MULTIPLE MODEL IMPEDANCE SPECTROSCOPY TECHNIQUES FOR TESTING ELECTROCHEMICAL SYSTEMS

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One critical problem in using batteries as a source of power for automobiles or for emergency backup systems is to know whether or not the battery will do its job. Is the state of health of the battery sufficient for the task demanded of it? Ohmic techniques, which measure changes in the impedance of a battery, have been implemented to monitor the battery's state of health (see Ref. 7 for a review; Ref. 1,2,5,10,11). These techniques, however, do have weaknesses. Here, I will explain the more critical problems associated with Ohmic testing and I will propose a novel solution.

WHAT IS AVAILABLE CURRENTLY?

Before understanding these weaknesses, it is necessary to know how Ohmic techniques are used to assess the battery's state of health. There are two main methods[1], each one used for a different purpose – repeated testing of the same battery (suitable for stationary, emergency backup systems) and 'first time' testing (suitable for automotive batteries).

Stationary batteries

Most commercial methods use only one frequency that is kept below 100Hz and only the real component of the impedance is used (Ref. 7,3). More advanced units measure complex impedance. Using these data, a particular battery is tracked across time and changes in the impedance of the battery are noted. These changes in impedance *may* result from the degradation of the battery and are used to determine which battery cells should be replaced.

In most applications, a technician tests each cell in the battery bank, imports the data into a software package, and then this software tracks the changes in impedance across time. Online monitoring systems are also available, in which the cell impedance or voltage are measured continuously, while the battery is still in operation. On-line testing requires a significant capital investment (specialized monitoring circuitry for automotive applications also available).

Automotive batteries

To determine the health of a novel battery, the impedance data is normalized using preset values to determine cold cranking amps (CCA). This technique is housed in a small portable unit, so that it may be used in automobile service centers.

THE 'ONE FREQUENCY' DILEMMA: PROBLEMS AND POTENTIAL SOLUTIONS

The one limiting factor in using these methods for stationary and automotive battery testing is that only a single frequency is used to excite the battery. This is not a trivial problem because it does not provide enough information about the battery to effectively judge its state of health. Consider an analogy. When visiting your family physician for a yearly physical examination, if your doctor only measured your temperature, would you believe that this is a sufficient assessment of your health? Unlikely. Yet, this is how a battery's state of health is measured.

Using only one frequency to measure state of health originates from a trade-off between two factors -- the sensitivity of the unit versus its complexity and cost. However, the restrictions inherent in using one frequency avalanches into a host of other problems, some of which are mentioned below.

If only one frequency is used, which frequency is the best choice?

Several factors are at play, the equipment available for testing, the type of battery, and the type of measurement required – state of health (stationary and automotive batteries) or state of charge (automotive).

[1] There are of course other types of test methods available, such as DC Ohm tests. This paper will mainly focus on techniques that have been known to the industry as impedance methods.

Battery capacity is correlated with ohmic resistance, with the best correlation obtained when impedance is at a minimum (the phase angle between the voltage and current waveforms is zero; Ref. 6). Accordingly, the best frequency to use (i.e., the one providing the minimum phase change) will change depending on the battery being tested. This explains why one battery analyzer may perform well for one type of battery, but performs poorly for another (Ref. 6). The correlation to capacity for the null reactance case is also less than perfect.

This is a significant problem for larger stationary batteries. For the accurate assessment, the excitation frequency should be less than 20Hz (Ref. 14). Most commercially available techniques excite the batteries at a relatively high frequency, though (83-90 Hz; Ref. 7). Doing so reduces the range of batteries that can be assessed with reasonable precision, only those with a capacity of 0 - 75% will be assessed precisely (Ref. 10), whereas batteries above 75% capacity will not. Considering, however, that IEEE 450 guidelines demand that all batteries below 80% capacity be replaced, the ability to detect a failing battery is in the same region that the analyzer is the least reliable. Moreover, it would be more desirable to predict when the battery will fail, as opposed to reacting to its failure. Accordingly, it would be desirable to precisely assess the capacity of a battery within this 75 – 100 % range.

For the automotive market, it is not always the case that a battery is at a 100% state of charge level when it is tested. The state of charge of a battery affects its impedance (Ref. 13). Because state of health is assessed through impedance, the state of charge will influence the obtained state of health if only one frequency is used.

