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Multiple model impedance spectroscopy techniques for testing electrochemical systems

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Abstract

In recent years, a number of fundamental problems associated with impedance spectroscopy techniques for testing electro-chemical systems have come to light. This paper will briefly attempt to explain some of these difficulties and propose a possible solution.

Keywords: Impedance spectroscopy; Battery state of health

1. Introduction

There are numerous studies that link ohmic techniques to battery state of health (SoH) analysis (Markle [1], Markle [2], Albèr and Migliaro [3], Feder et al. [4], Damlund [5]). Huet [6] gives an excellent overview of the current state of impedance analysis used on electrochemical cells. In recent years, a number of fundamental problems associated with these current techniques have come to light. Most commercial methods for impedance analysis described by the literature use only one particular frequency, usually kept below 100 Hz. The reason for this is an amalgamation of technical difficulties, interpretation and cost. In order to analyze the data, enough memory and computational ability is required to facilitate some type of usable result. In most cases, only the real component of the impedance is used. More advanced units provide complex impedance data but this still only produces a comparative measure to the user. For example, the user may track a particular battery over time and see how the impedance degrades. This method may only realistically be used with online monitoring systems. Another format is to normalize the impedance data and utilize a user defined multiplier in order to correlate impedance with values such as cold cranking amps (CCA).

An obvious problem is if only one frequency is used, which shall it be? To answer this question, the defining arguments will depend upon the equipment available, battery type, and the sort of measurement required such as state of health or state of charge (SoC). The literature suggests that battery capacity may be correlated to ohmic resistance (Hawkins and Barling [7]). This is described as the point where the impedance is at a minimum, which occurs when the phase angle between the voltage and current waveforms is zero. Unfortunately, the frequency that will provide this minimum phase changes with capacity. This means that some battery test equipment will perform better on one battery then another (Hawkins and Barling [7]).

One method to circumvent the frequency choice problem is to employ an electrochemical model equivalent of the cell. One that is commonly used is Randles model given in Fig. 1:

Using this model, the system may infer the impedance spectrum, thereby estimating the minimum impedance without directly exciting the battery at the required frequency. Without making estimates, different excitation frequencies are required since this is a multivariable problem. However, certain assumptions may be made to simplify the calculation such that it may be performed on common μ-controllers. The difficulty arises in the model itself. For example, what if we add an inductor or another RC network? There are

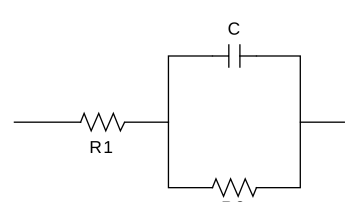

Fig. 1. Randles model of a lead-acid battery.

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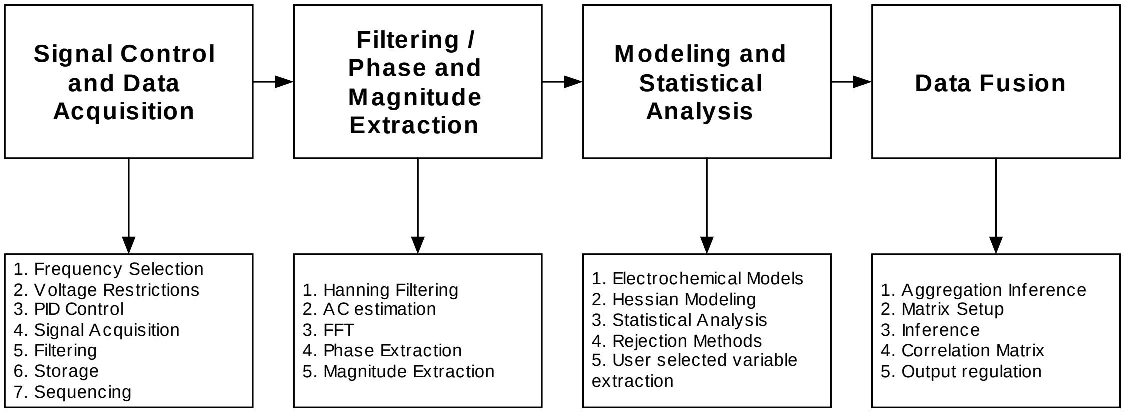

Fig. 2. System topology.

