Application Note

Impedance Modeling of Li Batteries for Determination of State of Charge and State of Health

Application Note SA100

Introduction

Li-Ion batteries and their derivatives are being used in ever increasing and demanding applications. As these demands increase, the need for more accurate determination of the health of the battery becomes a requirement. This is particularly true in applications in which the battery represents a significant cost component such as batteries for electric vehicles or for off-grid energy storage.

In the automotive segment, system engineers are seeking reliable methods to determine the State of Charge (SoC) of batteries such that, for example, the battery is not discharged to the point in which cold cranking is impossible. In addition, determination of the State of Health (SoH) is a critical parameter, especially when considering the lifetime running costs of electric vehicles versus traditional fossil fuel cars. Even during routine service and repair of electric vehicles it will be necessary to provide the consumer an indication of battery lifetime as this will represent a significant cost if the battery pack requires changing.

The use of impedance spectroscopy for SoC and SoH determination is increasing in popularity owing to the relative ease in which data can now be captured with modern instrumentation. It has been claimed that this technique can overcome some of the limitations of traditional SoC and SoH methods such as Coulomb Counting and Coulomb Counting with Kalman filters.

This short paper describes a novel approach to determine the state of health of a LiFP ($LiFePO_4$) battery from a generalized equivalent circuit model for Li-Ion batteries. We start with modeling the SoC of Li-Ion cells using the generalized model and then use this approach to develop a method to determine the SoH.

Experimental

Two types of cells were used for these studies. A 1500mA hr Li-Ion cell was used for SoC measurements and verification of existing models. For SoH measurements, a 500mA hr $LiFePO_4$ cell was selected since this is the chemistry receiving interest for EV applications.

All EIS data, Charge – Discharge and other electrochemical measurements were recorded using a Solartron Analytical ModuLab XM system fitted with a 1MHz FRA and a 2Amp internal Booster card. A Multisine /FFT technique in the frequency range of 10kHz to 10mHz was used since fast measurements are required in field applications such as on-board automotive analyzers. The AC stimulus applied was 50mA which was shown to provide excellent signal to noise while working within the linear region of the DC response of the cell.

Impedance measurements for State of Charge computations were recorded by discharging a fully charged battery at 10% charge intervals at 5C. The battery was left at open circuit for 10 minutes before the EIS spectra was recorded.

Impedance measurements for SoH were recorded as follows. The cell was cycled using a CC-CV technique at 5C for 25 cycles. At the end of the cycle, the cell was recharged and the impedance spectra were recorded in the same manner as that used for State of Charge measurements. The cell was cycled for 125 cycles in total. Using this approach, a matrix of State of Health as a function of cycle number and State of Charge was created and used for data analysis and interpretation of results.

Modeling State of Charge of Li-Ion Batteries

An equivalent circuit for the Li-Ion battery is shown in Figure 1 and is based upon that proposed by Howey et al. There are other models in the literature and it is advised that the these are consulted for more information.

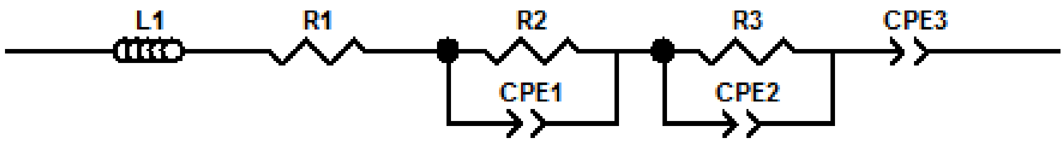

Figure 1: Equivalent Circuit Model for Li Ion Battery

Element	Description	Comment
L1	Inductance of cell and cables	Not usually of interest in models
R1	Equivalent Series Resistance	Ohmic Loss due to contacts and electrolyte resistance
R2	Solid Electrolyte Interphase Resistance	Reflects change in resistance of device due to SEI
CPE-2	Constant Phase Element - capacitance	Reflect non-ideal capacitance behavior of SEI
R-3	Resistance of charge transfer	Reflects fundamental electrode kinetics
CPE-2	Double Layer capacitance	CPR used rather than Capacitor due to non-ideal response
CPE-3	Diffusion Impedance	Can be represented by CPR or Warburg Element. CPE used in this instance as behavior was non-ideal for semi-infinite diffusion Warburg model

Table 1 list the circuit elements with a brief description of each and comments.