Modeling circumvents the ‘one frequency’ problem, but evokes another --which model should be used?

Electrochemical models have been used to circumvent the one frequency problem, in which electrical components are used to construct a circuit. The complex impedance response of the circuit will change depending on the components chosen. For example, Randle’s model (figure 2) infers the full impedance spectrum from a single frequency. Using a single variable to probe a multivariate problem requires many mathematical and electrochemical assumptions. These assumptions are beneficial insofar as simplifying the algorithm so that it may be used on inexpensive micro-controllers. However, there are an infinite number of possible combinations of models. How does one choose which model is the best candidate?

A SIMPLE SOLUTION? TESTING A SPECTRUM OF FREQUENCIES ACROSS NUMEROUS MODELS

The obvious way to circumvent the aforementioned issues is to use a wide range of frequencies to excite the battery and several different models to assess the data. Albeit simple in theory, a full spectrum analysis is not simple in practice. Producing an analyzer that can excite a battery over a spectrum of frequencies is expensive. Commercially available analyzers of this sort require costly laboratory equipment and a specialized technician to interpret the data.

Spectro reflects Cadex’s solution to this problem. Figure 1 depicts a system overview of the technique.

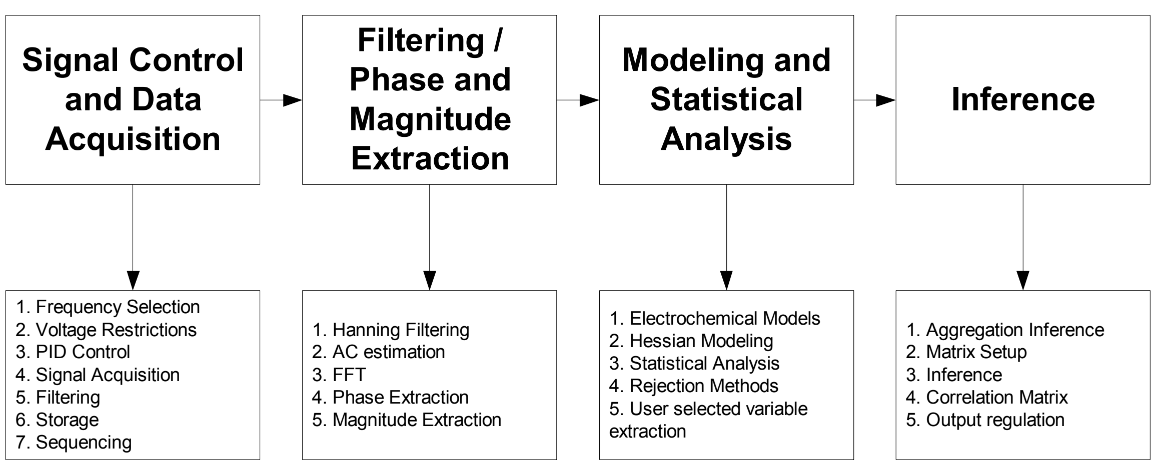

Figure 1: System Topology

A full frequency spectrum (20-2000) Hz is injected into the battery, which eliminates many of the aforementioned problems and provides a smooth impedance transition from one frequency to the next. This creates a full impedance spectrum of the battery, otherwise known as impedance spectroscopy.

However, the battery is an extremely complex system, involving coupled non-linear electrochemical reactions and transport processes (Ref. 8,9). This non-linearity will result in the production of a set of harmonic frequencies, when a fundamental frequency is applied (Ref. 9). When the battery is minimally perturbed (regulated to 10 mV across each cell), its response is may be viewed as linear through mathematical approximation. Potentiostatic, or voltage-controlled excitation (described above) is used to produce a pseudo linear response. Unlike galvanostatic, or current-controlled excitation, it scales automatically with the battery's capacity, so that as the battery capacity increases, the excitation required also increases. By contrast, galvanostatic excitation has some disadvantages if linear excitation is required. For instance, if the current is set too low, only small batteries will be adequately driven, whereas if the current is set too high, a pseudo linear approximation is invalid. By controlling the voltage directly, through potentiostatic excitation, the current is regulated automatically and the excitation is proportional for small and large batteries.

