Battery Performance and Electrode Corrosion

by

Ximo Chu

A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science in Technology

Approved November 2013 by the
Graduate Supervisory Committee:

Arunachalanadar Madakannan, Chair
Xihong Peng
Changho Nam

ARIZONA STATE UNIVERSITY

December 2013

ABSTRACT

Battery performance has been studied at different temperature, C rate. Different types of batteries have been used. Capacity and impedance are two factors, which are focused in the thesis. To evaluate battery performance and battery conditions, the SOC (state of charge) determination methods have been studied in the thesis. There are two types of batteries divided in three groups: group I. Ni-Cd battery (2V, 8Ah); group II. Lead-acid battery (2V, 8Ah); and group III. Lead-acid battery (2V, 25Ah). The impedance testing is using electrochemical impedance spectroscopy methods. AC impedance method has been used to test different state of charge (100%, 80%, 60%, 40%, 20%). For the corrosion part, the corrosion rate of metal material in the heat transfer fluids has been tested at different temperature. Hastelloys C-276 in eutectic molten salts a mixture of NaCl, KCl and $ZnCl_2$ using potentiodynamic method (swap from ± 30 mV in 0.2 $mV.s^{-1}$). The lowest corrosion rate of Hastelloy C-276 is 5.51 µm per year at 250 ^oC. Particularly, the corrosion rate of Hastelloy C-276 jumps up to 53.33 µm per year at 400 ^oC.

Dedicated to My Family

ACKNOWLEDGMENTS

First and foremost, I wish to express my profound gratitude to my advisor, Dr. Kannan, who taught me the knowledge I need and provided me the space to do research. I not only thank him for his critical role in my intellectual growth, but also for his consistent guidance that led me into well-defined problems for the present dissertation. Dr. Kannan has helped me understand battery system and research method and has helped me transition into a battery researcher and maybe a battery specialist in the future. He always supported me to go through difficulties and stress with consistent trust and patience to me. When I had questions, he taught me with clearly and easy understandable English. I appreciate for his patience. I want to thank my committee Dr. Nam and Peng, for valuable ideas and comments on my dissertation project. Dr. Nam gave many ideas about how to present and how to organize, spend a lot of time together with me. Dr. Peng provided many good idea and questions about the application of my research. They inspired me. Without my advisor, I could not have completed this work, and without my committees, I could not be confident and fully present my work.

Some of the work in this dissertation was carried out along with Dr. Vigna. Dr. Vigna also helped me with not only in the research, but also with tips on how to complete my thesis and presentation successfully. He taught me a lot of skills which I did not know. He also taught me what is important for a thesis work. Many other individuals gave me feedback, which helped me greatly in my research. I received many thoughtful and substantive responses from Vidya and Prashanth. We worked together. Vidya helped me and corrected my pronunciation.

I am also indebted to my community of colleagues and friends who always provided support.

Finally and the most importantly I want to dedicate this dissertation to my parents. I must express my deepest gratitude to my dearest parents, who have always supported me on whatever I want to do. Though I know you are happy that I am pursuing my dreams, at the same time I recognize you are worrying that I am getting far and far from you. I want you to know that I am like a bird. It doesn't matter how far I am from you because the thread has always been held by you.

This research on Batteries is being sponsored by SRP, Tempe AZ.

November, 2013 Ximo Chu

TABLE OF CONTENTS

Page

CHAPTER

LIST OF TABLES

Table Page

LIST OF FIGURES

Chapter 1

INTRODUCTION

Battery plays an important role in nowadays society. Battery as the energy source, has a stable output voltage, constant current, long time energy support, and less influenced by the environment. It has the simple structure and it is portable, easy operation, widely used in our daily life. With the technology development, there is more renewable energy being used. In Arizona, solar energy acts as an important role for the reason of the hot climate. Based on the Arizona climate, the work focuses on the battery performance and corrosion rate of metal materials in heat transfer fluids for concentrating solar thermal power system especially at high temperature.

1.1 Test & Evaluation of battery performance

1.1.1 Background and Introduction

Portable battery as the power supply of the electrical device is used more and more widely with the development of the electrical device. The battery is essentially a chemical energy system that, through the reaction it transfers the chemical energy into electrical energy. The battery consists of two different electrodes - positive and negative, and those two electrodes are put into the electrolyte. Once they are connected to the load, its internal chemical energy can transfer to outside.

In Arizona, the weather is extremely hot and dry, based on this climate. Do research to test and evaluate battery performance in hot and dry weather. SOC (state of charge) is important in battery technology, which can help user better use the battery, decide to charge or not and the charge time. And these will help to extend the battery life, reduce cost. Many people did a lot of work about SOC determination method [1-3], some of them did not take C rate into consideration, and some of their method could not be used in testing open circuit voltage. So it is necessary to do research about the different SOC determination method, which can support the portable battery tester for measurement SOC of the battery quickly. For the first part, different SOC determination methods have been studied in order to giving evaluation of battery performance and battery conditions.

Many people did a lot of work about the how the temperature and C rate influence the battery life, the degradation of the capacity, and the impedance. But the previous work, as my knowledge, did not do comparison study about the C rate and temperature affects to the battery. So it is necessary to study how aging, temperature, C rate affects the battery performance, do comparison study. And give suggestions to the user and charger manufacture for the using conditions and charger C rate design.

There are two issues the users will concern about the battery: State-of-charge (SOC), State-of-health (SOH).

State-of-Charge: the radio of residue capacity and the fully charge capacity [4].

State-of-Health: SOH reflects the condition of the battery, including age and the capacity degradation into consider, SOH shows the battery performance compare to a new battery [5].

Both SOC and SOH can give us information about the battery remaining run time. And the thesis focuses on the SOC.

The temperature will influence the battery life due to its affects chemical reaction speed inside the battery. Higher temperature, the internal chemical reaction is higher. The reaction speed almost double if the temperature grows up 10 ^{o}C (Developing Monobloc

Batteries for High Temperature Applications). The chemical reactions include wanted chemical reactions as well as the unwanted chemical reactions, and as a result, these lead to a reduction of the battery life. So it is helpful to prolong the battery life by keeping the battery working in properly temperature. C rate will decide the battery charging and discharging time, it will also affect the battery life, battery performance. Many work have been done on temperature and C rate influence to the battery performance. Some people did research about different C rate [6] and others did work about different temperature [7]. But they did not compare the temperature and C rate influence. So there is a needed to how aging, temperature and C rate influence the battery performance, take them into a general consideration.

For the two objects, there were a few methods have been used.

To determine the SOC, there are many methods, through discharge at particular C rate, EMF method, AC impedance measurement. These are what have been studied in the thesis. Other methods like pulse load method [8], specific gravity of the electrolyte [9].

To characterize the aging, temperature, C rate influences to the battery life and battery performance, impedance and capacity as well as HFR (high frequency resistance) have been calculated and analyzed. Impedance is the whole of the resistive and capacity and inductive resistance. The capacity reactance decreases with the frequency increases, while the inductive reactance increases with the frequency increases. EIS (Electrochemical impedance spectroscopy) has been used to test the impedance and high frequency impedance. There are a lot of advantages. It is a method widely used in impedance testing. It can be used in many types of electrochemical systems, and makes the electrochemical systems easy understand. EIS is a non-destructive method, will not harm to battery systems. It is also accessible to collect a plenty of data from this method. It gives us the impedance of the different frequency, and from that we can get the HFR to do more comparison of the aging, temperature and C rate affects to the battery. There are also some researches did research about the battery model based on EIS measurements [10]. This method is accurate and sensitive, and it can be influenced by testing conditions, which are the battery temperature or the connections between cable and battery. Thus it is important to keep the same testing condition.

1.1.2 Goals of Test & Evaluation of battery performance

i. SOC determination gives evaluation of battery performance- *a portable Battery tester can accurate test SOC for OCV*

One focus is to search the SOC determination, find a possible method to develop a portable battery test device to measurement battery condition and battery performance.

ii. Characterize aging, temperature, C rate to the battery performance

Another focus is to study how aging, temperature and C rate influence battery performance and compare the influence between the factors by studying the trends of impedance and capacity for three groups two types of batteries (lead-acid batteries, Ni-Cd batteries). Do comparison experiment of these factors to find which one affects more to the battery capacity and battery life. From the study of different kinds of battery performance under different conditions, Lead-Acid, Ni-Cd Batteries at RT and 50-55 ^{o}C at 1C , C/12 and C/3, it is accessible to get conclusion about the factors' affects and give suggestions to the users and manufactures about how to use the battery can prolong the batteries life as well as how to design the C rate of the charger.

1.2 Test & Evaluation of electrode corrosion

1.2.1 Background and Introduction

The heat transfer fluid is used in Concentrated Solar Power systems to transfer energy. The heat transfer fluid should be stable under high temperature, low freezing point, cheap and less corrosion. Both materials nowadays have a limited operating temperature range [11].

The pipe and vessels were used to contain those Heat transfer fluids. There will be corrosion of the metal materials, and the corrosion is mainly chemical corrosion. The corrosion was studied by design an electrochemical system, the metal materials as the electrode materials, the heat transfer fluids as the electrolyte. Some people did research about using different type molten salts as the heat transfer fluids, some of the work did not take chlorides salts into consideration, and few of them using Hastelloys materials [12]. There is needed to find the alloys can be stable at higher operating temperatures. The metal in the molten salts forms a battery electrochemical system. Study the corrosion behavior of Hastelloys in NaCl-KCl-ZnCl2 ternary molten-salt mixtures. HASTELLOY® C-276 alloy contains 57aNi-16Cr-16Mo-5Fe-4W-2.5**Co-1**Mn-0.35**V-0.08**Si-0.01**C, the corrosion resistance improves when percent of Ni grows in a certain range, and when Ni reaches high percentage over about 80, the corrosion is higher. When Cr is closed to 20, the corrosion is low [13]. What's more, Mo is also helpful to receive a high corrosion resistance. Other elements are also good for the stability at high temperature. HASTELLOY® C-276 alloy has excellent corrosion resistance [14], in oxidizing media and reducing media. HASTELLOY® C-22 alloy contains 56 aNi-22Cr-13Mo-3W-3Fe-2.5*Co-0.50*Mn-0.35*V-0.08*Si-0.010*C, and it can resist to a component which contains mix industrial chemicals. HASTELLOY® N alloy has little degradation with aging and robust. What's more, it can sustain in hot molten salts. The metal materials used in the thesis is the Hastelloy® C-276. The heat transfer fluid is a mixture of NaCl, KCl, and $ZnCl_2$. NACL molten rate is 58.44, melting point is 801°C, and boiling point is 1413°C. KCL molten rate is 136.315, melting point is 770°C, and boiling point is 1500°C. ZNCL2 motlen rate is 136.3 °C, melting point is 290°C, and boiling point is 732 °C. This mixture is relative stable at high temperatures, and cheap.

There are two methods to estimate the Corrosion rates, one is by faraday's law, and one is by testing the weight losses. For testing the weight losses, it needs a long time to make the difference of the weight measurable. And the corrosion rate is average corrosion rate during a long time. By using potentiodynamic method, an electrochemical method, can easily and quickly get the enough information for calculating the corrosion rate.

