



Investigation of Lithium-ion battery parameters using pulses and EIS

Bachelor Thesis, Electric Power Engineering

Awais Chaudhry

INVESTIGATION OF BATTERY PARAMETERS USING PULSES AND EIS

Awais Chaudhry

Department of Energy and Environment Division of Electric Power Engineering CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2017

AWAIS CHAUDHRY

©AWAIS CHAUDHRY, 2017

Examiner: Torbjörn Thiringer, Energy and Environment

Department of Energy and Environment Division of Electric Power Engineering Chalmers University of Technology SE-412 96 Gothenburg Sweden Telefon +46 (0)31-772 1000

Cover: Charge and Discharge curves

Chalmers Bibliotek, Reproservice Gothenburg, Sweden 2017

Abstract

Purpose of this thesis was to acquire a better understanding of different methods in low frequency area when doing measurements on a lithium-ion battery cell. Also, to compare the methods chosen for the measurements to each other and show how they differ. The methods that were used in this thesis are Charge and Discharge, open circuit potential (OCP) relaxation, Pulse tests and Electrochemical Impedance spectroscopy (EIS).

The measurements are done at room temperature, for most part in a temperature chamber with the temperature of 20° C and at current level of 0.25-30A and state of charge (SOC) level between 0-100%.

Charge and Discharge measurements are used to help identify SOC of different voltage level of the battery cell, to obtain the data of the resistance at different SOC level and to give an idea of how the charge and discharge curve looks like for different current levels. Open circuit potential curves are used to confirm the resistance retrieved from the charge and discharge measurements and also to better understand the relaxation of the battery cell. Pulse tests are then done and with the data obtained from the charge and discharge measurements, resistance of the pulse tests is calculated. The resistance from the pulse tests is then compared with the resistance from EIS measurements.

Acknowledgement

This thesis was done at Chalmers and would not have been possible without my supervisor and examiner, Torbjörn Thiringer, who showed great support and patience with the work in this thesis and gave insightful feedback. I would also like to thank my friends and family for their support and encouragement during my thesis and studies.

Awais Chaudhry Gothenburg, Sweden, 2017

Table of contents

Abs	tract	i			
Ack	Acknowledgementii				
Abb	revi	ationv			
1.	Intro	oduction1			
1.	1.	Background1			
1.	2.	Purpose1			
1.	3.	Limitation1			
2. T	heor	y			
2.	1. El	lectrochemical Impedance Spectroscopy2			
2.	2. St	tate of Charge			
2.	3. Eo	quivalent Circuit and Elements of the Battery			
	2.3.	1. Resistance			
	2.3.2	2. Capacitance			
	2.3.3	3. Inductance			
	2.3.4	4. Constant phase element			
3.	Met	hod and experiment set up			
3.	1.	Battery Cell setup			
3.	2.	Tests			
4.	Ope	en Circuit Voltage tests			
4.	1 Co	onstant Charge and Discharge tests			
4.	2 Of	pen Circuit Voltage relaxation			
5.	Puls	se tests			
6.	Elec	ctrochemical Impedance Spectroscopy tests			
7.	7. Method comparison				
8.	Con	clusion & Future Work			
8.	1 Cc	onclusion			
8.	2 Fu	ture work			
9.	Refe	erences			

Abbreviation

- EIS Electrochemical Impedance Spectroscopy
- SOC State of Charge
- OCV Open Circuit Voltage
- CPE Constant Phase Element
- Lithium-ion Li-ion
- OCP Open Circuit Potential
- Ah Ampere hours
- FFT Fast Fourier Transform

1. Introduction

1.1.Background

Lithium-ion batteries have taken quite a leap in the worldwide market and are one of the most important electric components whether it is in an electronic vehicle, a smartphone, solar panels or any miscellaneous device. Due to the increasing concerns of emission and effect on climate change, lithium-ion is looked upon as a solution, especially in vehicles.