Normally, impedance spectroscopy requires dedicated equipment and a computer to analyze the obtained data. To permit such analyses on a hand held unit, digital signal processing is used to analyze each frequency to produce a magnitude and an equivalent phase between the input and output waveforms. In addition, a self-correcting mechanism is also employed to identify any parts of the frequency spectrum that do not transition smoothly. This is combined with a cable impedance correction to deliver an accuracy of ±250 μΩ across the full spectrum.

Moreover, the system is robust against changes in DC voltage and noise in the system. The excitation and sensing of the unit is isolated from the DC voltage. This allows the analyzer to test a battery when it is under a charge/discharge condition. Digital signal processing techniques remove any other unwanted AC signals in electromagnetically noisy environments because the unit is aware of the frequency injected into the battery and will therefore only analyze the response for that frequency only. Finally, real time digital filters may further increase the repeatability of readings and remove all unwanted signals

Being able to collect data across many different frequencies is only half of the solution. An important issue is how to interpret the impedance spectrum for the user. The system houses a library of non-linear electrochemical models to which the data are fit, and solves the model coefficients quickly and with the least amount of calculations. A Levenberg-Marquart method is used for this task. One advantage of this method is its relatively low computation times because the solution converges rapidly. A second is that the initial seeding guess does not need to be in the neighborhood of the final solution. This gives the algorithm robustness when it encounters different battery types.

For example, there are three main components to Randle's model shown in Figure 2. These may be described by the following equation:

$$Z = R_1 + \frac{R_2 - j\omega C R_2^2}{1 + \omega^2 C^2 R_2^2}$$

Where $\omega=2\pi f$ and $j=\sqrt{-1}$. From here, the real (Z') and imaginary (Z") components can be easily derived:

$$Z' = R_1 + \frac{R_2}{1 + \omega^2 C^2 R_2^2}$$

$$Z'' = -\frac{\omega C R_2^2}{1 + \omega^2 C^2 R_2^2}$$

The non-linear algorithm finds the coefficients for the above equation with respect to frequency for both the real and imaginary components.

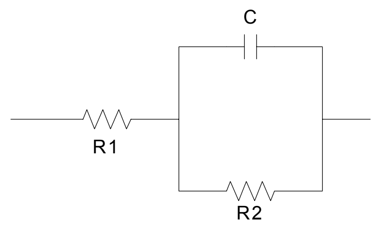

Figure 2: Randle's model of a lead acid battery

The frequency range is adjusted automatically to provide the most optimum fit and, if a particular model does not account for a specified proportion of the variance, the model is rejected. In general, each electrochemical model describes a portion of the impedance spectrum quite well. Mathematically this may be described as a piecewise continuous system. By incorporating a number of models, we can describe the entire spectrum with reasonable accuracy, which increases the repeatability and reliability of the calculated readings.

Once the fitting procedure is complete, the algorithm determines which elements of a particular model are correlated to the battery parameters that the user wishes to estimate. A second correlation library is used for this purpose. For example, if the user wishes to estimate the CCA of a battery (Fig. 3), then element R1 of model 1, elements R2, C1 of model 2, may be used. These values are processed in a data fusion algorithm and the estimated result is reported to the user.

