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Capacity Measurements of Li-Ion Batteries using AC Impedance Spectroscopy

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Abstract

This work presents AC impedance measurements (EIS) on a Li-Tec 40 Ah Li-Ion battery cell, including measurements in a climate chamber at different temperatures. The objective of this work is to provide a preliminary basis for estimating the potential of using EIS as a diagnostic tool for battery capacity measurements. In order to estimate the feasibility a Li-Ion battery cell is characterized by several EIS measurement, including measurements in a controlled temperature environment. From the measurements it can be seen that the impedance spectrum indeed changes as a function of State-of-Charge (SOC). However, measurements also show that the same spectrum is also strongly temperature dependent. Is is however concluded that EIS can potentially be used as a capacity diagnostic tool if a non-isothermal battery model based on EIS input data can be developed. The climate chamber measurements also features temperature data of the battery temperature compared to surrounding temperature, this data shows that a battery voltage drop will invoke a battery temperature increase. As the impedance measurements presented in this work are carried out on flexible low-cost Labview platform using conventional data acquisition equipment, suggestions have been presented on how EIS, as a diagnostic tool, preferably can be embedded in the battery management system.

Keywords: impedance spectroscopy, lithium battery, state of charge, battery model, data acquisition

1 Introduction

In order to obtain a widespread use of Battery Electric Vehicles (BEV) the users must be able to rely on the battery capacity. Preliminary experimental tests have shown that the battery capacity is hugely influenced by the load/recharge cycle that the battery is subjected to. Moreover, the derived battery capacity from performing the standardized load cycle test (EN61982) also differs significantly from the battery capacity derived from a real drive cycle. Indicators of the battery capacity, State-of-Charge (SoC) and the long term State-of-Health (SoH) are interesting parameters, but can be difficult to determine experimentally. In this study the feasibility of using Electrochemical Impedance Spectroscopy (EIS) to experimentally determine the SoC and SoH is assessed.

Research has shown that EIS potentially can help determining the SoC of a Li-Ion battery [1]. Unlike a lead acid battery [2], the high frequency resistance of a Li-Ion battery does not change as a function of SoC. Capacity estimating techniques from lead-acid batteries can therefore not be applied directly to Li-Ion batteries. The measuring conditions can also have large influence on the obtained results, especially the cell temperature of the battery is very important [3,4].

The HoC is by far more complicated to obtain than the SoC, however it is a highly interesting parameter and very relevant in cases where the ownership of a battery pack changes or in battery lifetime estimations. State of the art technology requires a battery-management-system that continuously supervises the battery for an estimate of the current battery capacity. Vetter et al. published a good overview of the different failure mechanisms of Li-Ion battery [5]. From this study and other studies [4,6] it was shown that the impedance of a Li-Ion cell rises during an aging test, this suggests that EIS may also be used to estimate the HoC of Li-Ion batteries. Equivalent circuit models have been suggested for extracting relevant physical parameters from the EIS measurements [7]. Models have also been suggested for estimating the aging of Li-Ion electrodes [8].

Lead acid batteries are still to date used as primary source of energy in various mobile applications. As Lithium-ion batteries continuously are improved both in terms of cost, size and durability many of the old type batteries will be replaced by modern high energy density batteries. Niche market segments, such as small transportation vehicles, such as scooters and pallet lifters, are already being converted into state-of-the-art Lithium-Ion battery packs.

2 Methods and Materials

In the present work a commercially available 40 Ah Li-Ion battery cell from Li-Tec was used. The cell features LITARION™ electrodes, which is a lithium nickel manganese cobalt oxide combination ($LiNi_xMn_yCo_zO_2$) for the cathode and carbon based anodes. SEPARION™ separators are used, which are ceramic based, in order to ensure safe operation.

2.1 Experimental Setup

The experimental setup features a TDI Dynaload (RBL488 50-200-800) electronic load, a Labview PC and a National Instruments CompactDAQ chassis with two 9205 and one 9215 analog input modules, one 9211 thermocouple module and one 9263 analog output module.