1.2.2 Goals of Test & Evaluation of electrode corrosion

The goal of the thesis is to do search about the performance of the metal materials made by Hastelloys C-276 in different temperature, 250°C, 300°C, 350°C, 400°C. By using the potentiodynamic method to get the corrosion rate and get a better understanding of the corrosion.

Chapter 2

EXPERIMENTAL

2.1 Materials & Equipment of battery performance

2.1.1 Equipment

Bench Power Supply

The CSI3020X Bench Power Supply was used to charge the batteries. The voltage can be adjusted from 0-30 Volts, and it can also provide a constant current adjusted from 0-10 Amps. This charger was used to charge 8 Amps constant current. User can preset the current. This bench power supply can provides precise output values as the user set.

Fig. 2.1 Bench power supply

DC Power Supply

Array 3631A Programmable Triple Output Dc Power Supply was used to charge 2 Amps constant current. The user can choose 0 – 6V, 5 Amps output mode or 0 – 25V, 1

Amps output. It has low ripple and noise and excellent load and line regulation. User can preset the voltage and current. It has USB, and RS-232 communications, which make it easily to control through computer.

Fig. 2.2 DC power supply

Electronic Load

3711A DC Electronic Load was used to discharge the batteries. This is a programmable device with high performance. Users can set the discharge current and voltage using computer control. The unit can be set for constant current, constant voltage or constant resistance, and it can be used for different types of batteries.

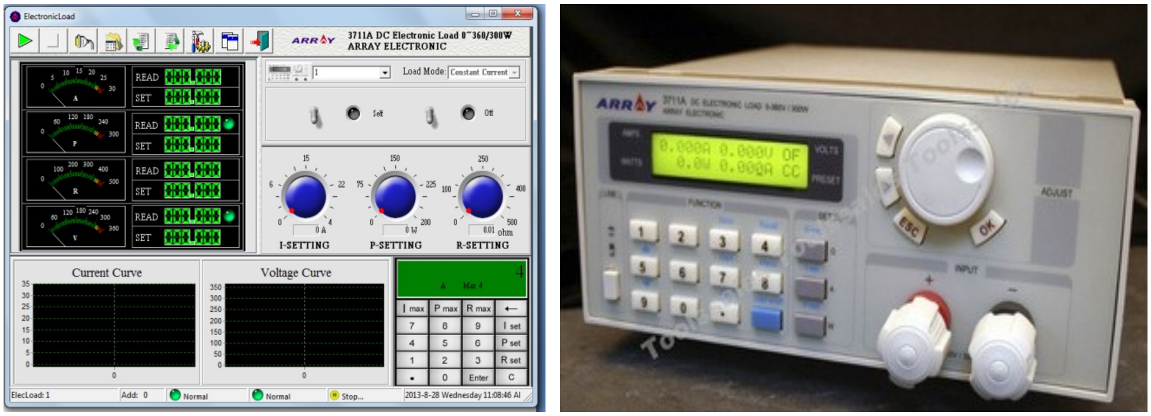


Fig. 2.3 DC electronic load

Computerized Battery Analyzer (CBA)

FThe CBA III and CBA IV were bought from West Mountain Radio, Waukesha, WI. Computer can set the parameters. The users can set up the discharge current and the cutoff voltage. When the discharge voltage reaches the cutoff voltage, it will stop itself. A temperature probe can be used additionally. By the temperature probe, it is possible to monitor the battery temperature and to keep it safe. The test method in the thesis is constant current discharge. CBA uses a solid-state switch and a fan as the cooling electronic load to make the constant current. The users can set the monitor time. Charging and discharging is the easiest way to measure the capacity and study the changes. Using CBA can easily do it. The CBA can be used to discharge from 0 to 40A, the thesis used 2A or 8A constant current.

Fig. 2.4 CBA IV unit

Cadex C7200

The Cadex C7200 has two stations, and it can be used for smaller battery and storefront operations. User can set the charge and discharge current for different kinds of batteries, it is suitable to test Lead-acid battery, NiMH battery, Ni-Cd battery, Li-ion battery and so on. After the user set the cycle number, the cutoff voltage, charge current, the Cadex C7200 can run automatically, and stop when the cycle number is reached. The testing battery voltage range is from 1.2 to 15Volts, the charge and discharge current is from 0 to 4Amps each station, and each station can charge power 40 watts maximum.

Fig. 2.5 Cadex C7200

Impedance Analyzer

PARSTAT 2273 Advanced Electrochemical System can be used to measure the battery impedance under room temperature. It can be used for EIS (Electrochemical impedance spectroscopy) method. Users can set the frequency range, AC amplitude, point number by using Powersuit, the software matched the equipment. The frequency range is 10 μHz to 1 MHz, the scan voltage range is -10V to +10V, the current range is -2A to +2A.

The frequency used in the thesis is from 10 μHz to 1 KHz, and the voltages were usually from 1.8V to 2.3V. The largest voltage used was 6V. The AC amplitude was chosen according to the 8% of the battery voltage. It will show three figure, the Nyquist plots and Bode plots can tell us the transition between the reaction proceeding under kinetic or transport control [10].

PARSTAT 2273 was used to test the electrochemical system by potential dynamic method. The PARSTAT can be used to test the electrode corrosion. It can be used to test many kinds of electrodes, it can be used to test microelectrode, mercury electrode.

Fig. 2.6 PARSTAT 2273

2.1.1 Battery types

Group I. Ni-Cd battery 2 V, 8 Ah (ACME #2, 3, 4)

In the thesis, ACME #2, 3, 4 were marked to easy discuss. ACME #1 already been used, in the thesis, not include ACME #1. Before 20 cycles, ACME #3, 4 were charged and discharged with at room temperature. From 20 to 25 cycles, ACME #3, 4 were charged at room temperature and discharged at 55 ^{o}C. After 25 cycles, ACME #3, 4 were charged and discharged at 55 ^{o}C. ACME #2 was always charged and discharged at room temperature. During the whole test, the batteries were charged at C/3 rate, discharged at C/3 rate. The capacities were calculated for each cycling and the impedances were measured for charge state and discharge state as well as different SOC, 20, 40, 60, 80, 100%.


Fig. 2.7 Group I. Ni-Cd battery 2V, 8Ah

Group II. Sealed-Lead CYCLON® battery 2 V, 8 Ah (SLA #3, 4)

In the thesis, SLA #3, 4 were marked to easy discuss. SLA #1, 2 already been used, in the thesis, not include SLA #1, 2. Before 55 cycles, the batteries were tested under room temperature. After 55 cycles, these batteries were charged and discharged at 55 ^{o}C. These batteries were charged at C/4 rate and discharged at 1C rate during the whole test. The capacities were calculated for each cycling and the impedances were measured for charge state and discharge state as well as different SOC, 20, 40, 60, 80, 100%.

Fig. 2.8 Group II. Lead-acid battery 2V, 8Ah

Group III. Sealed-lead CYCLON® battery 2 V, 25 Ah (SLA #5, 6, 7, 8)

In the thesis, SLA #5, 6, 7, 8 were marked to easy discuss. There were four experiments to compare temperature and C rate influences to the battery by testing them under different temperature and C rate. To compare the working condition affects, the capacities have been calculated and the impedances have been tested. The test details are showed below:

SLA #5: Charge in C/12 rate and discharge in C/3 rate at temperature 55- 60 ^{o}C

SLA #6: Charge in C/3 rate and discharge in C/3 rate at room temperature 27 ^{o}C

SLA #7: Charge in C/12 rate and discharge in C/3 rate at room temperature 27 ^{o}C

SLA #8: Charge in C/3 rate and discharge in C/3 rate at temperature 55- 60 ^{o}C

2.2 Materials & Methods of electrode corrosion

2.2.1 Materials

The NaCl, KCl and ZnCl2 were bought from Alfa Aesar. The weight for the electrolyte is 0.5gNaCl, 0.5gKCl, and 52.9gZnCl2. Melted them in 250 ^{o}C muffle furnace to obtain the molten salts. Silver and silver chloride powders were bought from Strem Chemicals (Strem Chemicals, Inc. Newburyport, MA, USA), the pure of them are 99.95% and 99.9% respectively, molten and solid them as the reference electrode. As the working and counter electrode, HASTELLOY® C-276 alloy was bought from Haynes International Inc. The thickness is 0.4mm. It has high corrosion resistance with in oxidizing media and reducing media. Within the electrolyte, the corrosion rates of Hastelloy C-276 were tested under 250 °C, 300 °C, 350 °C, 400 °C.

2.2.2 Experimental Set-up

First, make the electrolyte.

Weight the NaCL, KCL, ZnCl2, 0.5g 0.5g 52.9g

Put the solution into the muffle furnace, 250 °C for 2 hours make it become molten salts.

Second, make the reference electrode.

Weight Ag, AgCl, KCl 1:1:1 for 0.3g respectively.

Put into the frit with an Ag rod inside, the pore size is about 25 μm.

Put the frit into the muffle furnace and heat to 500 °C for 2 or 3 hours to make it solid.

Test the reference electrode potential, using a saturated calomel electrode (SCE) to calibrated in saturated aqueous KCl solution at room temperature.

Third, make the working electrode.

Cut the HASTELLOY® C-276 alloy 2cm*2cm.

Forth, make the counter electrode.

Cut the HASTELLOY® C-276 alloy 1cm*1cm.

Fifth, potential dynamic method

Wait them cool down and test the impedance and polarization for 250 °C, 300 °C, 350 °C, 400 °C.

In order to eliminate any mixed potentials in the three electrodes system, the counter electrode material was the same alloy used as the working electrode in every measurement.

