Application Note

solartron analytical

ModuLab XM ecs

Application Note

Electrochemical Impedance Spectroscopy - A Battery Monitoring and Fault Diagnostic Tool

Introduction

Integration of new battery technologies for portable devices and automotive applications necessitates development of reliable test and diagnostic algorithms. These include determination of the State of Charge (SoC), State of Health (SoH) for battery lifetime, internal temperature and fault finding within cell packs. Existing methods have some shortcomings. This short paper highlights some of the traditional techniques already used in the battery monitoring environment and how Electrochemical Impedance Spectroscopy (EIS) is being developed to improve the techniques and provide more accurate estimates of critical battery parameters.

This paper provides a brief introduction to EIS by contrasting the information EIS measurements can determine with respect to the traditional time domain techniques. The paper then discusses the commercial implications of battery warranty returns and how this is in part due to the test protocols in-use within the battery industry. Finally, we present examples in which EIS was used to help develop test procedures that should help engineers produce more accurate and reliable battery management and diagnostic tools.

Electrochemical Impedance Spectroscopy (EIS)

Our discussion will be limited to the differences between time and frequency domain techniques since this is the key differentiator between EIS and the other techniques.

It is useful to start with time domain techniques such as Cyclic Voltammetry, Current Interrupt and others. In such tests, the cell is polarised to a defined voltage or current and the response of the cell is recorded as a function of time. The benefit of these techniques are the simplicity of the hardware. However, the response is a composite of all electrochemical processes and for black box devices (batteries, fuel cells, supercapacitors), analysis of data is difficult as careful post-data analysis is required to de-convolve simultaneous electrochemical processes.

Systems employing EIS make use of the fact that processes in electrochemical devices can be deconvoluted by simply changing the measurement frequency. For example, applying a small AC sinusoidal wave to a battery at high frequencies measures only the ESR (equivalent series resistance) and inductance of the cell. At high to mid-frequency electrode reactions dominate the spectra. At lower frequencies, the AC input stimulates long time constant processes such as migration and diffusion. It is this ability to separate these processes in the frequency domain that makes EIS stand out from all other techniques. From this, models based upon passive circuit elements such as capacitors/resistors/inductors can faithfully simulate the internal electrical properties of the cell which in turn can then be used to fit real time data for improved diagnostic capability. We shall show examples of this in action in subsequent sections.

AMETEK

False Positive Readings in the Automotive and Consumer Electronics Sector

A false positive reading is one in which the device has failed a test procedure, but is subsequently shown to work according to the original manufacturers specifications.

Examples of false positive testing failures are numerous in the automotive sector. A recent AMETEK interview with a prestigious German car manufacturer highlighted the scale of the problem. They estimated that at least 3 in 5 reported warranty battery failures showed no sign of degradation or fault upon further inspection. Similar figures have been reported elsewhere. The situation is more pronounced in portable Lithium-Ion battery technologies in which > 75% of battery ‘failures’ were subsequently shown to be false positive readings. Such false readings are both expensive to the manufacturer and are bad for brand image.

Case Study:

- A manufacturer of portable devices, was suffering > 30% warranty returns as a result of suspected Li-Ion battery failure. Existing test methods could not help them differentiate good batteries from failures. They eventually concluded that EIS was the most powerful tool to help them develop past / fail algorithms.
- They estimated cost savings in the region of 2 million Euro’s per annum in warranty repairs if they could develop more accurate tester with fewer false positive results. In addition, the customer was especially concerned about the damage to their reputation, therefore, significantly reducing warranty returns due to suspected battery issues was a high priority.
- The customer implemented EIS into their test program and immediately determined their battery manufacturer had quality control issues.
- EIS testing is now used as part of incoming goods inspection.