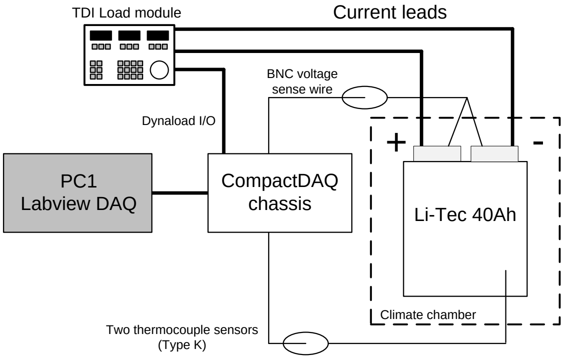

Figure 1: Experimental Setup

The CompactDAQ chassis will communicate with the electronic load using 0-10 V analog signals. The battery cell voltage is continuously logged, along with the cell temperature and the ambient temperature. The response signal from the battery cell is collected through a shielded BNC cable.

2.1.1 Labview-based EIS

Using the test rig Electrochemical Impedance Spectroscopy (EIS) measurements are periodically conducted. The Labview program will according to the user input conduct impedance measurements, the same program has previously been used for fuel cell measurements [9]. In this work the hardware was however changed to the CompactDAQ platform previously described, the Labview program remained unchanged. When conducting a measurement, the cycle charge is divided into a number of required measurements, for this case up to 10 EIS measurements were obtained for each discharge. The program logs the amount of Ah drawn from the battery, initially an expected battery capacity is given, in this case 40Ah, and when a certain threshold is reached an EIS recording starts.

Each EIS measurement was conducted from 2500 kHz – 0.02 mHz, using three points per decade. The resulting voltage amplitude was adjusted continuously in the program to obtain a voltage amplitude of at least 0.01 V RMS.

2.1.2 Climate Chamber Tests

In order to investigate temperature effects, the battery was installed in a climate chamber. The cell was tested at three different temperatures 0 °C, 20 °C and 40 °C, the relative humidity was kept at 50 %. The ambient temperature of the climate chamber was monitored by placing a thermocouple

(Type K) 4 cm above the battery cell. In order to monitor the battery cell temperature a second thermocouple was placed directly on the cell and covered with insulation.

2.1.3 Experimental Test Matrix

The complete test matrix is listed in Chronological order in Table 1. The experiment M6 is similar to experiment M3, however after completion of experiment M5, a program bug failed to switch off the electronic load, the battery was therefore subjected to a depth discharge. Therefore, to investigate the consequence of a depth discharge experiment M3 was redone.

Table 1: EIS Test matrix

Test #	Current [A]	Temperature [°C]
M1	5 (C8)	Amb. (20)
M2	2 (C20)	Amb. (20)
M3	10 (C4)	20
M4	10 (C4)	40
M5	10 (C4)	0
M6	10 (C4)	20

3 Results and Discussion

The results from the experiments listed in Table 1 are presented in the following.

3.1 Discharge Curves

A typical discharge curve is shown for experiment M6 in Figure 2. The discharge rate was C4 (10 A) and the impedance measurements can be seen as tiny fluctuations on the voltage curve. The experiment was shut off after accumulating 38 Ah, which is indicated by the small rise in voltage.

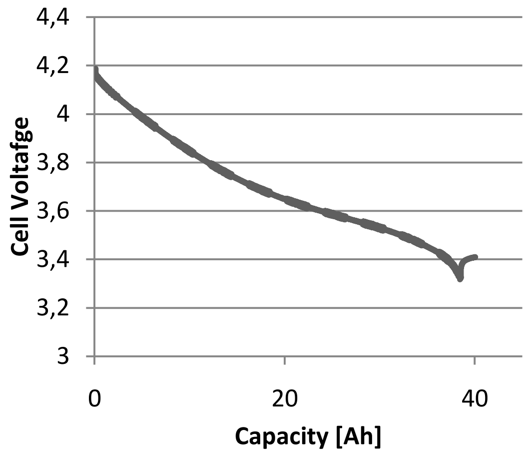

Figure 2: Typical C4 discharge curve for experiment M6

Figure 3 shows all the experiments using the 10A discharge rate (C4). The figure shows that the temperature has a significant influence on the battery capacity, especially at low temperature (0 °C, M5), the capacity is drastically lowered. A higher temperature (40 °C, M4), than room temperature, only has an minor influence on the capacity. Moreover, it can be seen from the data that depth discharge, which occurred in experiment M5, did not have any influence on the capacity, as the M3 curve is right on top of the M6, which has similar experimental conditions.