This thesis will aim on understanding and comparing different methods used for characterizing the lower frequency part of the Li-ion battery. When it comes to charging a battery, industries nowadays mostly focus on fast charging [1] [2]. The charging time of an electric vehicle is considered as one of the negative points when purchasing an electric vehicle and therefore electric vehicle companies are focusing on making electric vehicles faster to charge [1]. However, there are other areas within battery usage where faster charging is not needed but rather slower charging and discharging. Such as battery facility could be connected to solar energy plants that might charge or discharge slowly, which are increasingly being built [3]. Therefore, both slow and fast charge and discharge. Different methods that are going to be used are Electrochemical Impedance Spectroscopy (EIS) and Pulses with help of charge and discharge curves. While characterizing battery impedance several factors affect the result, such as state of charge of the battery, temperature and batteries life state.

1.2.Purpose

The purpose of this thesis is to test and compare different methods such as pulse tests and EIS with focus in the low frequency area and present the result from both methods. This is done with the goal of pushing the equivalent circuit models of batteries forward.

1.3.Limitation

While characterizing the battery impedance several factors affect the result, such as state of charge of the battery, temperature and batteries life state. Different SOC will be taken into consideration and most of the measurements will be done at a fixed temperature of 20°C, however, the batteries life state is unknown and will not be taken into account neither will any other temperature.

2. Theory

2.1. Electrochemical Impedance Spectroscopy

EIS is one of the most common methods used to gain a deeper insight into electrochemical systems and is often used within battery research. One advantage with EIS is that it measures in a wide frequency range. By applying sinusoidal signals with a certain frequency range, in this case 0.001-20kHz and measuring the characteristic response, the impedance of the battery can be measured. The input signal can be either current or voltage.

The voltage u(t) and the phase shift δ are the responses of the measurement recorded and using the following expression.

$$Z(\omega) = \frac{u(\omega)\cos(\omega t + \alpha)}{i(\omega)\cos(\omega t + \alpha - \varphi)}$$
(1)

2.2. State of Charge

The state of charge is equivalent to fuel gauge when comparing an electric vehicle and a combustion engine. SOC is measured in percentage which means it is the ratio of the battery's present capacity and its maximum capacity. Where 100% means it is fully charged and 0% it is fully discharged, according to

$$SOC = \frac{Q_c}{Q_m} 100\% \tag{2}$$

where Q_c is the present charge and Q_m is the maximum charge. A way to explain how fast a battery can be discharged or charged can be done by the C-rate. For example, if a battery has 1000mAh and discharges at a rate of 1 C-rate (C/1) it means that the battery will be fully discharged in an hour. At 5 C-rate (C/0.2) it will be fully charged or discharged in 0.2 hours or 12 minutes [2].

SOC can be found in a few different ways, one of them is using the Open Circuit Voltage (OCV). It is done by measuring the difference in electric potential between two terminals with no load. Another way is by integrating the current flow in and out of the battery, also known as coulomb counting [6].

2.3. Equivalent Circuit and Elements of the Battery

Different parts of the EIS curve represent different parts of the internal impedance of the Li-ion cell during cell operation, and this will be explained in this part of the chapter. A circuit model is used to identify the different parameters of the total impedance. However, in this thesis a circuit model will not be used to identify any parameters. The impedance model from [4] will be used to explain the different part of the EIS curve seen in figure 2.



Figure 1 Semi physical impedance model of a battery

2.3.1. Resistance

There are four resistances being used in this circuit model R_o , R_{ind} , R_1 and R_{ct} . R_o is the ohmic resistance and is in series with the other components. R_o can be measured in the Nyquist graph, its value is given when the impedance curve intersects with x-axis, see figure 2. It is the total resistance of the battery cell.



Figure 2 Synthetic data for impedance based model

2.3.2. Capacitance

There are two capacitances in this model, the capacitance is used in these models to give a clearer picture of the low and medium frequency spectrum which consists of a semicircle. At the end of the semicircle a 45° slope starts which is typical of Warburg impedance [7]. Both capacitances combined with alpha (α) are modelled as a CPE.