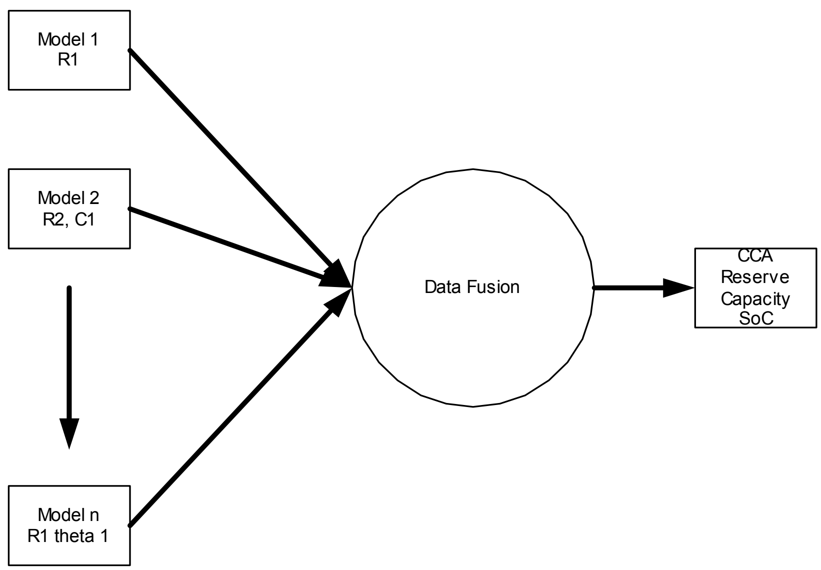

Figure 3: Data fusion algorithm

The data fusion algorithm relies on a set of numbers, or a matrix, to produce the result. A generic matrix may be constructed for large classes of battery types -- for example, all automotive lead acid batteries[2]. Although this provides sufficiently high accuracy for most users, it can be further optimized for a particular battery model.

[2] More then likely a different type of generic matrix would be required for AGM batteries.

EFFECTIVENESS OF SPECTRO.

To date, over 190 automotive batteries have been evaluated under various conditions. Figure 4 shows the test between CCA and reserve capacity for each battery and the system's estimated CCA[3].

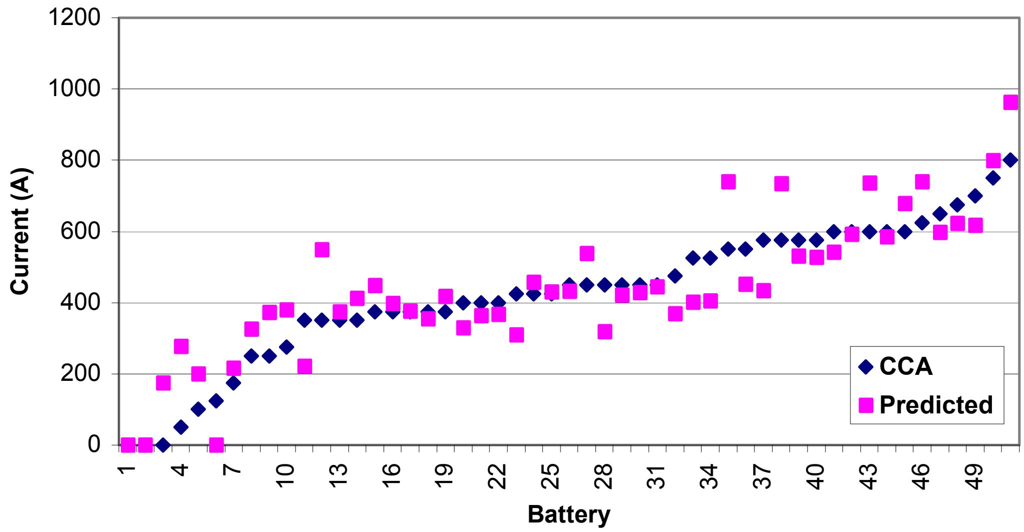

Figure 4: Cumulative test results of 50 different batteries, of various types and state of health levels.

The diamonds in this figure represent the true CCA of the battery. CCA was determined using the procedures outlined in SAE J537 sec 3.7. Because CCA is a pass/fail test, a stair case technique was used to find the exact CCA within ±50A. The battery was charged, cooled, and then tested at a set current level. If the test failed, this procedure was repeated, but at a lower current, until it passed. The squares in the figure indicate the CCA estimates using 14 separate electrochemical models. The accuracy with respect to the measured CCA was ±10% A. For this test, the data fusion matrix used was generic, meaning that it was not optimized for a particular battery model.

In most instances, the user wants to know whether the battery has a CCA rating less than 80% of that indicated by the manufacturer (a failure). For every battery tested under these conditions, the system has identified 83% of all failed batteries. This is a 3-fold improvement over competing commercial units.

These results improve when the data fusion matrix is optimized for a particular battery type. The results from an optimized matrix are shown in Figure 5 for a population of batteries from the same manufacturer, but at varying state of health levels. This optimization procedure involves 'showing' the matrix one healthy battery and the implementation of a learning algorithm that extends this 'ideal' case across the population of batteries tested.

[3] Not all 193 batteries are shown in order to reduce clutter. The results are similar and available upon request.