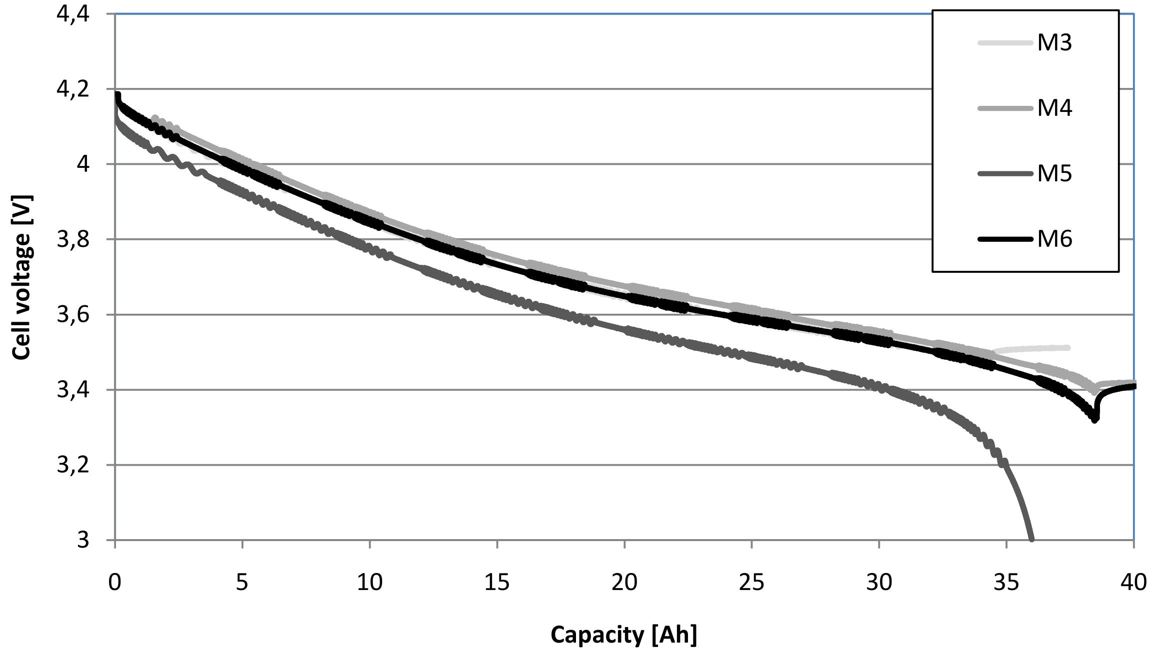

Figure 3: Discharge curves for C4 experiments (M3-M6)

From the data it can also be seen that the battery lives up to the rated capacity of 40 Ah at room temperature.

3.2 Impedance Spectroscopy Data

EIS data are typically presented in the form of a Nyquist plot, a typical Nyquist plot for the 40 Ah Li-tec Cell is shown in Figure 4. The shape of the Nyquist plot matches similar Li-Ion Nyquist plot found in the literature [5,6] very well.

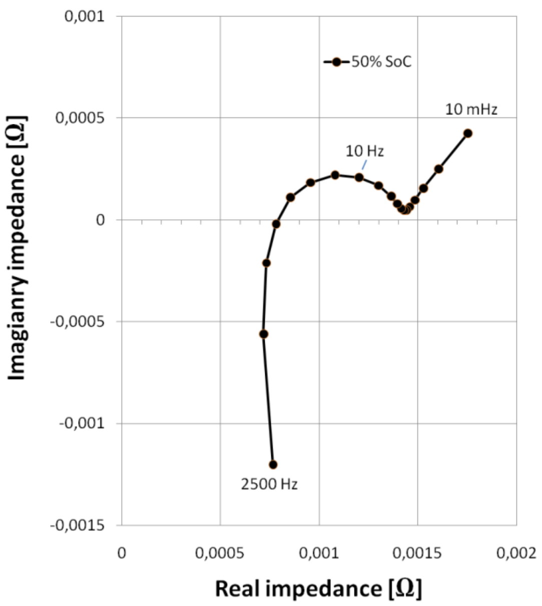

Figure 4: Typical Nyquist plot of 40 Ah Li-tec cell, 50% State-of-Charge (SoC) from experiment M3

According to Jossen [6] the Nyquist plot of a battery can roughly be divided into three parts. The high frequency part, with negative imaginary impedance, is caused by conductance in wires ect., the mid-frequency semi-circle can be related to charge transfer and the electrochemical double layer, this therefore represents the kinetics of the electrochemical battery reactions. The low frequency part, characterized by the 45° slope is caused by limitations in mass transfer, also known as the diffusion limited part.