The data was modeled using the ModuLab Impedance modeling software. A typical result is shown in Figure 2. Clearly there is excellent agreement between the model and the data.

It was noted that the impedance results showed a marked response as a function of SoC with decreasing frequency. A simple correlation as shown in Figure 3 demonstrates this point in which the impedance magnitude at 50mHz showed a near linear correlation with SoC. Since this frequency is within the linear region of the plot (the diffusion region), we can infer that the diffusion of Li ion was impeded during the discharge process. This effect has been noted elsewhere and was attributed to the expansion of the lattice at high SoC which facilitates faster rates of diffusion.

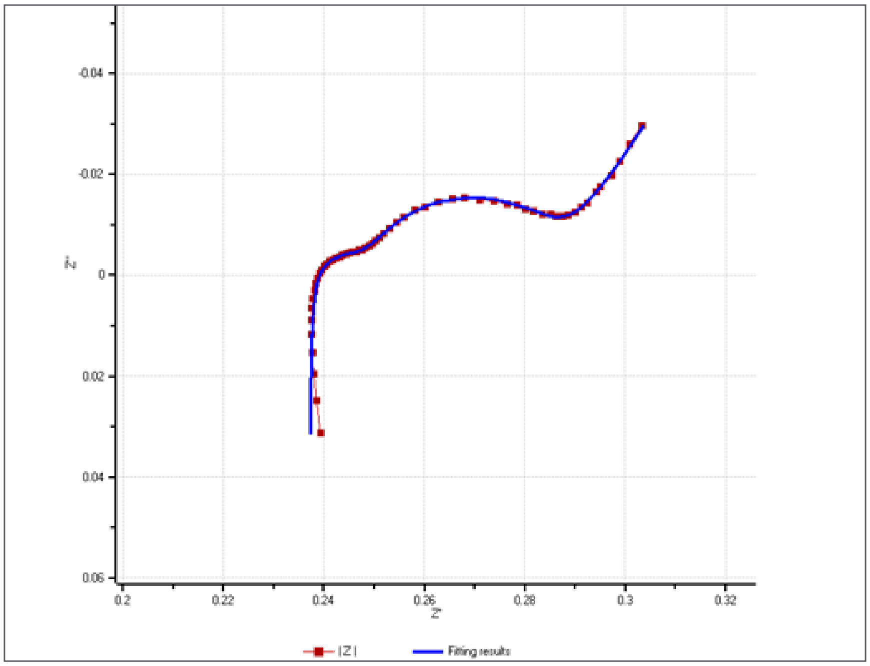

Figure 2: Fitting of data for Li Ion battery to equivalent circuit. Battery had been cycled at 5C for 40 cycles

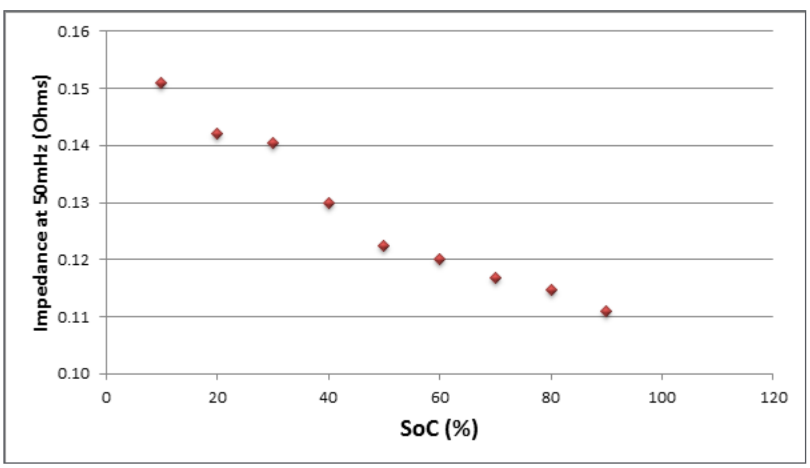

Figure 3: Impedance of Li-Ion battery at 50mHz as a function of State of Charge.