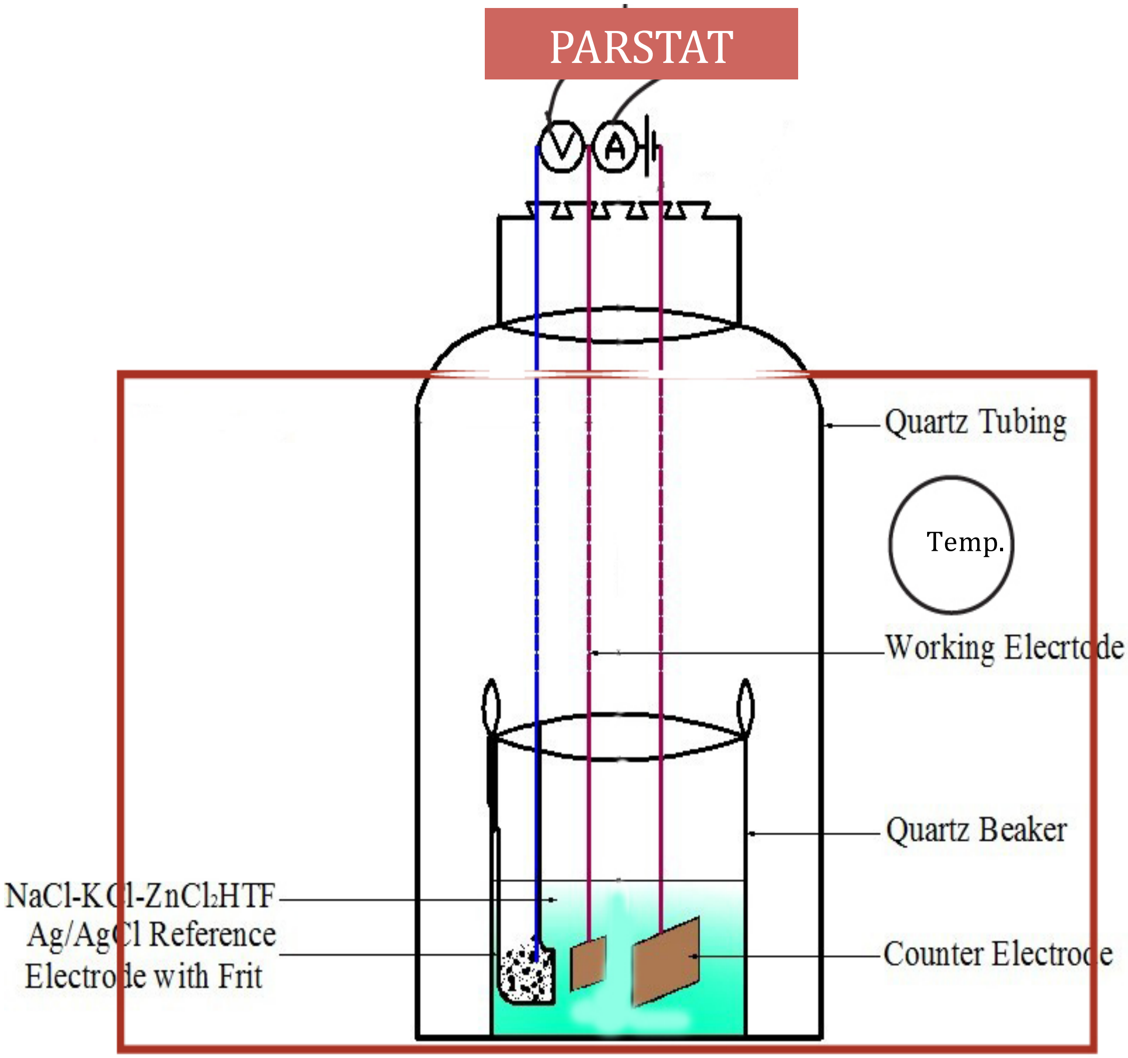


Fig. 2.9 Schematic of experimental set-up

It is for conducting high temperature corrosion by potentiodynamic method for Hastelloys in NaCl-KCl-$ZnCl_2$ eutectic molten salts.

The tubes were put into the muffle furnace. There was a thermometer on it. Through the thermometer, it is convenient to control the temperature. Thermocouple was not needed.

The test system is three electrodes system. The three-electrodes system has two loops. One is consisted of working electrode and counter electrode that is for testing the electrochemical reaction of working electrode, testing the current. Another one is consisted of working electrode and reference electrode to create a loop for transmitting electrons, testing the voltage. The counter electrode provides a stable potential during the testing progress. The counter electrode is needed for the reason that the potential of working electrode and reference electrode changes sometimes and they are not always stable during the test. In order to know the exactly working electrode potential, it is needed to use a non-changed potential electrode as the counter electrode. During testing, there is an extremely small current through the counter electrode and it will not influence the potential change. The counter electrode was the same materials as the working electrode to avoid mixed potentials in the system.

2.2.2 Method of caculation corrosion rate

Potentiodynamic Method

Under the extra electric field, the electrochemical reaction speed is slower than the movement of the electrons, and it causes the electrode potential changes in electric double layer. This process we call it electrochemical polarization. Feature of the electrochemical polarization is, there are superfluous electronics accumulated on the surface of the positive electrode, then it potential is nearly negative.

Test steps:

First, clean the working electrode and the counter electrode.

Second, connect PARSTAT 2273 to the working electrode, counter electrode, and reference electrode.

Third, wait 1 hour for a stable voltage.

Forth, test the electrochemical polarization for different temperature.

Corrosion rates formula:

$$CR\ (in\ \mu m\ per\ year) = \frac{K_1 \times i_{corr} \times EW}{\rho}$$

This formula is from ASTM Standards G 59 and G 102 [15]:

Where $K_1 = 3.27$ in $\mu m.g.\mu A^{-1}.cm^{-1}.yr^{-1}$, i_{corr} is the corrosion current density in $\mu A.cm^{-2}$, EW is the equivalent weight. The ρ is the density ($g.cm^{-3}$) of the Hastelloy. The current density is from the projected area but not real area, so it will not influence by corrosion.

Weight losses method

Another corrosion rate calculate is by weight losses.

Mils penetration per year (mpy)

$$mpy = \frac{534W}{D * A * T}$$

Where, W = weight loss (gms)

D = density of the specimen, g/cm3 A = area of specimen, sq. in.

T = exposure time, hr.

The drawback is this method takes a long time to make the difference of the weight be measurable. And the corrosion rate is the average value during the time.

Chapter 3

RESULTS OF TEST & EVALUATION OF BATTERY PERFORMANCE

3.1 Results of SOC determination give evaluation of battery performance

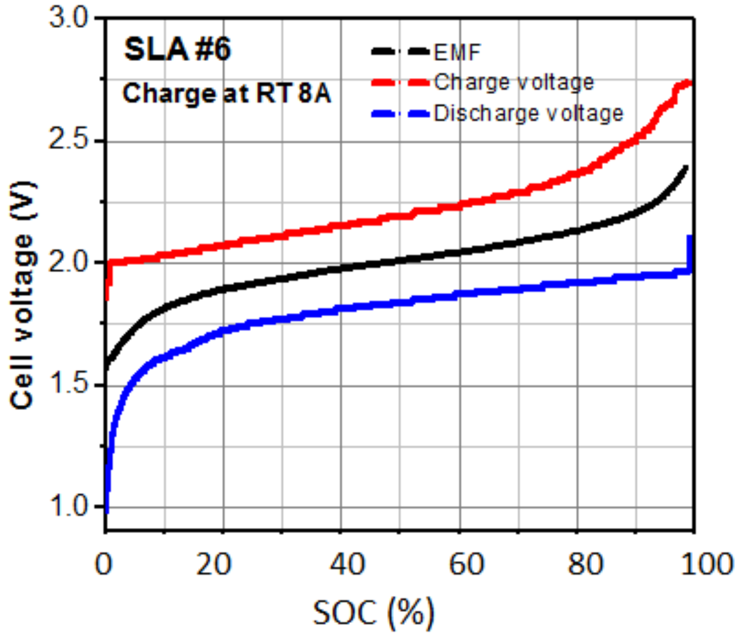


Fig. 3.1 SOC determination by EMF

The SOC can be decided by using the discharge graph at particular C rate, EMF method, pulse load method, specific gravity of the electrolyte, AC impedance measurement [3].

For the EMF method, the graph shows that there are two curves, charging and discharging, the average of these two curves are calculated, and the SOC can be calculated from the run time. Then it can be used to judge the SOC in a charging or discharging circuit. The EMF method does not provide continuous indication of the SOC, and the battery should be charging or discharging, in other words, the EMF method can only be used when the battery is working. But it is a widely used method, easy and convenient. The EMF curve does not depend on aging and temperature of the battery.

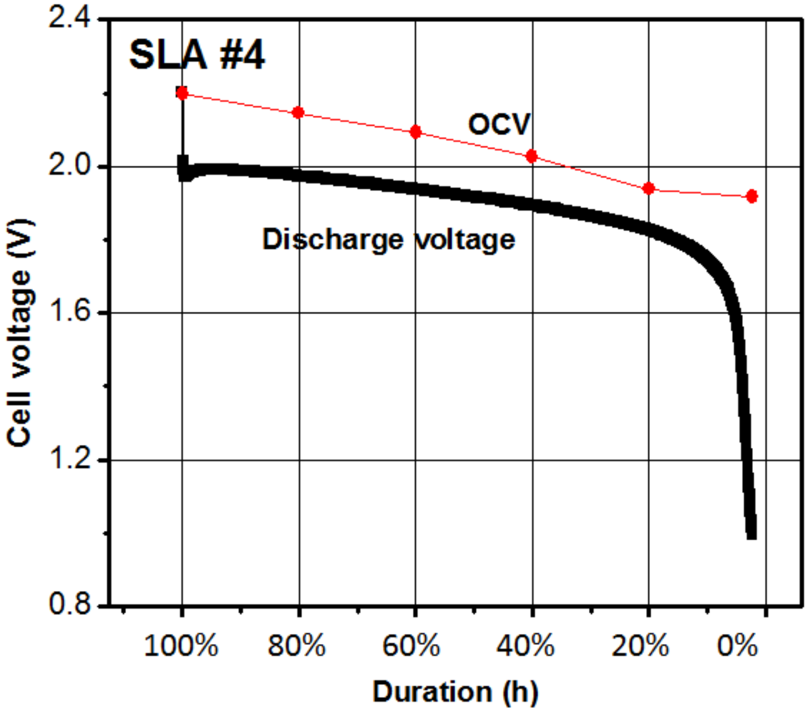


Fig. 3.2 SOC determination by discharge at particular C rate

Another method is to decide the SOC through discharge graph at particular C rate [2]. This figure is the OCV at different SOC and the discharge curve. It is easy but the voltage discharge curve strongly depends on the discharge rate. If collect different C rate discharge open circuit voltage, it will be easier to decide the SOC. Temperature also should be taken into consideration. The figure shows that the voltage when it is discharging is different from the open circuit voltage. So for the EMF method, it cannot be used to decide the OCV. Through discharge at particular C rate is a convenient method but the main drawback is it is hard to know the battery using history, the discharge C rate.

The third method is based on the impedance. Impedance is the whole of resistive, capacitive and inductive resistance. Capacitive reactance decreases with increasing frequency. Inductive reactance increases with increasing frequency. Resistive resistance is influenced by temperature.

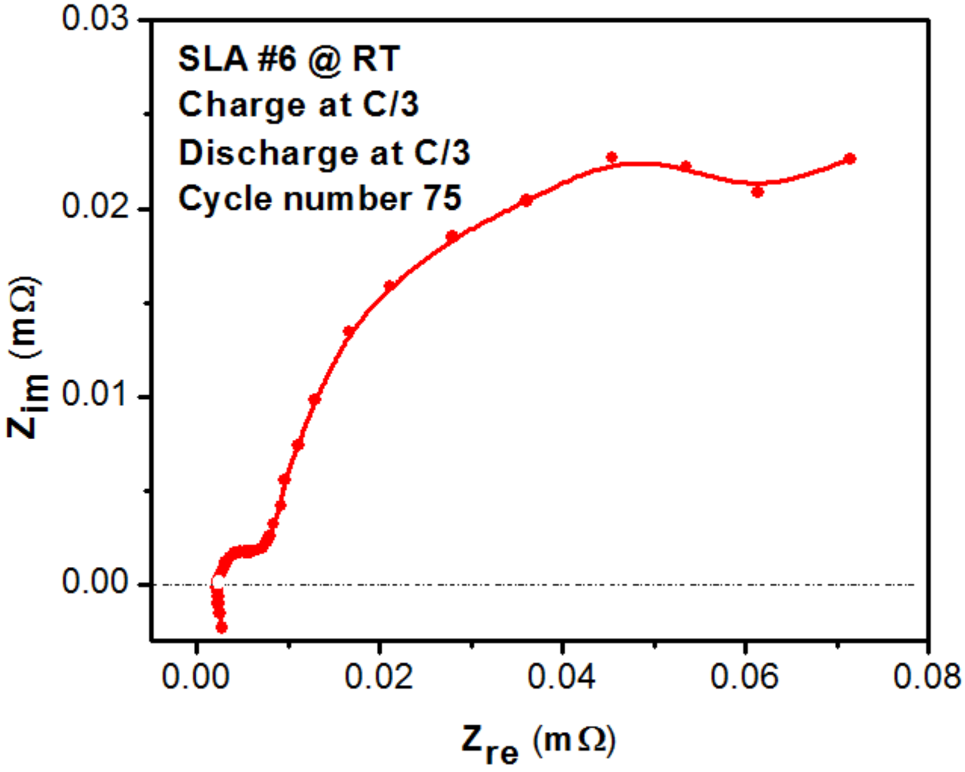


Fig. 3.3 SLA #6 impedance Nyquist diagram

Here is a typical impedance graph based on EIS method. This is a Nyquist diagram of lead- acid battery in full charge state. The point cross zero is the HFR. The HFR: 2.3 mΩ, Frequency 138.9Hz. HFR becomes higher as the battery capacity degrades with cycling.