2.3.3. Inductance

Only one inductor is included in this model, they are used for the higher frequencies areas of the spectrum. However, a pure inductance is a straight line in the impedance spectrum so alpha is added for the semicircle shape.

2.3.4. Constant phase element

The CPE (alpha) is a mathematic tool. It was discovered (or invented) to achieve the semicircle shape on x-axis [8]. A CPE can be between zero and one, but it is a mathematic tool therefore it does not exist in the battery. The CPE is used to adjust the height and the shape of the capacitance and inductance in the circuit model. An RC circuit is usually a semicircle but sometimes it needs help by a CPE for a better curve fitting.

3. Method and experiment set up

3.1. Battery Cell setup

A Li-ion battery cell with capacity of 26Ah is used for the measurements with an operation voltage range of 2.8V to 4.15V. However, in this thesis, limit will be set at 2.9V to 4.1V due to a wish to avoid cell ageing behaviour below 2.9V and above 4.1V. A battery cell at 2.9V will be considered to be 0% SOC and 4.1V to be 100% SOC.

The battery cell is put onto a bakelite board with contacts to reduce the risk of short circuit. Then the board with cell is put into a temperature chamber where different temperature can be selected, as can be seen in figure 3. In this thesis the temprature is kept at 20° C with temperature chamber.

The contacts of the board are then connected to a Gamry reference 3000, Shown in figure 5, which is the main part of the measurements.



Figure 3 Battery cell inside temperature chamber

A Gamry reference 3000 is a sensitive instrument that requires calibration before usage to avoid distortion noise [5]. It operates in two modes when charging and discharging, galvanostat mode as well as in potentiostat mode. During galvanostat mode the Gamry charges and discharges the cell. During potentiostat mode the voltage is kept at its nominal value to make sure the cell is kept at the desired voltage level.

Figure 4 shows all five steps for charging and discharging the cell properly. Point 1 in the graph of figure 5 shows the initial potentiostat, which is the part where the voltage is kept constant at 2.9V, 0% SOC. Point 2 is a galvanostat charging part, where the cell is fed with the current applied through Gamry reference 3000 until it is at 100%SOC, in this case 4.1V. Point 3 is the potentiostat part where the voltage is kept at 4.1V. Point 4 is the galvanostat discharging, where the battery cell is discharged to 2.9V and then point 5 is potentiostat mode again which keeps the voltage level to 2.9V. Together they show how the battery cell charges and discharges, and the length of the different parts in Ah, as shown in figure 6.



Figure 4 Different sequence in charging and discharging Li-ion battery cell for SOC of OCV curve

Additional Open Circuit Potential (OCP) mode can be added after the battery cell has been fully charged and discharged to make sure battery is completely relaxed. OCP does not control the voltage or current at any desired level but only shows if the battery is relaxed or not by indicating if there is an active current, thereby showing if voltage level is shifting.

Gamry reference 3000 can only be used for currents up to 3A, therefore for every measurement above 3A, a Gamry reference 30k, shown in figure 5 together with Gamry reference 3000, will be connected in between a Gamry reference 3000 and the battery cell. Gamry 30k is a booster that allows currents up to 30A. As with Gamry reference 3000, the booster is a very sensitive device and needs calibration before usage. Even with calibration, the results on measurements below 3A might differ when measured with and without the booster.



Figure 5 Gamry reference 3000 and Gamry reference 30k Booster

3.2. Tests

In this chapter the different tests that are done in this thesis will be described and later in this thesis results from each test will be shown.

The charge and discharge measurements are made for 0.25, 1.25, 2.5, 10, 20 and 30A. All the measurements are made in a temperature chamber where the temperature is kept to 20°C. These measurements provide the SOC over the voltage and thereby give the resistances for different current levels. These measurements also provide an OCV curve which is used as a base curve for longer pulse tests where the SOC for the pulse tests varies.

The OCV relaxation tests are done for four different current levels, 2.5, 3, 10 and 30A to evaluate the time it takes for the battery cell to become completely relaxed and measure resistance for comparison with the resistance from the charge and discharge measurements.