3.2.1 State-of-Charge (SoC) Measurements

EIS measurements were performed at several SoC levels for each experiment. Figure 5 shows the impedance measurements for selected SoC levels from experiment M3. From the figure it can be seen that the ohmic internal resistance of the cell remains constant for all the measurements. The charge transfer part of the spectrum, characterized by the semi-circle, changes as a function of SoC. Unfortunately, it is far from a linear relationship, as the 100% SoC semicircle is almost the same magnitude as the 20% SoC semicircle. The change in the charge transfer semicircle as a function of SoC is not in coherence with the data from Jossen [6], as this work shows a more linear relationship between the SoC and charge transfer kinetics.

A better parameter for estimating the SoC might be the slope of the linear diffusion limited part of the spectrum, as this also changes as a function of SoC. Another possibility is to combine the two parameters to create a more rigid parameter.

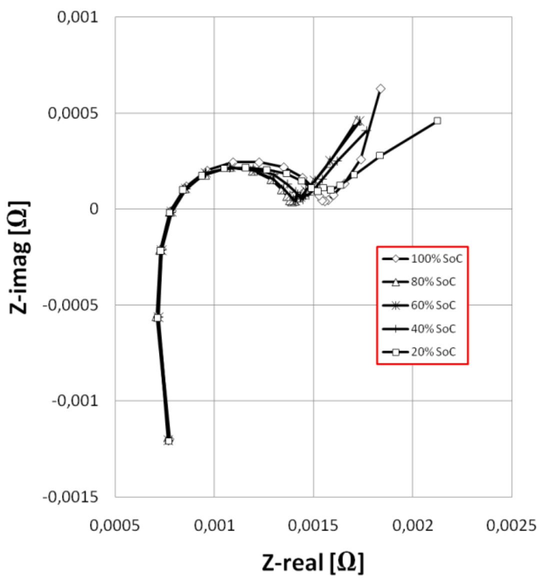

Figure 5: State-of-Charge measurements for experiment M3

3.2.2 Effects from discharge rate

The different impedance spectra at SoC (State-of-Charge) 50% for the different discharge rates used in the experiments are shown in Figure 6. The figure shows that the discharge rate has virtually no affect on the impedance spectrum at low currents (2A and 5A), however at 10A, the spectrum is shifted to the right in the complex plane, which indicates a change in internal ohmic resistance of the cell. This could be caused by the experimental conditions of the experiment, as the four latter experiments (M3-M6) was conducted in a climate chamber. The movement to the climate chamber required disassembly of the experimental setup, this may have cause extra ohmic resistance in the wires and connections to the cell.

The two 10A plots shown in Figure 6, are the spectrum before (M3) and after (M6) the depth discharge occurring in experiment M5. From

Figure 3 the cell seemed unaffected by the depth discharge, however the Nyquist Plot reveals a change in the internal ohmic resistance of the cell (shifted to right in the complex plane).

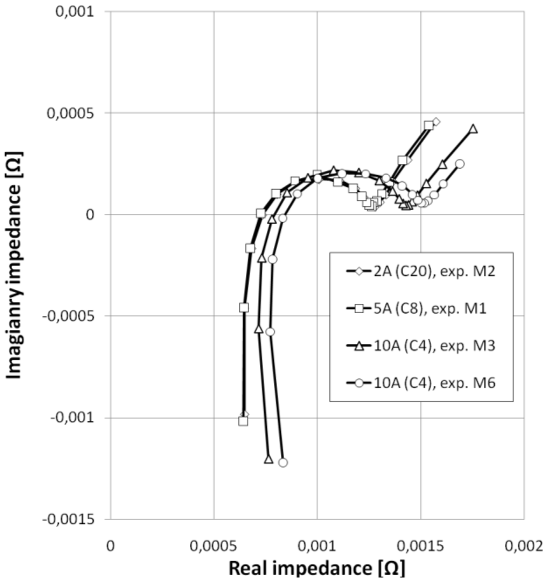

Figure 6: Nyquist plot at 50% SoC at different discharge rates

3.2.3 Effects from ambient temperatures

The battery cell was placed in climate change during experiments M3-M6, in order to investigate the effects from changing the surrounding temperature, Figure 7 shows the Nyquist plot at 50% SoC for these results.