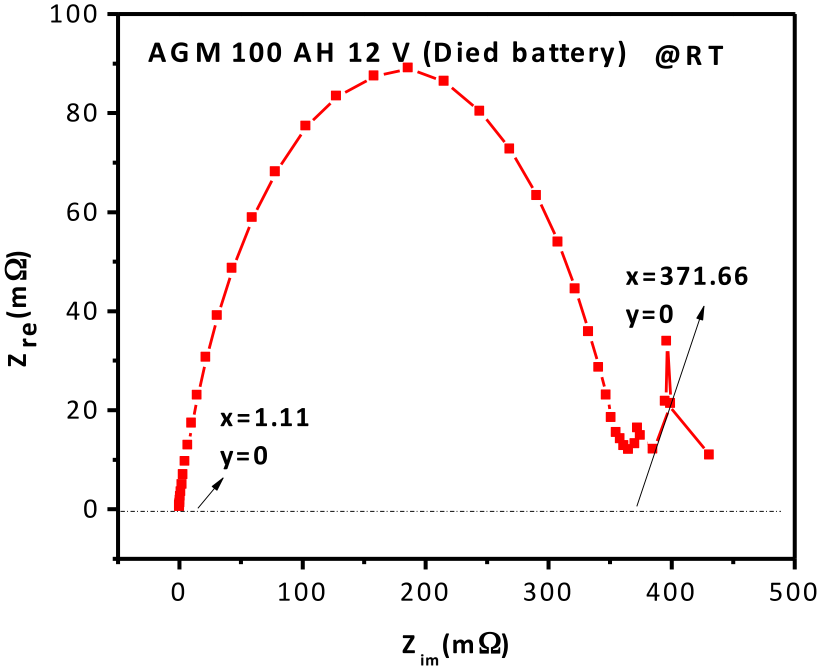


Fig. 3.4 The EIS data in old battery

This is the EIS data in old battery. VRLA battery has capacitance100 Ah 12 V. The battery almost lost the all capacity. The Nyquist plots can show the transition between the reactions proceeding under kinetic or transport control

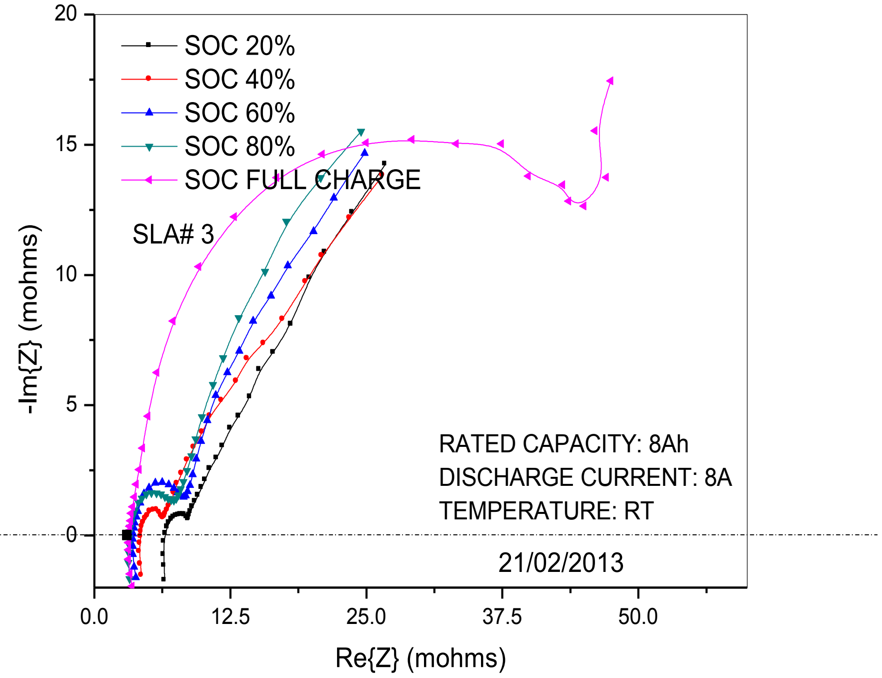


Fig. 3.5 Impedance characteristics of different SOC for SLA #3

The graph shows the full charge high frequency resistance is lower. The impedance change with different SOC shows that at different SOC, the curve is different. It provides another method to test the SOC. However, this method is not practical for SOC indication in a portable device. Because a frequency sweep signal should be applied to the battery, the device will be large. And EIS method to test the SOC will take a longer time. One method to solve this problem is to collect a plenty of data for different C rate, HFR and make a look up chart. By using the chart into a portable battery device, it is accessible to test the battery SOC.

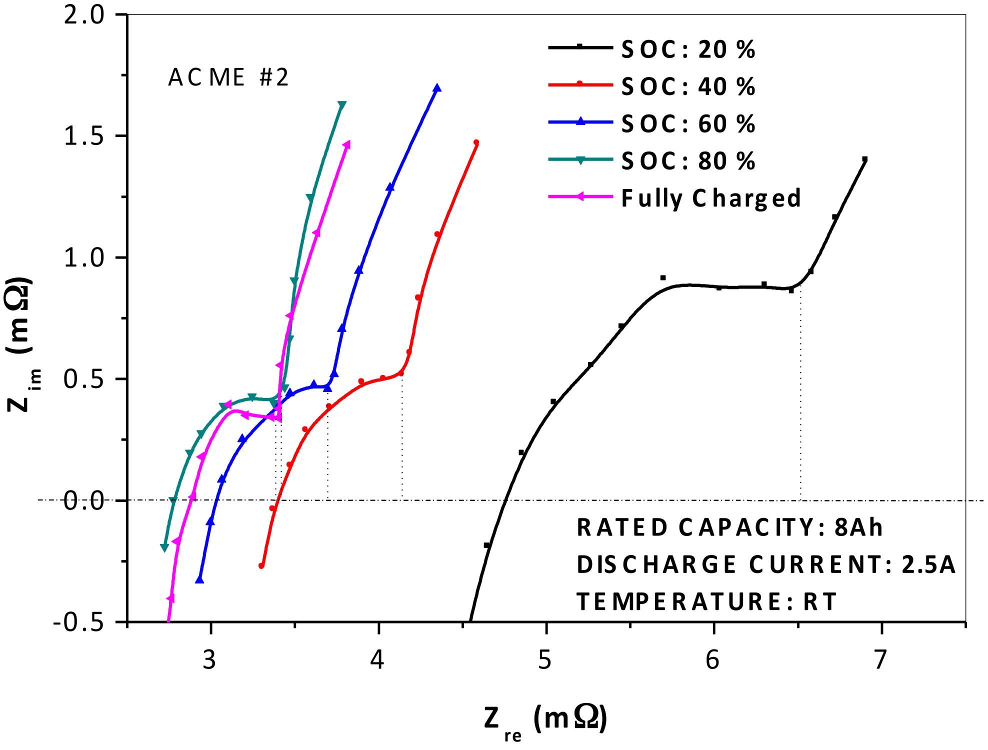


Fig. 3.6 Impedance characteristics of different SOC for ACME #2

The impedance characteristics of various SOC for Ni-Cd batteries are similar to the graphs of SLA batteries. From the impedance change with different SOC, it can be seen that the 20% SOC has higher HFR than 40%, and the 40% SOC has higher HFR than 60%, the full charge HFR is near the 80% percent curve. It provides an accessible method to measure the state of charge.

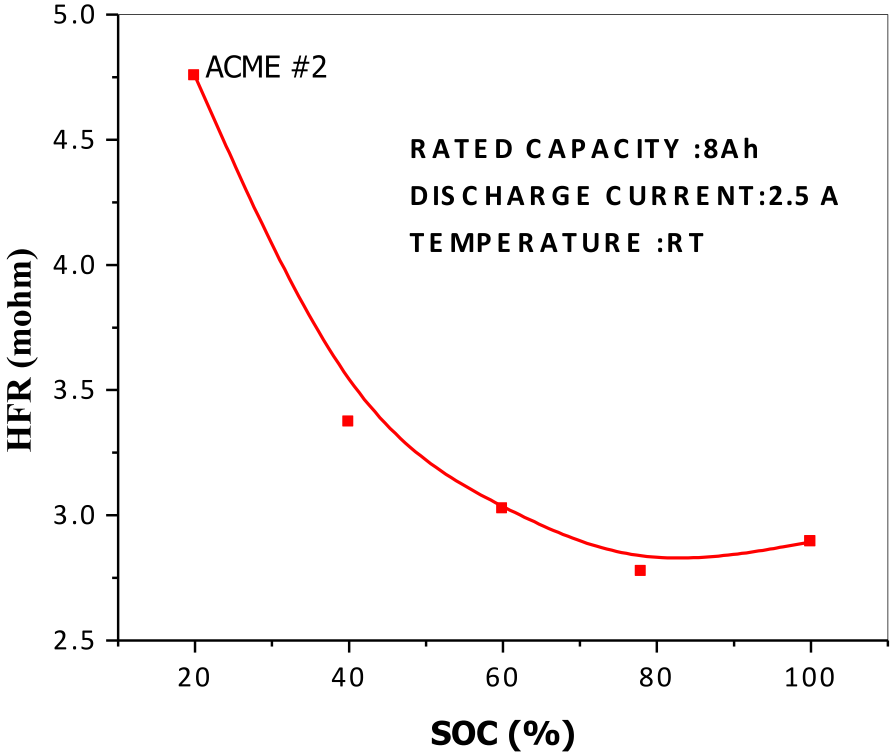


Fig. 3.7 ACME #2 HFR change with SOC

This figure shows that the HFR is lower when SOC higher. The HFR of the full charge state is a little bit higher than the HFR of 80% percent. This figure clearly shows that the HFR changes with the SOC.