EIS measurements are made at different SOC levels from 10% to 80% at 1 mHz-20 kHz with 3mV. Additional EIS measurements at 50% SOC are done with voltage level of 1, 5 and 20mV. EIS is used as one of the methods to obtain the resistance of battery cell for comparison with the pulse tests over frequency.

Pulse tests are done at different SOC levels and different pulse lengths. Pulse tests for different SOC, between 10-90% are done with the length of 20 second pulses at 30A and the longer pulse tests are done at 50% SOC with 13-minute pulses at 3A and 2 and 9-minute pulses at 30A. Results from the pulse tests are used to obtain the voltage difference between pulse tests and OCV curve in order to obtain the cell resistance. This resistance will then be compared with the resistance from EIS measurements in chapter 7.

4. Open Circuit Voltage tests

In this chapter charge and discharge curves will be shown together with OCV curves and comments regarding them will be given. OCV curves will be compared to other OCV curves with different current levels, how the charge and discharge process changes and how this affect the resistance of the OCV curve. The OCV relaxation test will also show the duration for the battery cell to get completely relaxed.

4.1 Constant Charge and Discharge tests

Figure 6 shows total potentiostatic and galvanostatic charge and discharge for current level of 2.5A. Charge + potentiostatic for 4.1V reaches 25.4Ah which is almost the battery cell capacity. Discharge + potentiostatic for 2.9V does not completely go back to 0Ah, which means it is smaller than the charge + potentiostatic for 4.1V, which will be shown in Table 2.



Figure 6 Total charge and discharge curve for 2.5A

Figure 7 shows the difference of charge and discharge of all the current levels that were used and an OCV curve, except for 1.25A since the difference between 0.25A and 2.5A is so small it would get clustered. It can be seen for the larger current, ΔV increases and decreases for lower current. It also shows that for larger current, galvanostatic charge and discharge goes quicker therefore larger potentiostatic charge and discharge period are needed.





The charge and discharge curves are used to calculate 50% SOC by dividing the total Ah (25.4) by two. Which in this case is 12.7Ah. ΔV for 50% SOC is then the difference between the voltage levels of charge and discharge at 12.7Ah. The resistance can then be calculated by the following expression

$$\Delta V = 2RI \Longrightarrow R = \frac{\Delta V}{2I} \tag{3}$$

The resistances from these charge and discharge curves are referred to as the long-term resistances.

Figure 8 shows the long-term resistance over different current levels for all the charge and discharge measurements done in this thesis.



Figure 8 Long-term resistance over different current levels at 50% SOC

The resistance declines exponentially, however the graph shows that the resistance is becoming constant for higher current levels. The current capacity for the equipment used for measurement is 30A so another measurement at 45-50A could not be done. Table 1 shows the amount of time it takes for the charge and discharge measurements for different current levels.

Current level [A]	Resistance $[m\Omega]$	Time per test [days]
0.25	50	11
1.25	16	4
2.5	9	3
10	4.75	1.25 (potentiostat time
		reduced to 12hours)
20	4	1.1 (potentiostat time
		reduced to 2 hours)
30	3.66	2.1

1 1	01 1	11 1	4 1 1	• • •	1 4 4 4 *		11 1	4
l'anie i	Charge and	discharge	current level	with resistance	and test time	(harge	discharge ± 7	noten i
Lanc L	Unai gu anu	uischarge	current never	with resistance	and use unit	Unar zu,	uischarge i 🖬	pouli,
						\ O /		. /

As can be seen in table 1 the amount of time it takes for OCV measurements accelerates greatly at lower current levels. It would take about 24 days for a complete charge and discharge curve of a current level of 0.1A. The potentiostatic part was set for 24 hours however, after an assumption that there might be a current offset and that complete charge and discharge might be complete within 12 hours potentiostatic part was set for 12 hours. This was only done for current level of 10A and 20A.

Table 2 shows the different lengths of the galvanostatic charge and discharge together with the potentiostatic charge and discharge in Ah. It also shows the start value for OCP in red and end value for OCP in blue, this measurement was not done for 30A and low SOC side for 1.25A.