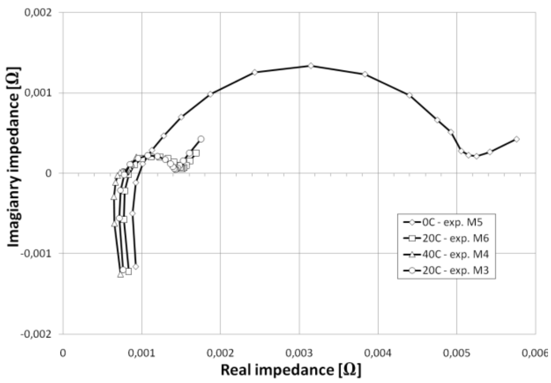

Figure 7: Effect from different ambient temperatures at 50% SoC.

From the figure it is clear that the temperature indeed have a massive effect on the impedance spectra, this was also the case for the capacity graphs shown in Figure 3 and measurements made by Abraham et al. [3].

The largest change in the spectra is change in the charge transfer loop, the low temperatures makes the electrochemical reactions sluggish, however also the internal resistance of the cell is slightly increase at low temperatures. These changes are in coherence with the findings of Abraham et al. [3]. It is important to notice that the temperature effects seen in Figure 7 are fully reversible and does not cause any permanent improvement or degradation to the cell.

3.3 Temperature Measurements

During each measurement in the climate chamber (M3-M6), the ambient temperature of the climate chamber and the battery temperature were monitored. Figure 8 shows the temperature measurement from experiment M3, it shows a steady increase in cell temperature, in comparison to the surrounding temperature, during the first hour of the experiment, hereafter it levels out and begins to increase again after 2.5 hours of operation, until the load is switched off at 3.5 hours of operation. There is a minor coherence between the battery cell temperature and the voltage drop shown in Figure 3. A battery voltage drop will therefore result in a battery temperature increase.

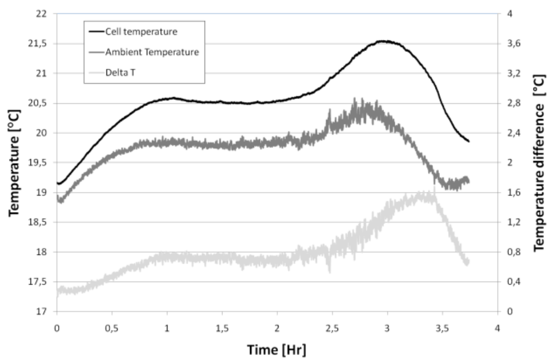

Figure 8: Temperature development during experiment M3

3.4 EIS as a Tool for Estimating Li-Ion Battery Capacity

From the data obtained in this work, it is clear that capacity measurements using EIS as input tool requires detailed modelling of the impedance output data. From the data potential parameters for estimating the current capacity of the model was identified and models such as Equivalent Circuit models could provide a potential modelling platform, it is however a prerequisite for such a model that it a non-isothermal model, as the EIS measurements on the Li-Tec Lithium-Ion battery are strongly temperature dependent.

In this work the EIS measurements are done a Labview platform and with conventional DAQ hardware, this opens the potential for building an embedded EIS diagnostic tool, maybe even embedded in the battery management system. The battery managements system is interesting, as it already features single cell measurements and most likely temperature control of the battery pack. Therefore the battery management system would be an ideal platform for incorporating an EIS diagnostic tool.

4 Conclusion

A lithium Ion battery cell was characterized using Electrochemical Impedance Spectroscopy at different temperatures and discharge rates with the objective of using EIS as a diagnostic tool for battery capacity estimation.

The data obtained from the experiments shows that the battery capacity potentially could be estimated using EIS as a diagnostic tool. It is however not straightforward and requires a substantial knowledge of the battery in question. As the measurements showed, Lithium-Ion batteries are strongly temperature dependent, therefore it would be a prerequisite for a potential EIS model that extensive characterization work is carried out on the battery. This characterization data will then serve as empirical data for a potential battery model.

Suggestions are given on how EIS may be used as a tool for capacity estimation was presented, including the potential for having an embedded EIS tool in the battery management system.

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