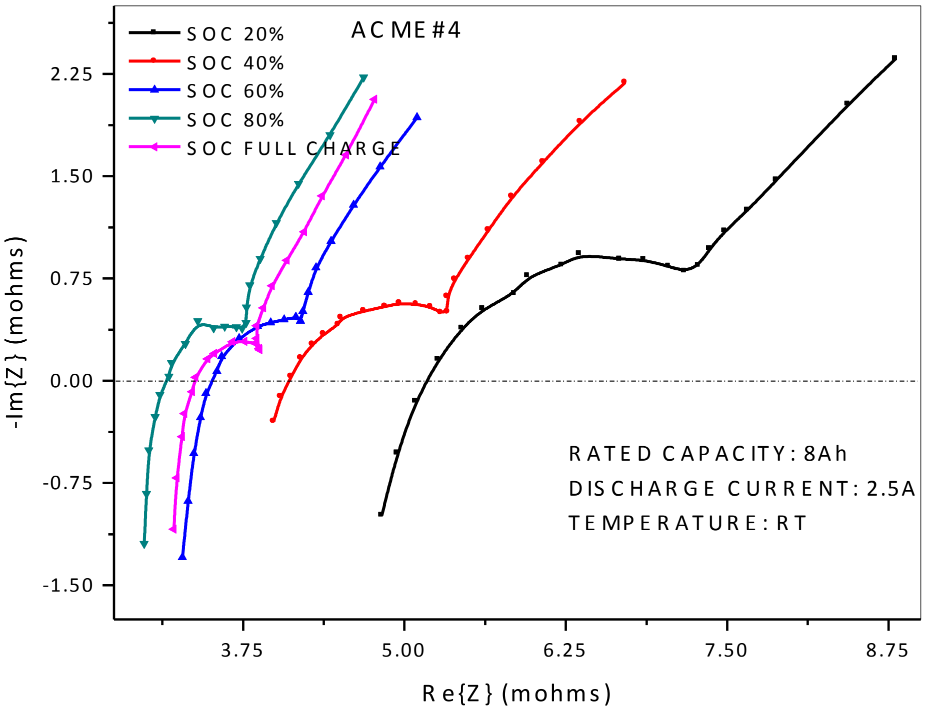


Fig. 3.8 Impedance characteristics of different SOC for ACME #4

ACME #4 SOC figure is similar to ACME #2, the full charge SOC is between the 80% and 60% curve.

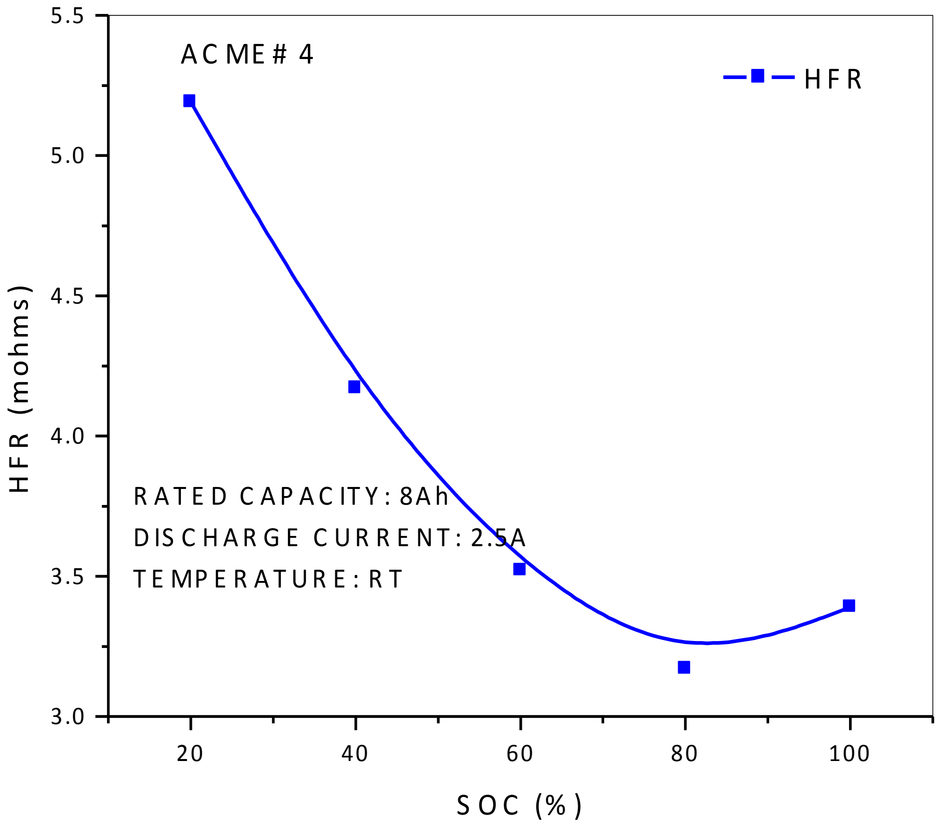


Fig. 3.9 ACME #4 HFR change with SOC

Again, the graph shows that different state of charge, different high frequency resistance.

This method can be used for open circuit voltage, and it is not dependent on temperature.

The chart below shows the SLA #4 charge and discharge impedance with cycling as an example to show that HFR change with cycling.

By collecting the HFR values and the frequency for different SOC, it can be used to make a reference table for the portable device to test the battery state of charge easily and accurately. So it is a widely used method.

Table 3. 1, take SLA #4 charge and discharge impedance with cycling as an example, from the table, the charge impedance of the SLA #4 is keeping increasing, the impedance of the discharged battery is increasing but only one point. It might be caused by the different time interval between the discharge finish and impedance test. When the battery is discharging, the cutoff voltage is 1.0 V.

Table 3.1 SLA #4 charge and discharge impedance with cycling

		Charged		**Discharged**	
Cycle number	Temperature	HFR(mΩ)	High Freq.(HZ)	HFR(mΩ)	High Freq.(HZ)
26	RT	3.128	372.8	5.957	372.8
35	RT	3.294	372.8	6.433	719.7
40	RT	3.370	517.9	6.535	1000
55	RT	3.478	517.9	5.526	719.7
70	50C	6.732	517.9	13.25	10,000

The impedance of the fully charged battery is increasing with the cycle number. Some people developed modeling based on impedance [16]. When the battery finished discharge and immediately test the voltage, the voltage is 1.85 Volts, when put the battery for 10 minutes, the voltage will grow up to 1.9 Volts, so it make it hard to use the discharge impedance to test the battery condition. So the later discussions in this thesis use the full charge impedance.

3.2 Results of Characterize aging, temperature, C rate to the battery performance

This is a typical discharge graph. In this figure, the battery was charged at the rate of C/4, discharged them at the rate of 1C rate at room temperature.

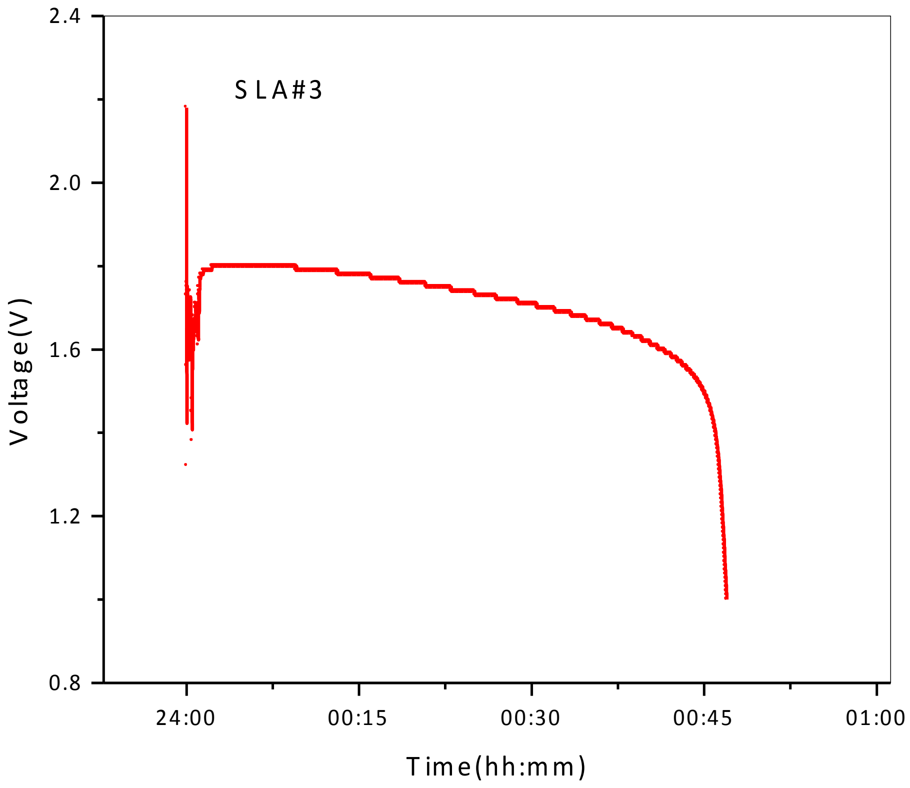


Fig. 3.10 Discharge graph of the SLA #3

In the figure above, according to the discharge time, the capacity is about 80 percent. There is a sudden drop at the beginning of the battery discharge stage.

It is caused by the electrochemical reactions within the battery; the reaction name is coup de fouet. The coup de fouet can be seen in the fully charged battery, so it is a signal to show that the battery is fully charged. In a very short time, the voltage recovers [17].

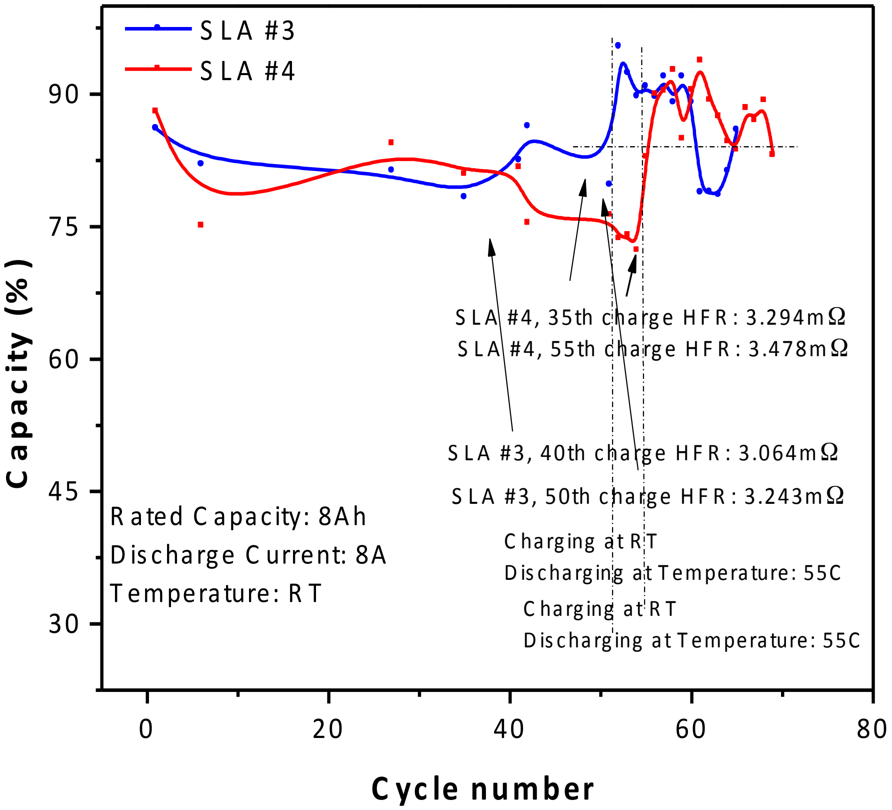


Fig. 3.11 Capacity of the batteries SLA #3, 4

Figure above is Group II. Seal Lead-acid battery 2 V, 8 Ah (SLA #3, 4). It shows that the battery capacity decreases from about 87 percent to 75 percent in 55 cycles of charge and discharge. The high frequency resistance for SLA #3, 40th cycle, charge HFR was 3.064mΩ, 50th cycle, charge HFR was 3.243mΩ. The high frequency resistance for SLA #4, 35th cycle, charge HFR was 3.294mΩ, 55th cycle, charge HFR was 3.478mΩ. It showed that HFR becomes higher as the battery capacity degrades with cycling.