It can be seen that the galvanostatic charge decreases as the current level increases. However, for galvanostatic discharge it does not change so much. This is due to that the potentiostatic low is much smaller than the potentiostatic high. But the total charge and total discharge is approximately the same which is the desired result. Some measurements were done twice for assurance, hence the (1) and (2).

	Galvano	Potentiostatic	Charged	OCP	Galvano	Potentiostatic	Discharged	OCP
	charged	high	+	High	discharge	low	+	Low
			Pot.	Start			Pot. low	Start
			high	End				End
(1)	25.3443	0.2113	25.5556	4.1009	25.3408	0.0804	25.4212	2.8996
0.25[A]				4.1002				2.9014
(2)	25.2939	0.1953	25.4892	4.0996	25.3309	0.0837	25.4146	2.8996
0.25[A]				4.0094				2.9014
(1)	24.9307	0.5424	25.4731	4.0998	25.2288	0.2104	25.4392	
1.25[A]				4.0996				
(2)	24.9678	0.5222	25.4900	4.0999	25.2460	0.2036	25.4496	
1.25[A]				4.0998				
(1)	24.7821	0.6951	25.4772	4.1000	25.1492	0.2572	25.4064	2.8997
2.5[A]				4.0999				2.9014
(2)	24.8140	0.6685	25.4825	4.0999	25.1832	0.2556	25.4388	2.8997
2.5[A]				4.0998				2.9013
10[A]	23.5641	1.9034	25.4675	4.0994	25.1341	0.3875	25.5216	2.8998
				4.0993				2.8996
20[A]	22.0338	3.3776	25.4114	4.0993	24.8943	0.5680	25.4623	2.8994
				4.0993				2.8998
(1)	20.7885	4.5074	25.2959	4.0994	24.6070	0.6141	25.2211	2.8994
30[A]				4.0993				2.8996
(2)	20.8274	4.4815	25.3089		24.6082	0.8054	25.4136	
30[A]								

Table 2 Table of total charge and discharge values for different currents of OCV graphs

4.2 Open Circuit Voltage relaxation

OCV relaxation tests were done by charging the battery cell up to 50% SOC with current levels of 3A, 10A and 30A. After being charged up to 50% SOC, the battery is put in relaxation mode for 20 hours. These tests show how long it takes for the battery cell to become completely relaxed and can also give more confidence in the result of the resistance measurements obtained from the OCV curves.

It is quite clear in figure 9 that as soon as the relaxation mode starts, the voltage drop is quite large and after 5 hours the decline in voltage level slows down. However, the voltage does not become constant even after 20hours.

At 12.5 hour point a small spike in the voltage level can be seen, which is believed to have often caused, due to the instrumentation.



Figure 9 OCV Relaxation test at 3A

Figure 10 shows that for larger currents, the voltage drop entering relaxation mode is larger and quicker. The relaxation test for 30A was the only one to not show any spikes in the curve.



Figure 10 OCV Relaxation test at 30A

As can be seen in both figure 9 and 10, the battery cell does not get relaxed ever during 20hours of the measurement. A suspicion is that this is due to a current offset in the equipment.

In figure 11, the relaxation test of both 3 and 30A with absolute values can be seen simultaneously. A current level of 30A has a larger drop as expected. However, after a few hours of relaxation time, the relaxation looks equal for both current levels.



Figure 11 OCV relaxation test of 3 and 30A, absolute values

Tabell 3 Resistance over different current levels from relaxation and OCV tests

Current level [A]	Charge and Discharge resistance $[m\Omega]$	50% SOC Relaxation resistance [mΩ]
2.5	9	5.692
10	4.75	4.706
30	3.666	3.719

Table 3 shows the resistance gained from OCV relaxation measurements at 50% SOC and charge and discharge measurements at 50% SOC. As can be seen the relaxation test confirm the resistance at 10A and 30A, the difference is minimal, indicating good quality in measurements. However, the result for 2.5A is incorrect due to the difference in between the result from charge and discharge measurement and relaxation measurement. Reason for this is unknown.