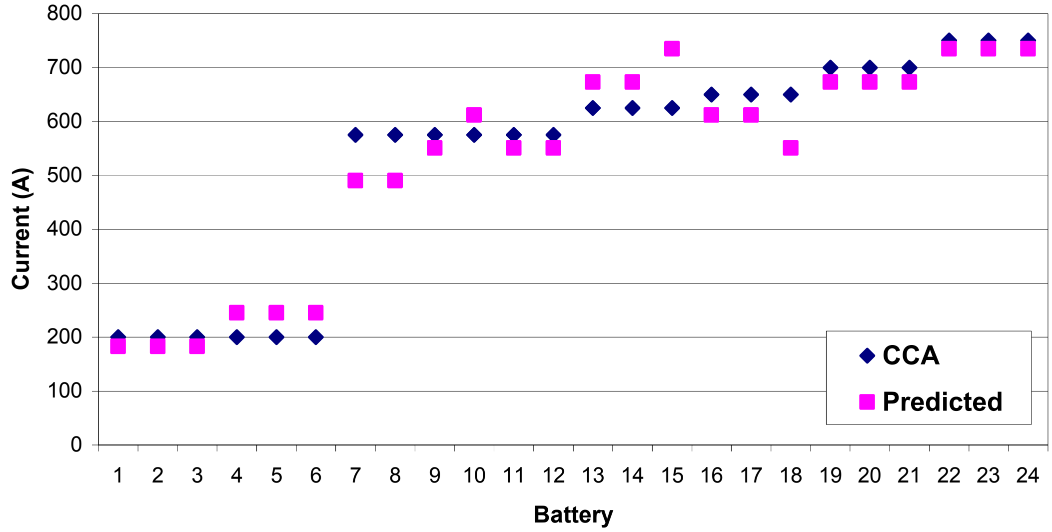

Figure 5: Optimized output using learning.

In this case, the error in CCA estimates was ±7% A, and the system identified all batteries that were performing less than 80% CCA. The results were very stable between (50-100)% SoC levels.

As the sophistication of automobiles increases, more demand is placed on the capacity of the battery, as opposed to its cranking ability. For instance, electric braking methods demand that the battery's capacity is maintained at a sufficient level. Estimating the capacity of an automotive battery is much more difficult task, however, because capacity is more sensitive to changes in battery architecture than cold cranking ability. For stationary batteries, determining the capacity of a cell with high reliability, without needing to remove it from the bank, may fundamentally change how stationary battery banks are monitored.

Several of the models in the system's present library correlate well with capacity measurements. Figure 6 demonstrates the reserve capacity estimation for 40 batteries using a generic reserve capacity matrix. For capacity, each battery is rated in minutes, which can reach 180 minutes when under a constant 25A discharge. In this instance, the system estimated the reserve capacity within ±13% of the actual capacity.