After 55 cycles, the batteries were charged and discharged at 55 ^{o}C. The capacity grew up to about 10 percent.

From this experiment, there were three questions:

Is all kinds of battery will have better performance when charging and discharging at high temperature?

Is charging temperature influence the battery performance or discharging temperature?

What could be the results if there are more cycles? How long will this better performance remain in higher temperature?

When the batteries were put into higher temperature, the capacity increased, in order to figure out how the temperature and C rate influences the battery capacity and impedance, the thesis investigated and designed experiment: charging and discharging the battery under different temperatures for different C rates.

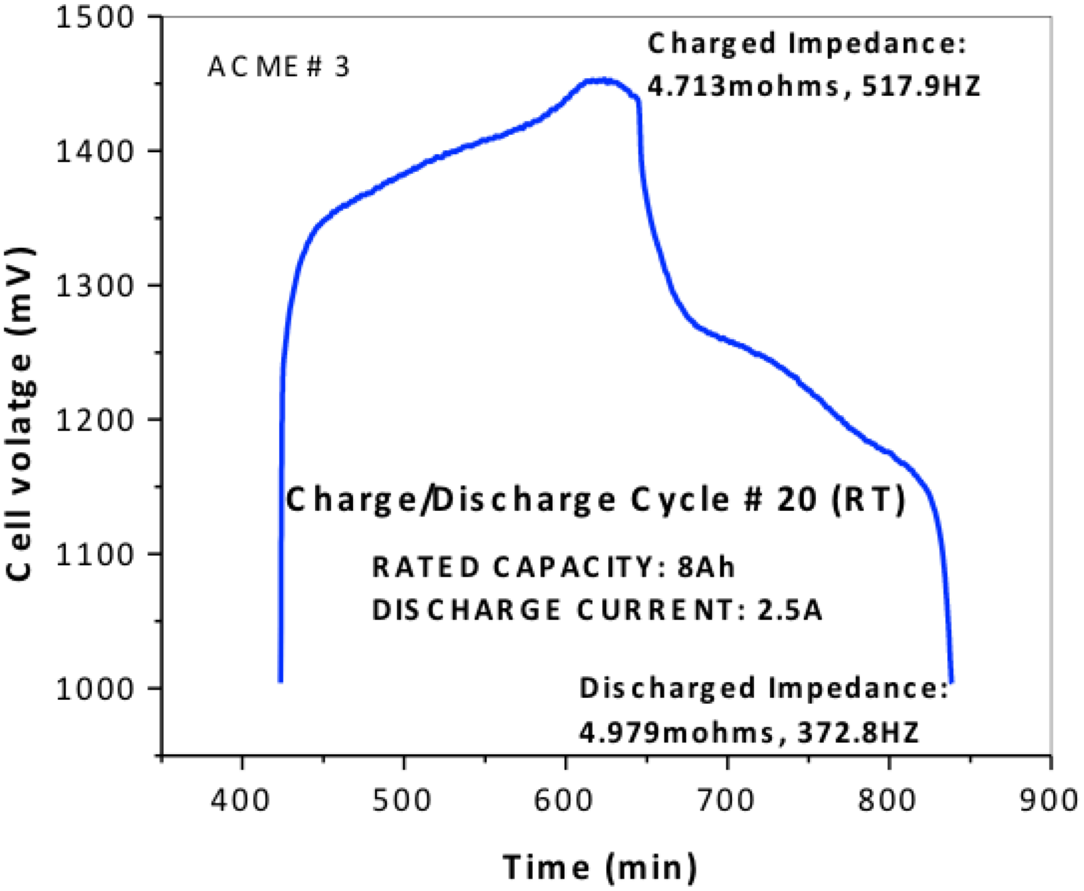


Fig. 3.12 Charge and discharge of battery ACME #3

The figure is Group I. Ni-Cd battery 2 V, 8 Ah (ACME #2, 3, 4). The battery was charged and discharged in 2.5A at room temperature in this figure. It is the charge and discharge graph of Ni-Cd with the cycle number 20. The charge impedance is 4.713mΩ at 517.9Hz and the discharge impedance is 4.979mΩ at 372.8Hz. The full charge impedance is higher than discharge impedance.

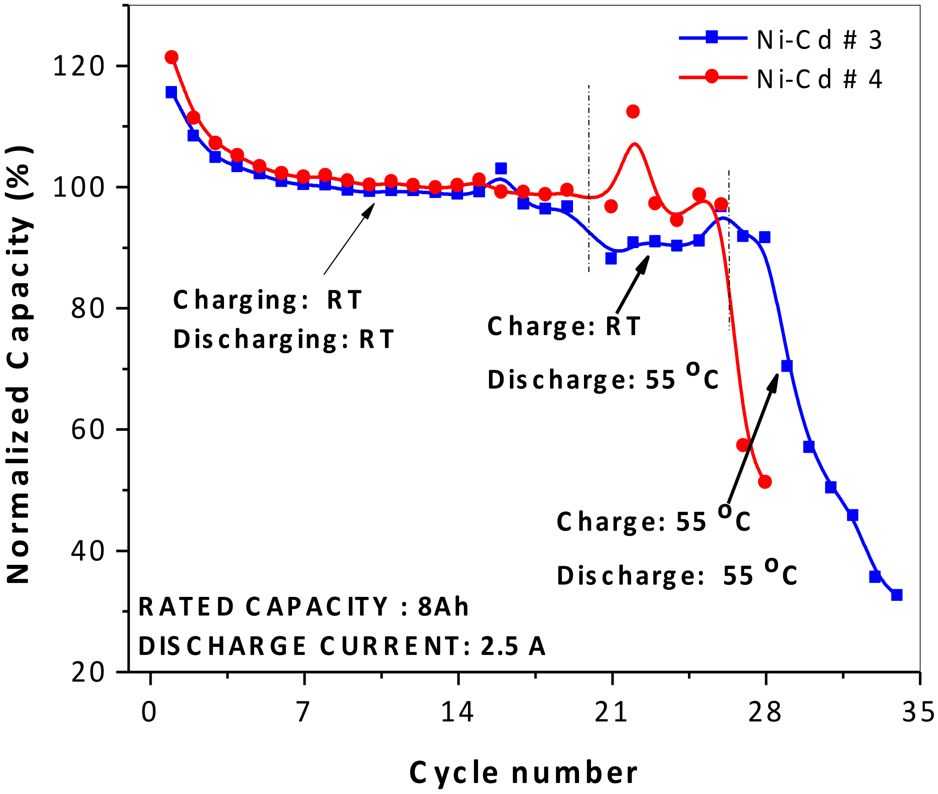


Fig. 3.13 ACME #3, 4 capacities degrade

The ACME Ni-Cd batteries were tested, marked them as ACME #3 and ACME #4. The testing was divided into three parts, first part was tested under room temperature for about 20 cycles; the capacity was 8Ah, discharge current 2.5A. The second part was charging at room temperature and discharging at high temperature for about 5 cycles. The third part was charging and discharging at 55 ^{o}C.

For the first part, the first 3 cycles drop quickly from 120 percent to 100 percent, and then it remained rather stable around 100 percent.

For the second part, the capacity has a little decrease when charge the battery at room temperature and discharge at 55 ^{o}C.

For the third part, capacity drops quickly and finally stays about 40 percent.

When the batteries are put into the oven for charging and discharging, the capacity decreases quickly. When the Ni-Cd batteries are put at 55 ^{o}C, it is hard to make it fully charged. When using 2.5A and charge for 3.2 hours and discharge, it shows 40 percent or 60 percent capacity.

This experiment solved the first two questions in the last experiment:

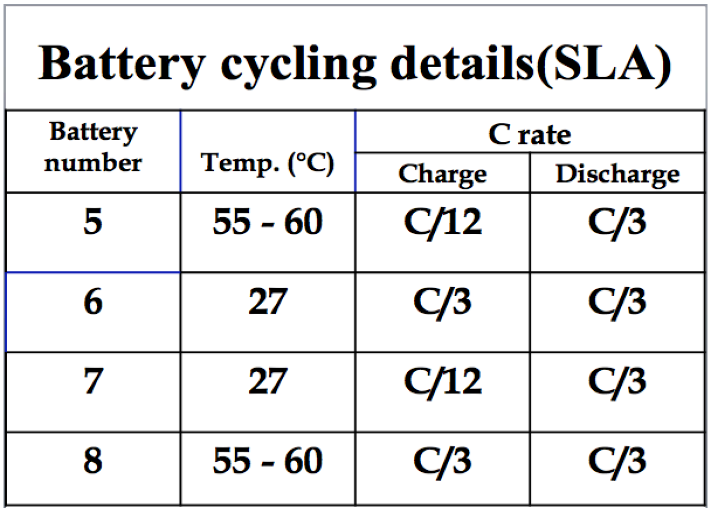
First, not all batteries will have batter performance under a higher temperature.

Second, Charging temperature has more affects on the battery performance. Since the batteries were charged at room temperature and discharge at high temperature did not have an obviously capacity degradation. While when the batteries were charged at room temperature, the degradation is quickly.

The figures below are batteries for Group III. Sealed-lead CYCLON® battery 2 V, 25 Ah (SLA #5, 6, 7, 8).

In order to study the temperature and C rate influence to the batteries, the batteries were charged and discharged under different conditions. Below are the test details.

Table 3.2 Group III Seal-acid battery 2 V, 25 Ah cycling details



Battery cycling details(SLA)

Battery number	Temp. (°C)	C rate	
		Charge	Discharge
5	55 - 60	C/12	C/3
6	27	C/3	C/3
7	27	C/12	C/3
8	55 - 60	C/3	C/3

There are four experiments under different conditions. SLA #5 and 8 were tested under high temperature.

SLA #6 and 7 were tested under room temperature. SLA #6 and 8 are charging in high C rate (C/3). SLA #5 and 7 are charging at low C rate (C/12).