5. Pulse tests

In this chapter, the results from the pulse tests will be shown. The pulse tests were done from 90-10% SOC with 40 pulses of 30A with the length of 20 seconds at each SOC point, an example of a pulse can be seen in figure 14 with a length of 120 seconds. For this measurement, the battery cell was charged to 100% SOC and then discharged 10-20% depending on SOC level for each measurement. Between the SOC levels, EIS tests are done as well, as can be seen in figure 13.



Figure 13 Procedure of Pulse and EIS tests at different SOC levels

In addition, pulse tests of different lengths were also done at 50% SOC with 30A and a series of pulse tests with 3A at 50% SOC with the length of 13 minutes.

It is very hard to get the precise SOC especially with larger currents as 30A. As expected SOC's shown in figure 13 were not accurate and new SOC for each measurement was calculated and the result can be seen in figure 15.

Expected SOC [%]	Actual SOC [%]	Error [%]
10	8.16	1.84
30	28.14	1.86
50	48.43	1.57
70	69	1
90	89.58	0.42

 Table 4 Expected SOC and Actual SOC during decreasing SOC pulse tests

The measurement started at 100% SOC and went down to 0% SOC. Since the measurement start at 100% SOC the error gets larger as the SOC gets smaller.

Pulse tests were done by looping four current pulses over a short selected amount of time, which is the length of the pulse. The loop consists of a positive current pulse, relaxation mode, negative current pulse and relaxation mode again. During relaxation mode the current is zero as can be seen in figure 14, together with a full period of the pulse test, each pulse part is 2 minutes, and the total period is 8 minutes.



Figure 14 A 30A pulse of 2 minutes

The pulses in figure 15 start off with an amplitude at 3.88V and over time decline to 3.87V. This is due to that the battery cell did not have enough relaxation time between when the battery cell was charged up to 50% SOC and the pulse tests. Therefore, the amplitude declines a bit over time. During the pulse tests in figure 13 the voltage amplitude increases instead over time, due to the fact the test is started at 100% SOC and the cell is discharging instead of charging. Therefor it has the reversed effect. There is also an offset in the Gamry current, which slowly discharges the cell which can be seen in figure 16.



Figure 15 Pulse test of 30A with 2-minute length at 50% SOC

Unlike the other pulse tests in this thesis, the pulse test in figure 16 was done when the battery cell had been completely relaxed. The battery cell was charged with 3A until it reached 50% SOC, afterwards it was put in potentiostat mode to keep it at 50% SOC for 12 hours and relaxation mode for another 4 hours. Therefor the voltage amplitude should not decline over time like it does in figure 16. The reason for this is probably due to that the current charge was slightly lower than the current discharge during pulse test.



Figure 16 Pulse test of 3A with 13-minute length at 50% SOC

For the longer pulses, SOC is taken into consideration. The 13-minute pulse test with 3A at 50% SOC charges the battery cell by 0.65Ah, up from 12.7Ah to 13.35Ah. Therefor when calculating the voltage difference, it is done accordingly to the change of Ah as shown in figure 17 and 18.



Figure 17 Result of 13-minute pulse test with OCV offset.



Figure 18 Voltage difference between 13-minute pulse and OCV.

The voltage difference from figure 18 is used to obtain the resistance by dividing the voltage with current for the pulse which is 3A. The sampling time used for the 13-minute pulses is 50ms, therefore the highest frequency is 20Hz. Figure 19 shows the charging and discharging resistance from the 13-minute pulse test. The discharge resistance for the higher frequency is smaller than the charge resistance, as can be seen in figure 19. Discharge resistance over frequency is also more linear than the charge resistance. However, this resistance result is not quite accurate but used to show the difference between charge and discharge resistance. For a proper resistance measurement, the fast fourier transform (FFT) was utilized over a period of a pulse, as can be seen in chapter 7. The FFT does not show charge and discharge resistance separately however.