The following sections discusses how researchers are using EIS to improve cell diagnostics. We will focus on three specific issues:

State of Health

State of Charge

Fault Diagnosis in Stacks

State of Charge

State of Charge (SoC) indicates the lifetime of the battery BETWEEN charges. As such, it is a critical tool for providing information to the end user about anticipated battery usage at current discharge rates. For example, full EV automotive applications require accurate on-board determination of charge to avoid running out of power unexpectedly! While perhaps less critical for handheld applications, inconsistencies between the calculated SoC and real SoC are a concern for the device manufacturers and annoying for end users.

The most common method of determining the State of Charge is with a technique known as Coulomb Counting. In essence, the battery monitoring system calculates the amount of charge used and compares with the C-rating or capacity of the battery. Whilst this method has the required accuracy for new batteries, the method becomes more inaccurate as the battery ages. Efforts to improve this accuracy include more complex fitting algorithms such as Coulomb Counting with Kalman Filters. Whilst these are a general improvement, there is certainly a need to further improve the accuracy of measurements.

Recently researchers have turned to EIS as a tool to improve accuracy. Typically experiments begin with new batteries and are discharged to defined SoC values. The broadband EIS measurement is recorded at predefined SoC levels. This can either be done at the open circuit voltage of the cell or under constant load – thus simulating real world conditions. The data is then fitted to an equivalent circuit model such as the one shown in Figure 1. It has been shown that for some Li cell chemistries, the variation of one or more of the circuit elements in the model shows a repeatable relationship with the State of Charge (see Figure 2) . In addition, some studies indicate that such measurements are independent of the age of the battery particularly when coupled with EIS data of aging tests (c.f. the issues with age related coulomb counting methods)