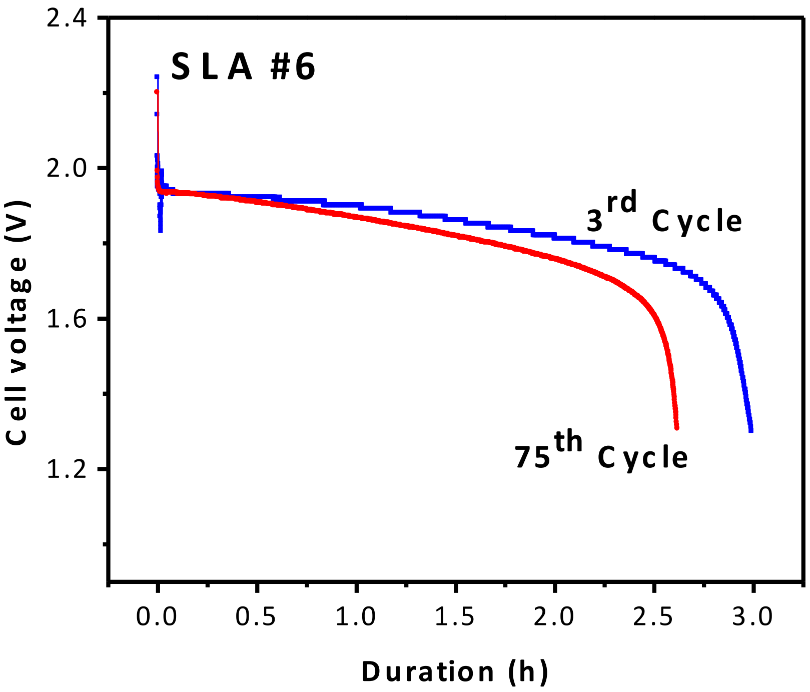


Fig. 3.14 SLA #6 discharge

To study the capacity degradation with aging, the figure shows the discharge graph of different cycle number, one is collected when the battery was fresh, and one is old. The run time of 75th cycle is lower than the run time of 3rd cycle, it can be concluded that the capacity decreased. Capacity has a little degradation after about 70 cycles, the capacity changes from about 100 percent to 85 percent even at room temperature.

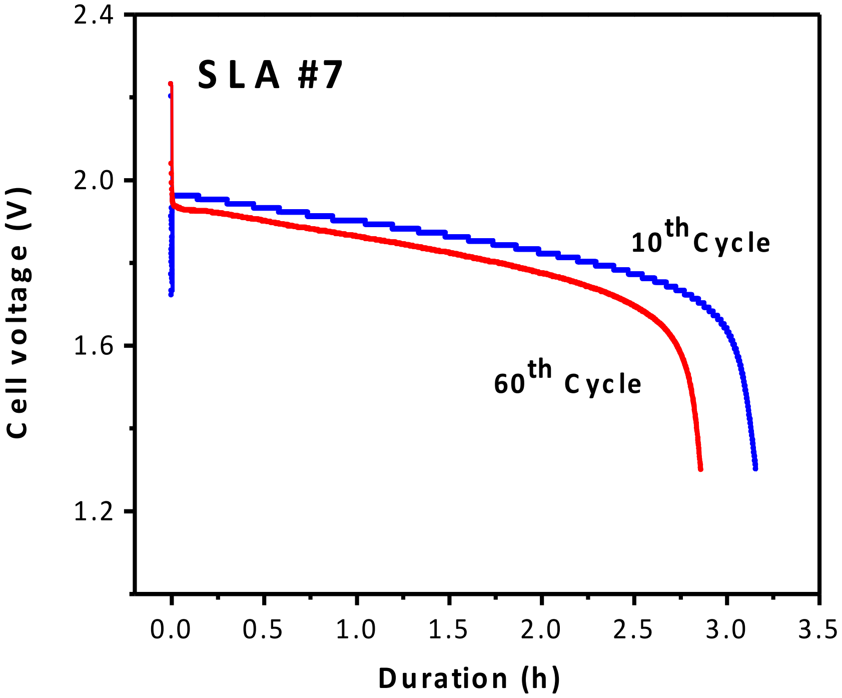


Fig. 3.15 SLA #7 discharge

SLA #7 capacity has a little degradation after about 50 cycles, the capacity changes from about 100 percent to 90 percent.

From figure.21 and figure. 22 it can be concluded that relatively, the battery charges at higher rate degrades fast, at room temperature.

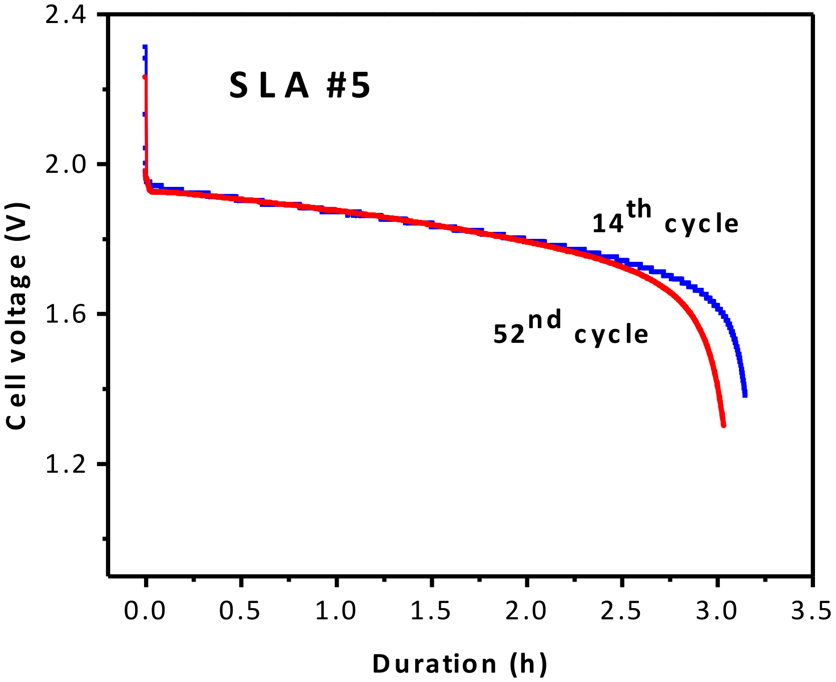


Fig. 3.16 SLA #5 discharge

SLA #5 capacity has a little degradation after about 30 cycles discharge. The capacity changes from about 104 percent to 99 percent.

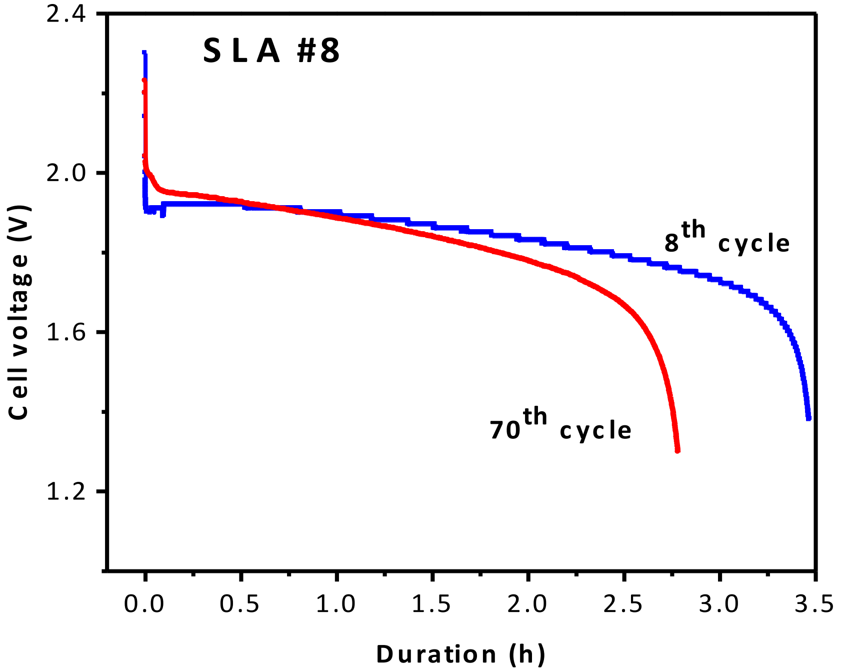


Fig. 3.17 SLA #8 discharge

SLA #8 capacity has an obvious degradation after about 50 cycles discharge. The capacity changes from about 110 percent to 85 percent. At elevated temperature, higher electrolyte conductivity, the higher current migration ability and the migration resistance will be lower. These lead the improvement of discharge performance. However, the degradation is fast.

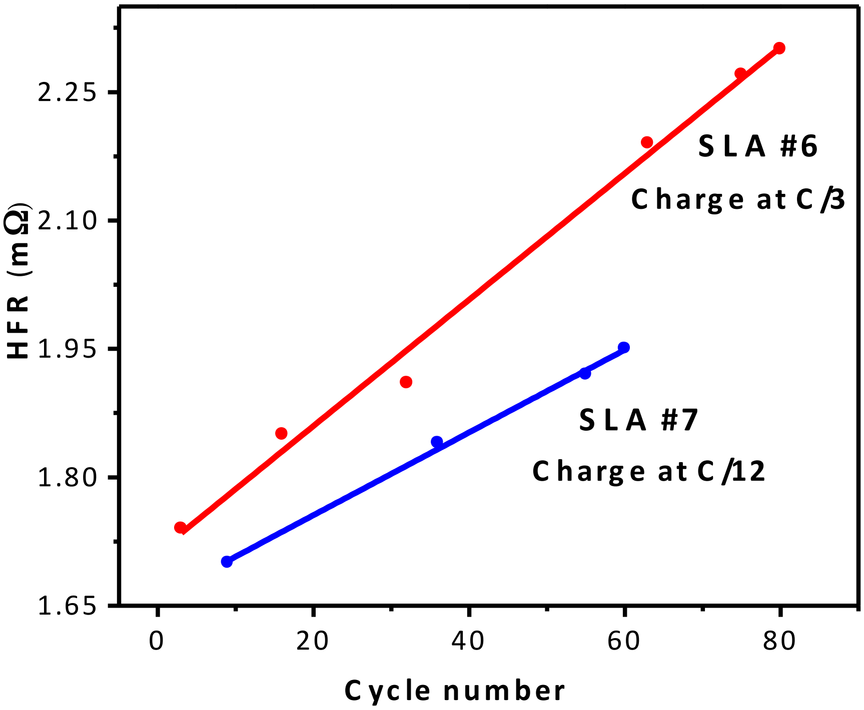


Fig. 3.18 HFR values of SLA #6 & 7

HFR becomes higher as the cycle number higher.