Figure 19 Resistance of a 3A charge and discharge, 13-minute pulse over frequency

6. Electrochemical Impedance Spectroscopy tests

In this chapter EIS measurements will be presented. Measurement of how EIS impedance changes over frequency and time, where EIS measurements are done over time directly after Li-ion cell is charged up to 50% SOC according to figure 21. The measurements of EIS at different SOC has been done as well according to figure 13.



Figure 21 Three EIS test of 1, 10 and 100 mHz

For 1 mHz there is only 5 loops instead of 10, this is due to the amount of time it takes for each EIS measurement done at 1 mHz in comparison with 10 and 100 mHz. Which can be seen in table 5.

As can be seen in the figure 22, the Warburg impedance, which is 45 degree ends at the low frequency part of EIS. It also shows where the different frequency starts and ends, squares in the plot represent the highest frequency and end when the frequency reaches 1Hz, then diamond shape start at 1Hz and end at 0.1Hz and so on.



Figure 22 EIS measurement at 1 mHz for 10% SOC

Further measurements could not be done to show more of the bending from 45 degrees due to the limitation of time. The lower the frequency, longer the time it takes for Gamry to gather data. As can be seen in table 5 that shows different time, voltage and frequency level of each EIS measurements made. EIS tests from 10-80% show to have taken a lot longer time than the 50% SOC tests. The reason for the time difference might be the sampling time, that was much lower for EIS 50% at 1mV.

EIS [%]	Voltage [mV]	Frequency [mHz]	Time per EIS sweep [s]
10-80	3	1	15 000
50	1	1	1684
50	1	10	183
50	1	100	32
50	5	1	7299
50	5	10	704
50	5	100	118
50	20	1	6507
50	20	10	704
50	20	100	118



Figure 23 EIS plot for various SOC from 10-80% at 1 mV

80

In figure 23 EIS measurement from the procedure in figure 13 is shown. The SOC error from table 4 also applies to this EIS measurement. The ohmic resistance is almost the same for all the SOC. However, the charge transfer differs for each SOC. As the SOC declines, charge transfer impedance grows. The end resistance at charge transfer for each level of SOC can be seen in table 6.

SOC [%]	Resistance $[m\Omega]$
10	1.132
30	1.065
50	1.013
70	0.9996

Table 6 Lowest point of EIS at the end of transfer charge impedance

The reactance does not change much, except for the 10% SOC. However, the resistance changes step by step at each SOC. It can also be seen that EIS-curve at 80% SOC pivots a lot more than the other curves and does not give the 45degree angle for most of the Warburg impedance part of the curve. Whereas for 10% SOC the EIS-curve Warburg impedance does not last for very long.

0.9740

7. Method comparison

In this chapter, results from pulse and EIS measurements will be shown and compared to each other.

In figure 24 EIS resistance plot at 50% SOC is shown for 5 and 20mV. As can be seen there is a slight difference in resistance at lower frequency. The resistance for 5mV is slightly higher than the resistance for the 20mV and the distance in between them grows as the frequency declines.



Figure 24 EIS resistance for 5mV and 20mV

The Gamry does not gather the data for current when doing EIS-sweep therefor it is hard to compare it with pulse tests done at a certain current level. However, during the EIS-sweep current level can be seen on the Gamry program window and for 20mV it reached the maximum current level of 30A and 5mV reached approximately 7A. Therefor the 20mV can be compared to the 30A pulse levels.

Figure 25 shows the resistance of EIS measurement of 5 and 20mV and the resistance of pulse of 3 and 30A. As can be seen, the pulse resistance is quite similar to the EIS resistance. For both EIS and pulse tests, the lower current/voltage gives higher resistance. The results from the pulse tests do not reach the resistance levels from the charge and discharge measurements, this is believed to be due to the length of the pulses. For longer pulses it is believed that they will reach the same value as the charge and discharge measurements, which can be seen at the slope for 30A pulse, as it is heading towards the resistance value of charge and discharge measurement.