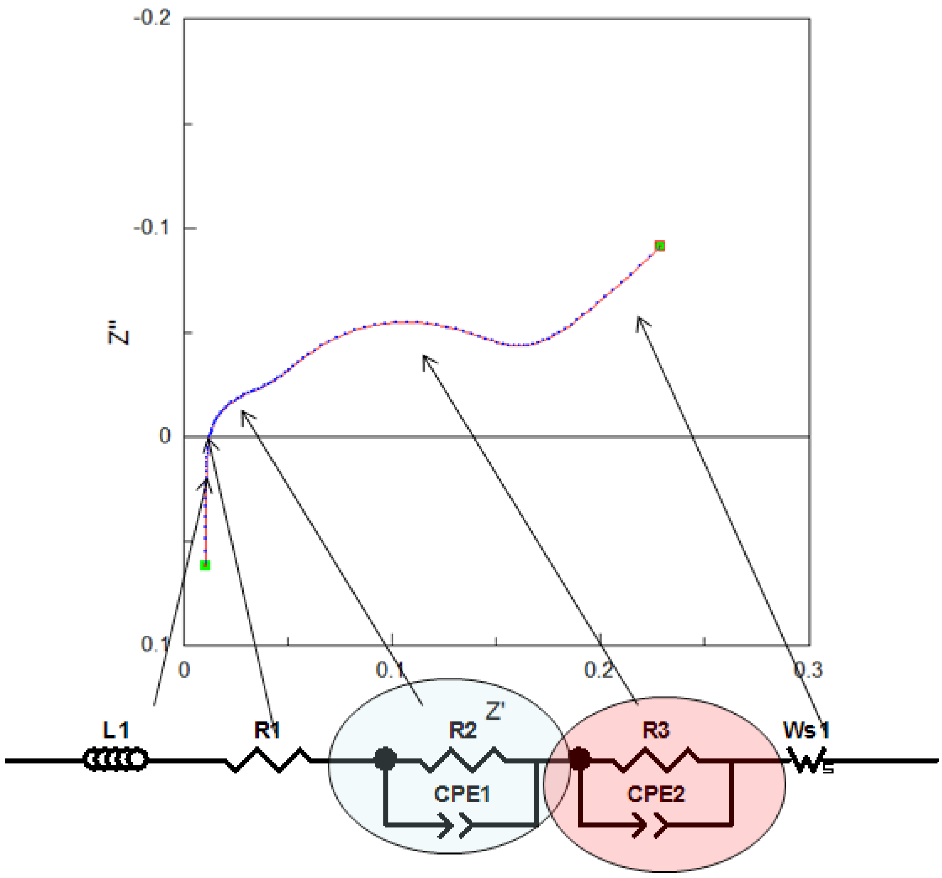

Figure 1: EIS results in Nyquist form from a Li-Ion battery at 100% SoC. The equivalent circuit model is used to simulate the EIS response of the cell. The circuit elements corresponding to the features in the EIS plots are shown. The data is modelled in the industry standard analysis platform ZVIEW. Note- R2 is the charge transfer resistance - Rct and R3 is the Solid Electrolyte Interface Impedance - Rsei

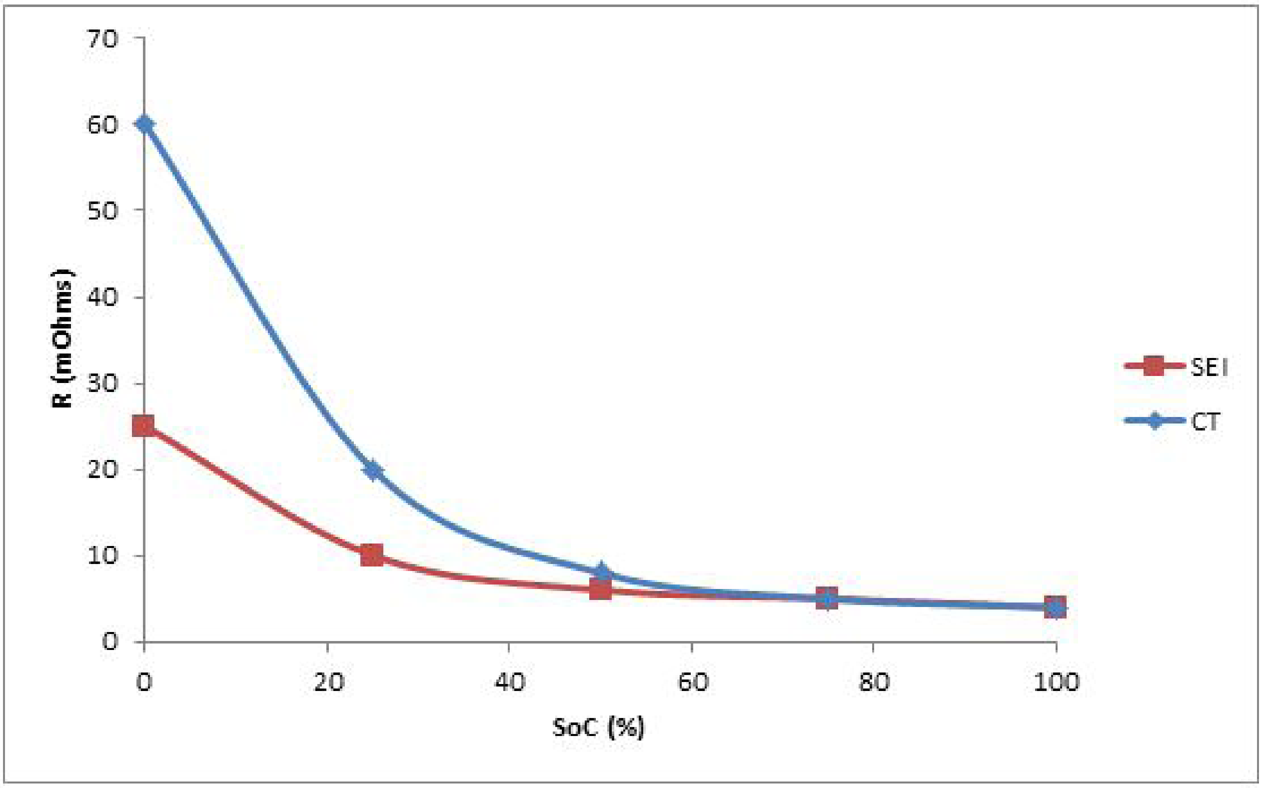

Figure 2: Impedance values calculated for circuit elements RCT and RSEI (Figure 1) as a function of SoC. Note how both values increase with decreasing SoC.