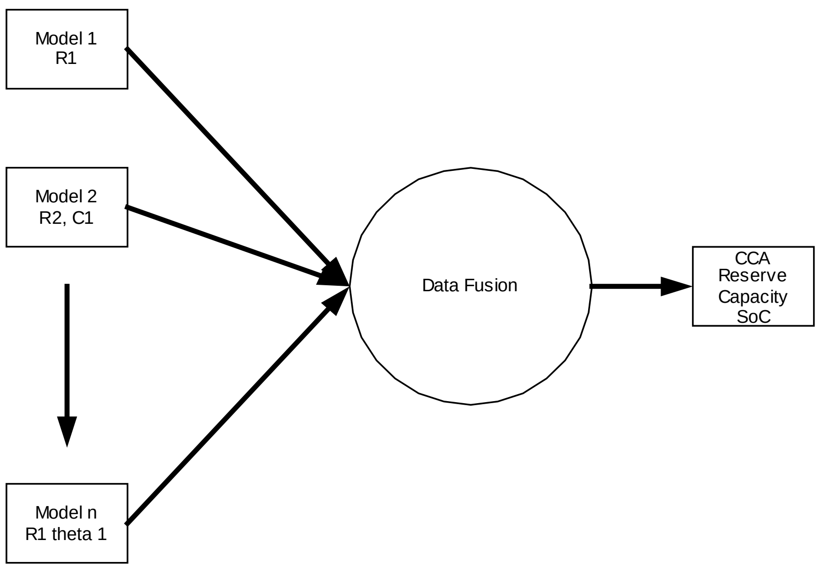

Fig. 3. Data fusion algorithm.

an infinite number of possible model combinations so how does one choose which is the best candidate?

2. The Spectro equipment

Spectro, being developed by Cadex Electronics Inc., attempts to rectify these problems considered above in one unit. Fig. 2 depicts a system overview of the technique.

The first unit is a signal control and data acquisition block. A full frequency spectrum (20–2000 Hz) rather than just one particular frequency is employed. This overcomes a number of difficulties listed above. Moreover, it provides the ability to measure both the SoC and various other battery parameters. An added advantage is the reliability of readings is increased since we can assume a smooth transition from one frequency to the next.

The battery is an extremely complex system involving coupled non-linear electrochemical reactions and transport processes (Liaw and Bethune [8], MacDonald [9]). Non-linearity will in general produce a set of harmonic frequencies in response to a perturbation of a fundamental frequency (MacDonald [9]).

If, however, the battery was excited with a minimum amount of perturbation, a pseudo-linear regime may be approximated. The system regulates the excitation voltage to a level of 10 mV across each cell ensuring linear operation.

To deal with the data collection on such a scale, a digital signal processor is used to process the data off line for each frequency to produce a magnitude and an equivalent phase between the input and output waveforms. We also take advantage of using real time digital filters to increase repeatability of readings and remove any unwanted signals in electromagnetically noisy environments.

Even if data collection is performed on a number of separate frequencies, the problem of how to analyze the result is still difficult to answer. The system uses a library of different electrochemical models[1] to fit the data. The frequency range is automatically adjusted to provide the most optimum

[1] At the time of writing, 14 models are currently in the library.

fit. If a particular model fails to attain a certain quality of fit, the model is rejected. In essence, each electrochemical model tends to describe a portion of the impedance spectrum quite well. By incorporating a number of models, we describe the entire spectrum with reasonable accuracy, which is beneficial in increasing 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 parameter the user wishes to estimate. This is accomplished by using a secondary library. For example, in Fig. 3, if the user wishes to estimate the CCA of a battery, then element R1 of model 1, element R2, C1 of model 2, etc. may be used. These values are processed in a data fusion algorithm and the estimated result is reported to the user.

3. Results

The current test results using this method are quite promising. To date over 100 standard automotive batteries in various conditions have been evaluated. Before being tested with the Spectro technique, the CCA and reserve capacity of all batteries was established using SAE J537. Results are shown in Fig. 4.