This body of work shows that the model is sound and that a simple correlation between Impedance and State of Charge could be used to develop a simple on-board battery analyzer.

With this knowledge we can now approach a much greater problem in battery diagnostics, that of State of Health monitoring.

Modeling State of Health of $LiFePO_4$ Batteries

The generalised circuit model for the battery was simplified from the case of the Li-Ion battery. It was noted that the Nyquist response showed an apparent single time constant (see Figure 4). It is known that if the time constants of two or more Randles circuits in series are such that;

$$\frac{(R_1\, C_1)}{(R_2\, C_2)} \sim 1$$

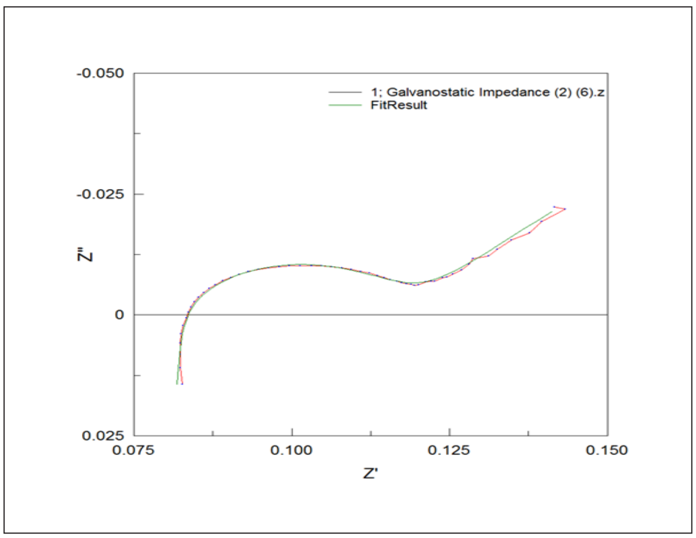

Figure 4: Nyquist Plot of a $LiFePO_4$ battery with data fitted to the model. Note only one apparent time constant (semi-circle) for this system.

The two time constants appear as a single time constant in the Nyquist plots. Therefore, we have represented the time constants of the device in a single Randles circuit as shown in Figure 5. We shall call this an 'apparent time constant' and show how we can relate this to the SoH of the battery

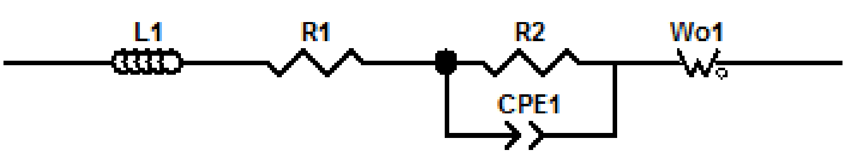

Figure 5 : Equivalent circuit model showing the composite Randles circuit for a $LiFePO_4$ cell.

Figure 5: Nyquist Plot of a $LiFePO_4$ battery with data fitted to the model. Note only one apparent time constant (semi-circle) for this system.

It was necessary to determine the SoH of the battery as a function of cycle number. The state of health in this study was defined as follows:

- Cell was cycled using the CC-CV technique in which the voltage cut-off was 4.1V. At this point the cycler switched from constant voltage to constant current
- The initial cell capacity of a new battery was determined using this method and State of Health of the battery as a function of cycle number was expressed as the capacity of the battery vs. the initial measured cell capacity
- A plot of the State of Health in % as a function of cycle number is shown in Figure 6