Therefore, by measuring the full frequency response of the battery and then applying an auto-fit routine to the data, it is possible to automatically determine the two resistance values from the equivalent circuit model and compare with a look-up table to determine the state of charge.

Fault Diagnosis in Cell Packs

It has been shown that EIS is a simple tool to determine faults within cell packs. This is particularly applicable to EV applications in which the battery unit consists of many repeat cells. When batteries approach their end of useful life, the OCV (open circuit voltage) may not deviate significantly from that of a new battery. Therefore using voltage monitoring may not always be a suitable method to determine faults. Furthermore, the series resistance may not also change appreciably with time and therefore current interrupt measurements may not be a suitable diagnostic test.

EIS overcomes these limitations since it measures the entire electrochemical properties of the cell using a broadband frequency stimulus. To demonstrate this, we measured the EIS response of 3 simple Ni-HM cells connected in parallel. Further details of testing batteries in a stack can be found on the Solartron Analytical website.

Figure 3 shows the EIS response of cells within the stack. This clearly shows that while 2 cells have a low impedance, the third cell (red line) has values that are double the others. It is important to note that the cell voltage for all cells were approximately the same (within 2mV). In this instance, the third cell limits the current (power) that the system can produce and therefore should be removed. Clearly, this approach can be scaled to battery modules meaning that engineers and technicians can use EIS to quickly identify packs with high impedance cells AND only remove those packs.

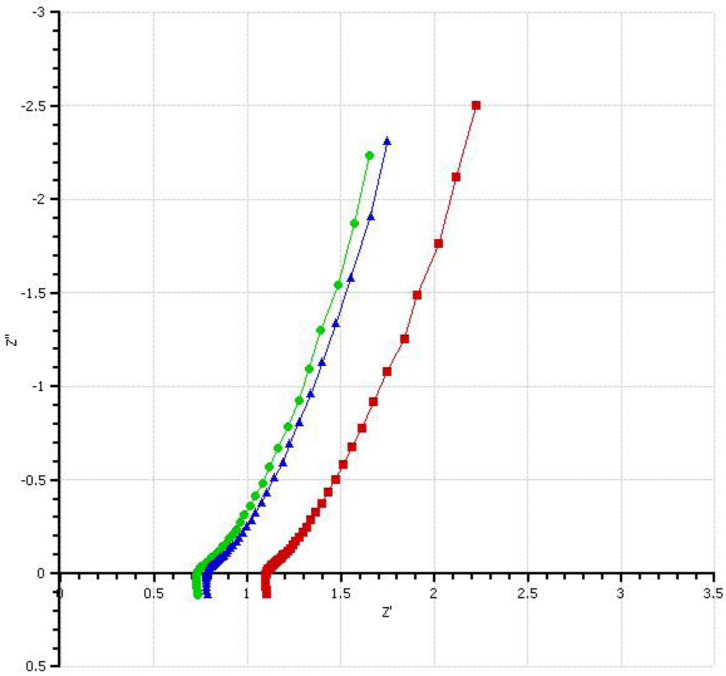

Figure 3: In-Stack Cell measurements for 3 Ni-MH batteries connected in series. The blue and green lines are the EIS responses of 'good cells' whilst the red line is an example of a 'bad cell'

State of Health

An estimation of the reduction of lifetime of the battery for a specified application is an important parameter in battery management and battery diagnostics. This State of Health (SoH) is a very difficult parameter to determine and is an area that requires further work.