Figure 25 Resistance plot of EIS 5 and 20mV and pulse of 3 and 30A

Figure 26 shows the result of measurement from figure 13, where pulse tests of 10,30,50,70 and 90% were done together with EIS tests of same SOC except 90% which was done with 80% SOC instead due to the EIS sweep reached the battery capacity limit and aborted the test at 90% SOC. All the pulse tests were done at 30A with 20second pulses and all the EIS tests were done at 3mV. However, to show the results more clearly only 10, 50 and 70% SOC results are shown in figure 26.

It can be seen in the figure 26 that the resistance increases as the SOC decreases for both pulse and EIS tests. At the lower frequency area, the resistance for pulse tests is larger than the resistance for the EIS.



Figure 26 Resistance plot of EIS and Pulse tests with different SOC levels

8. Conclusion & Future Work

8.1 Conclusion

This thesis focused on studying different methods which makes it possible to characterize the impedance a battery cell. As expected, the results from EIS and pulse tests were not identical. For all the EIS and pulse tests the resistance gap in between the EIS and pulse measurement grew as the frequency decreased. However, the resistance at the ohmic region from the EIS plot described in the Theory chapter were quite similar for both the EIS and pulse tests. Furthermore, both EIS and pulse tests show that the resistance increases as the SOC decreases.

Charge and discharge tests were done to obtain OCV curves and the long-term resistance which was used as the base resistance for comparison with pulse test resistances. However, 30A pulse tests of 2minute length did not give the same result as the resistance obtained from 30A charge and discharge test. A reason for this could be that the temperature is higher for pulse tests since it consists of a lot of 30A pulses and the battery cell does not get enough time in between to cool down.

One of the reason for the OCP tests were done was to confirm the long-term resistance of charge and discharge curves, which gave the same results as the pulse tests.

Another reason for OCP tests were to see how relaxation for a battery cell progresses for different current levels. However, even after 20 hours, the voltage level continued to fall, the reason behind this is current offset in the equipment. This was also noticed during pulse tests, where Gamry charged the battery cell with 29.99A and discharged it with 30.05A. After this discovery it was noticed for 10 and 20A charge and discharge tests that 12 hours for relaxation was enough.

8.2 Future work

Much is still unknown when comparing both methods. Future work can be done on additional current levels for pulse testing where EIS tests are also done at the same current level for better comparison. Pulse tests for 30A for longer pulses can be investigated further in future work and how the temperature affects the measurements, which is believed to be a big part in the measurements. Also tests at current below 3A can be done with and without the Gamry booster for the investigation of how much it affects the results. Furthermore, the parameters given from different measurements can be applied to a real model and the difference can be analysed further, to evaluate which method that is preferred.

[1] ABB Fast-charging. (2017)

http://www.abb.cz/cawp/seitp202/EF3999A3159A21E1C125816F00473D7A.aspx?_ga=2.89 701723.1157850579.1505220497-93609199.1472114234

[2]Reuters, Toyota fast charging electric cars.(July 2017) <u>https://www.reuters.com/article/us-toyota-electric-cars/toyota-set-to-sell-long-range-fast-charging-electric-cars-in-2022-paper-idUSKBN1AA035</u>

[3] The Guardian, Solar power growth leaps by 50% worldwide thanks to US and China. (March 2017) <u>https://www.theguardian.com/environment/2017/mar/07/solar-power-growth-worldwide-us-china-uk-europe</u>

[4] Avnish Narula, "Modeling of Ageing of Lithium Ion Battery at Low Temperatures", Department of Electric Power Engineering Chalmers, Gothenburg, 2014.

[5] Sandeep Nital David, "Pulse power characterisation for lithium ion cells in automotive applications", Department of Electric Power Engineering Chalmers, Gothenburg, 2016

[6] Freddy Trinh, "A method for Evaluating Battery Sate of Charge Estimation Accuracy", Department of Signals and Systems, Gothenburg, 2012.

[7] Gamry Online. (2017) Basics of Electrochemical impedance spectroscopy [Online]. https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/

[8] Research Solutions & Resources LLC. (July 2014) The constant Phase Element (CPE). http://www.consultrsr.net/resources/eis/cpe1.htm