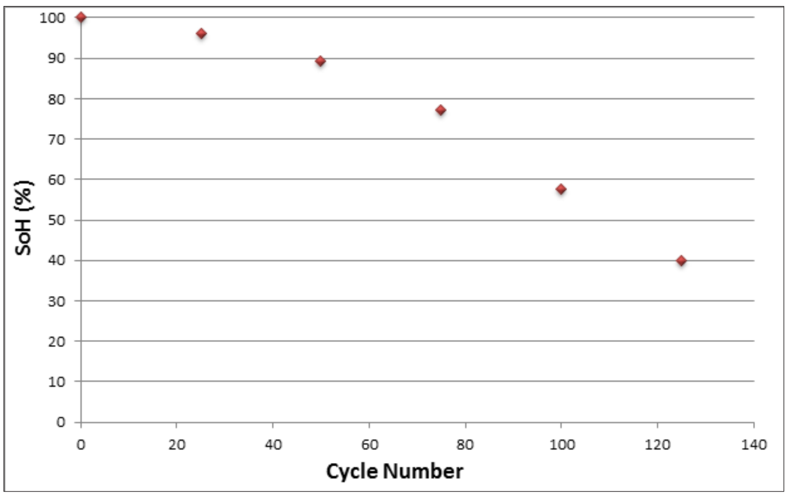

Figure 6 : State of Health as a function of cycle number for a $LiFePO_4$ cell

It can be seen from this plot that the SoH decreased rapidly after 50 cycles. This represents an important observation particularly for the automotive application. It is important to know the SoH of the battery during the early life of the cell –as many as 70% of warranty returns due to reported battery failure are subsequently shown to be within specification. The goal is therefore to improve the accuracy and resolution of SoH during the early life of the battery to reduce the false positive warranty returns.

The EIS data at each SoH was analysed according to the model shown in Figure 5. Each element of the model was analyzed and compared with the SoH to determine if there was a simple correlation. No clear correlation was observed. However, a strong correlation between the time constant of the electrode process and the SoH was noted. Furthermore, as demonstrated in Figure 7, the correlation became more pronounced as the state of charge at a given cycle decreased. Figure 7 shows clearly that at 20% state of charge, the RC constant provided sufficient resolution up to 90% SoH. This means the SoH can be determined using EIS when the battery has only reached 10% of its life. This could have significant implications for improving the SoH determination for warranty returns since in principle, the method has the ability to determine if the battery is at fault early within the warranty period of the car and thus significantly reduce unnecessary battery warranty replacement.

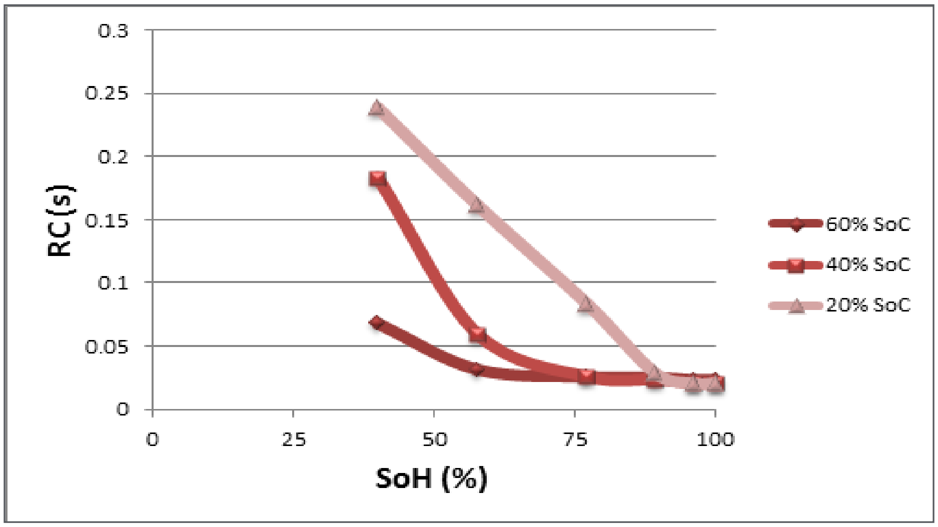

Figure 7: SoH vs cell time constant recorded at different SoC.

Summary

This short paper has described a method of EIS analysis to determine both the SoC and SoH of Li Batteries. While building upon the work of others, we believe we have demonstrated a unique, simple method to determine the SoH of a LiFP battery using the time constant of the cell at low SoC.

Bibliography

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