The diamonds in Fig. 4 represent the true CCA of the test battery. The CCA was determined using procedures outlined in SAE J537 sec 3.7. The squares indicate Spectro CCA estimates using 14 separate electrochemical models. The accuracy with respect to the measured CCA is ±80 A. The data fusion matrix is static and has not been optimized for an individual battery model. This data purely represents the output with a known indicated CCA of the battery provided by the user.

Most users are primarily interested in battery failure detection. A failure in this case is defined as a CCA rating less than 80% of that indicated by the manufacturer. For the current population, Spectro was able to identify 83% of all failed batteries. This is approximately a three-fold increase to competitive commercial units.

When the data fusion matrix is optimized for a particular battery model, a sufficiently higher degree of accuracy may be established. Indeed, such a function has been incorporated into the device. The batteries contained in Fig. 5 are of one model type but at varying SoH levels.

The error with respect to CCA in this case is (-10 ± 30) A. Learning was performed on one healthy battery. It appears with proper initial calibration fairly reasonable CCA estimates may be obtained. We have also found that the results are relatively stable between 40 and 100% SoC levels.

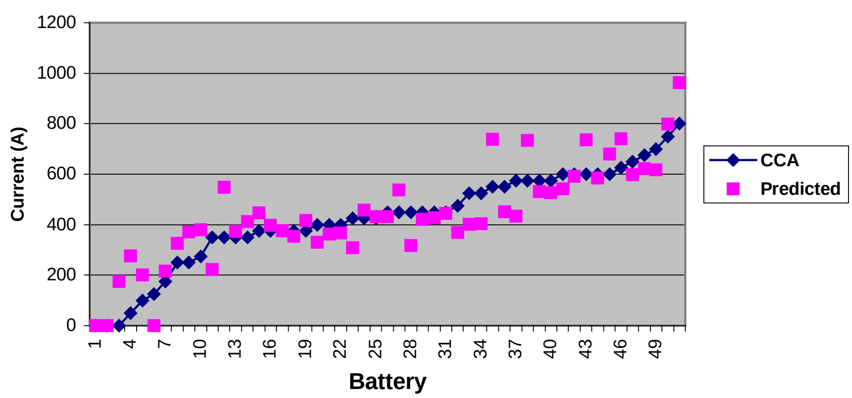

Fig. 4. Cumulative test results of 50 different batteries of varies models and state of health levels.

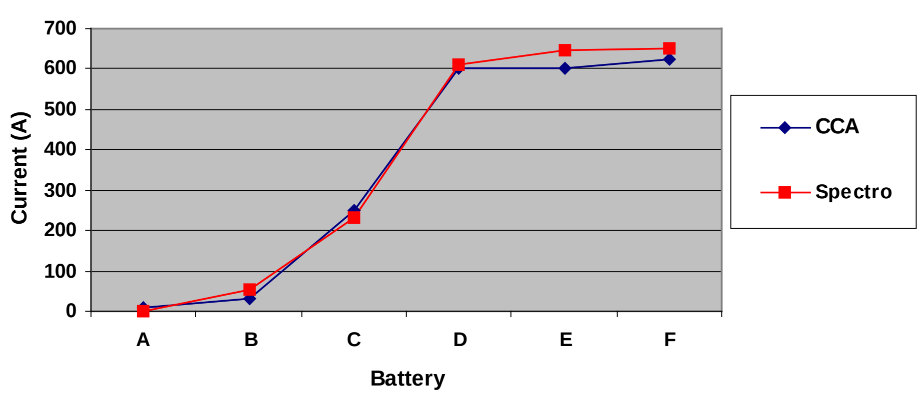

Fig. 5. Optimized output using learning.

The method supplies the user with a result that is simple and understandable in a minimum amount of time. The algorithm may be easily upgraded to include new electrochemical models for other battery types or applications such as fuel cells. The converging results provided by a number of electrochemical models may potentially provide a robust tool in establishing reliable CCA and SoC estimates. Further work is ongoing to also provide estimates for battery reserve capacity.

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