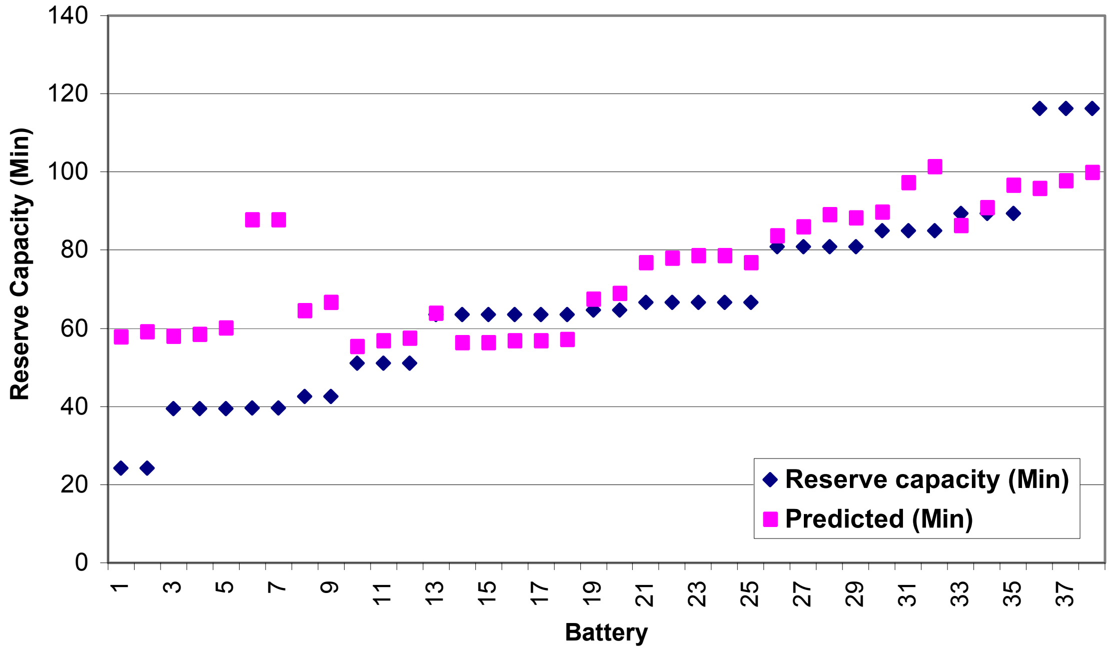

Figure 6: Reserve capacity estimates for 40 batteries using a generic matrix

As with case of CCA results, optimizing the matrix for a particular battery type increases the accuracy of the result. An example of this is shown in Figure 7. Here, the error was reduced to ±9 %. Of course, the accuracy of this result will vary depending on the type of batteries tested.

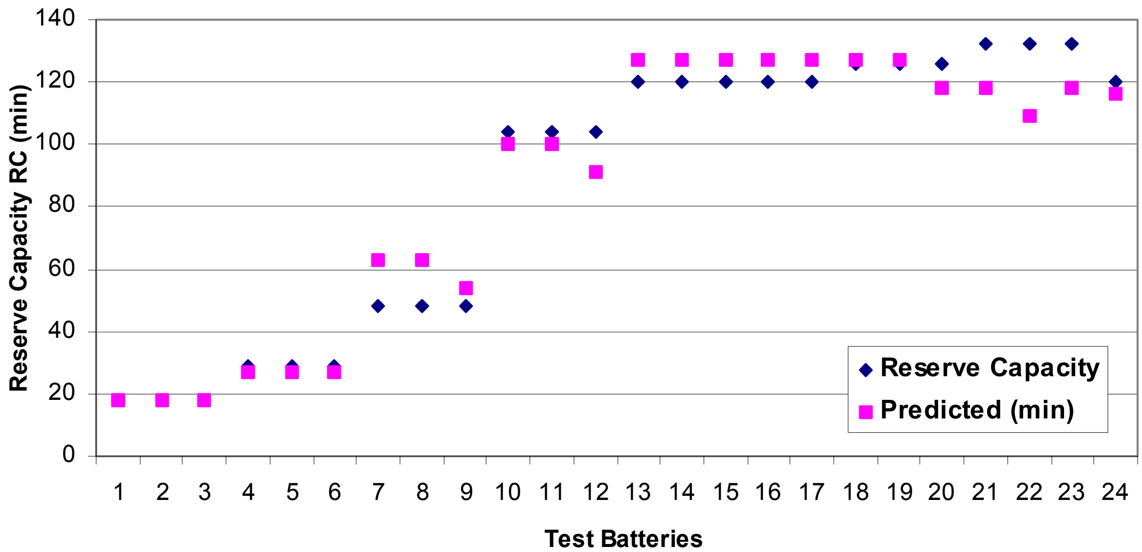

Figure 7: Reserve capacity estimates for a model specific battery

For stationary batteries, the frequency used to excite the battery should be lower than 20Hz when testing batteries with capacities higher than 80% (Ref. 12). Lowering the frequency produces a practical problem, however, because it increases the time required to test each cell -- ~1 minute per cell using standard techniques. This timeframe is not feasible, as it is 6 times longer than other commercially available test. Recently, we have developed a technique, specific for stationary batteries, that excites the battery at as low as ~1Hz waveforms and completes the test within 15 seconds.

For both automotive and stationary batteries, the method described provides the result to the user in a short amount of time and in a format that is simple to interpret. Currently, we are implementing new electrochemical models so that other battery types, such as fuel cells, may be tested as well. All told, our results indicate that this method, which uses a spectrum of excitation frequencies in combination with several electrochemical models to fit the out-coming data, is an effective tool to estimate the CCA and reserve capacity of batteries.

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