance measurement techniques for onboard monitoring of energy storage devices.



William H. Morrison is a Visiting Research Scientist with Montana Tech. Mr. Morrison's interests are in the development of control software for real time measurement and control systems, intelligent prognostic and diagnostic solutions and algorithms,

and finding new and innovative ways to apply them. Past projects include data normalization for the Pratt & Whitney F119 engine; fault diagnostics and prognostics for the F/A-18 C/D aileron servoactuator, including the development of a complete nonlinear Simulink model of an electrohydraulic servovalve; development of a data driven prognostic solution for the Advanced Airborne Sensor as part of the Airborne Laser Theater Missile Defense Program; and prognostic monitoring of the nozzle and actuation hardware for the F135 engine for the Joint Strike Fighter. Mr. Morrison is also interested in intelligent prognostic and diagnostic solutions and algorithms and finding new and innovative ways to apply them. Mr. Morrison received his Bachelors of Science in Electrical Engineering (2003) and his Master of Science in Electrical Engineering (2012) from the University of Connecticut. He also received an R&D 100 Award in 2011 for the Impedance Measurement Box, which offers innovative breakthroughs on rapid impedance measurement techniques for onboard monitoring of energy storage devices.