The pioneering work of Alvin Salkind showed that EIS with a combination of fuzzy logic could determine the state of health of Li batteries. This stimulated much interest in the use of EIS for SoH measurements. Since the development of his work, researchers have developed a range of algorithms that determine the SoH of different cell chemistries. It should be noted that it is likely that this approach is not a 'one size fits all' and models may apply to specific battery types. In the following section we describe one such example.

A recent example of SoH determination using EIS was successfully implemented for a Lithium Manganese Nickel Cobalt Oxide (LiMNCOs) cell. The cells were discharged at their C rate and the EIS spectrum were recorded periodically. The resulting EIS spectra were fitted to an equivalent circuit model similar to the one shown in Figure 1. It was shown that the SoH showed a clear relationship with the series resistance of the cell. (See Figure 4). This is perhaps the easiest data to analyse since the ESR is simply the impedance magnitude at the high frequency intercept for the Nyquist plot as shown in Figure 1.

Further work is now focusing towards the development of algorithms which compare the SoC, SoH and temperature of the cells. If has been shown that the SoC and SoH EIS measurements depend somewhat on the temperature of the cell. It is suggested that a knowledge of two of the parameters can predict the third. This is an area of great interest in the automotive sector considering that battery systems will be expected to operate in a wide range of temperatures. Therefore a knowledge of the SoC and SoH as a function of temperature using the EIS response of cells is likely to become requirement in this sector.

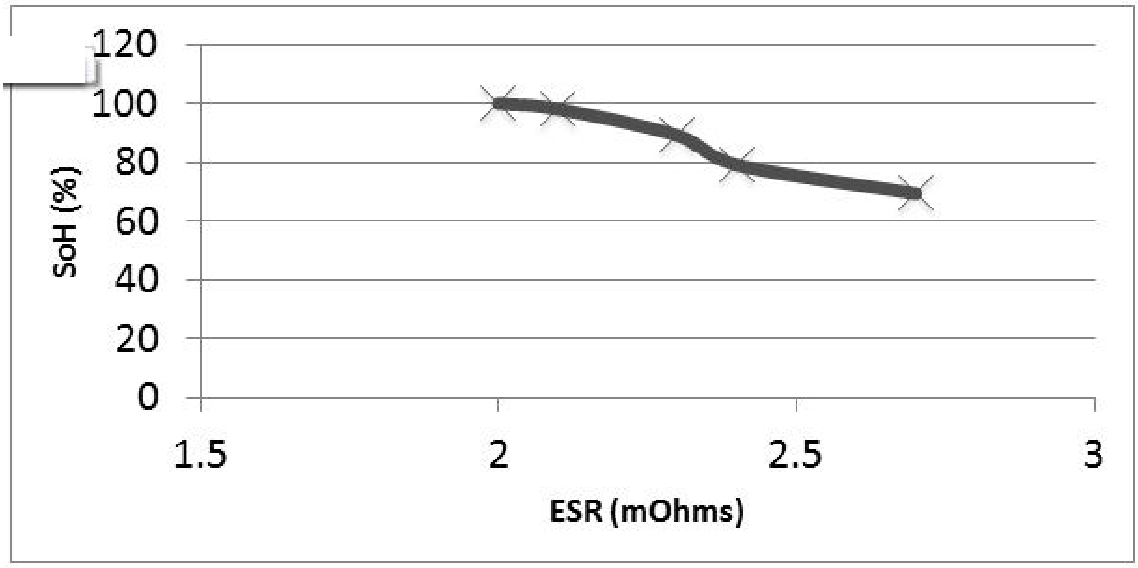

Figure 4: SoH (%) plotted vs the ESR (series resistance) of the cell as determine by analysis of the high frequency intercept from the complex plane / Nyquist plots.

Conclusions

This brief application note has described some of the limitations of traditional battery monitoring technologies and how EIS diagnostic tools are being researched and implemented in the field. The use of impedance analysis should greatly improve the accuracy and reliability of battery management and battery test systems resulting in fewer false positive results and fewer unnecessary battery warranty returns.

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