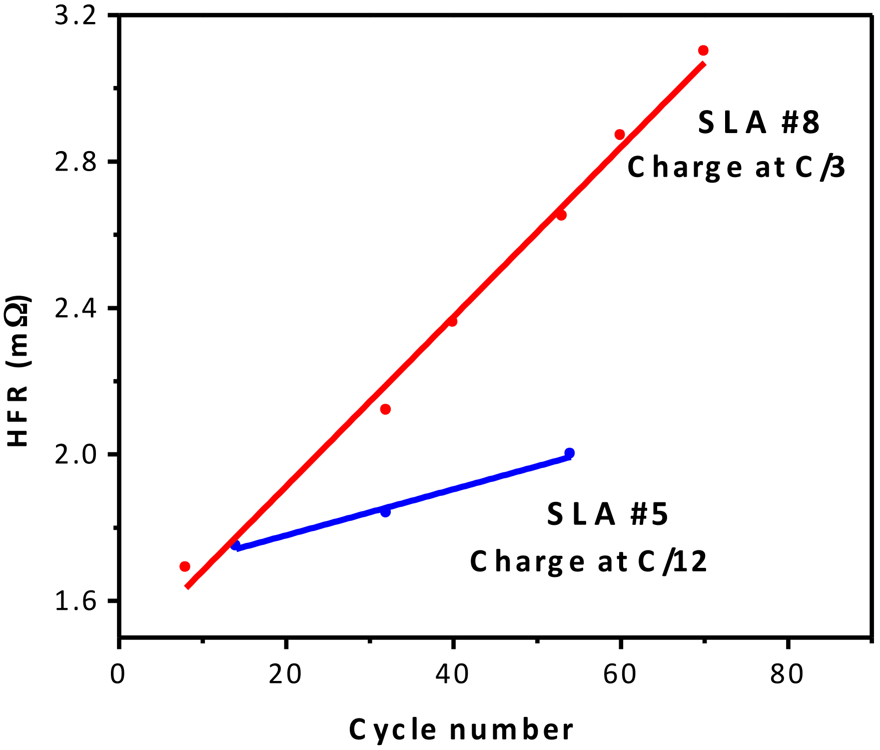


Fig. 3.19 HFR values of SLA #5 & 8

The figure shows that the rate of increase in HFR is higher for a battery with faster charging rate.

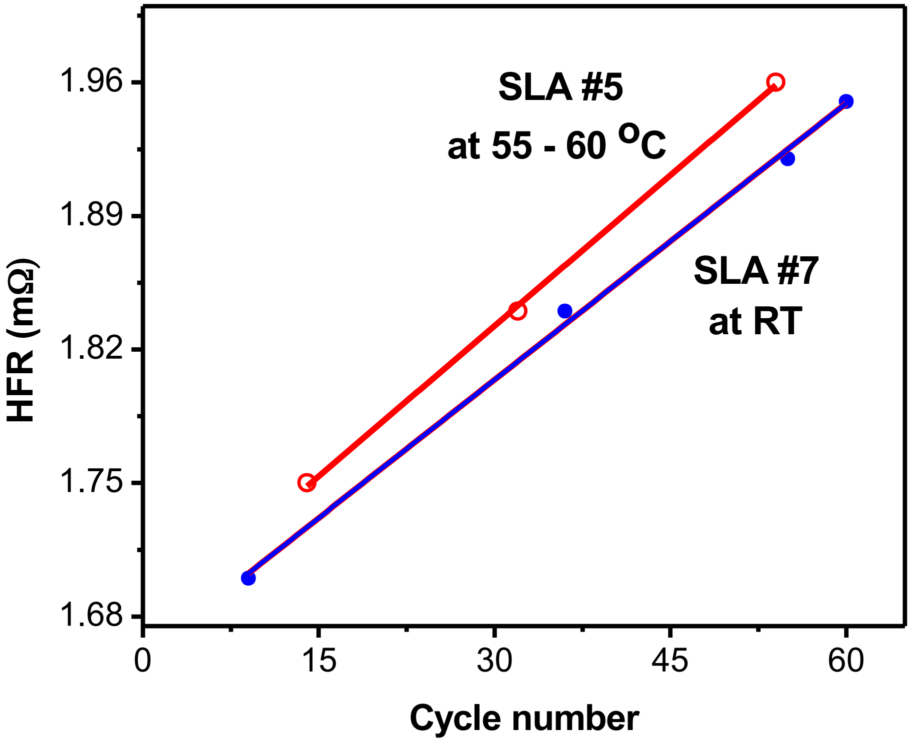


Fig. 3.20 HFR values of SLA #5 & 7

It is interesting to note that the rate of increase in HFR is not high even at 60 ^{o}C, if the charging slowly.

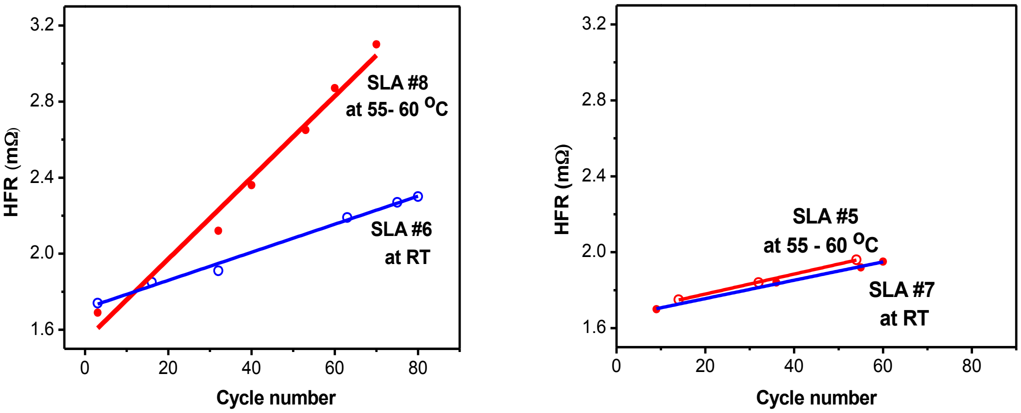


Fig. 3.21 The contrast of the influences of the C rate and temperature

Temperature influences the internal chemical reactions of the battery. The hotter the battery, the faster chemical reactions will occur.

The Battery degrades fast at elevated temperature only when the charging is carried out faster (C/3 rate).

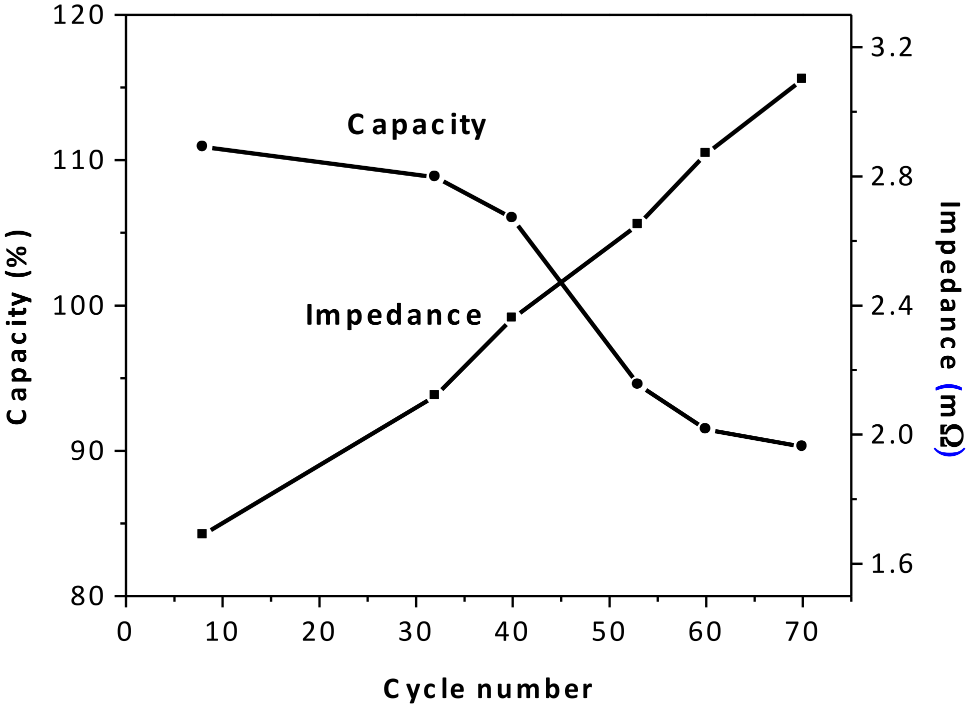


Fig. 3.22 Capacity degradation with impedance change

This is the capacity degradation and impedance increasing of SLA #8 as an example. The graph shows that the more cycle number, the lower capacity, and the higher impedance. The capacity losses for lead acid batteries are caused by sulfation, the grid corrosion and lower density of the electrolyte [18]. Self-discharge can lead to sulfation. Sometimes recharging can reduce it. However, if the sulfation is remained long time and too much, it will be hard to reduce. The chemicals in the electrolyte lead to the grid corrosion. When the temperature is higher, these unwanted chemical reactions speed will be higher, in other words, the corrosion reaction speed increases.

Chapter 4

RESULTS AND DISCUSSION ON CORROSION OF METALLIC ALLOYS

The figure below shows the polarization for the Hastelloy C-276 in molten salt $NaCl-KCl-ZnCl_2$ at 250 °C by potentiodynamic method. The left branch is anode polarization and the right branch is cathode polarization. Draw tangent for each branch and the crossing is the i_{corr} values [18-20].

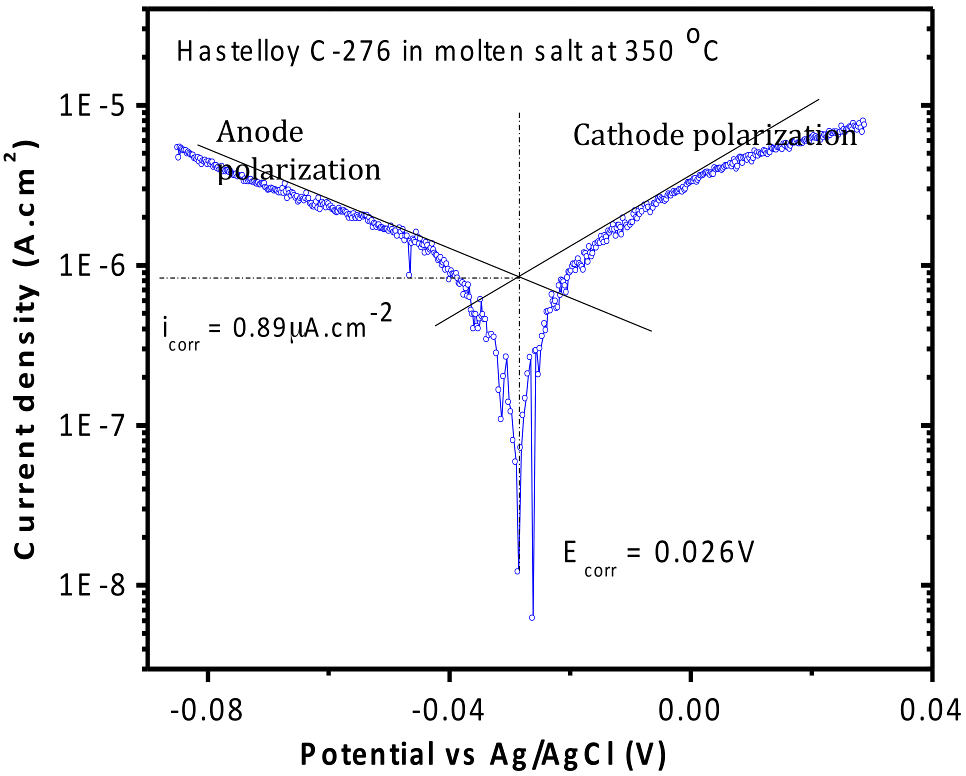


Fig. 4.1 Polarization curve of Hastelloy C-276 in molten salt

The corrosion of the Hastelloy is mainly caused by chemical corrosion. The metal has oxidation-reduction reaction with electrolyte and the electrode, metal will lost. So it asks for high corrosion resistance. The higher operating temperature, the higher thermal transfers efficiency, while higher corrosion of the metal.

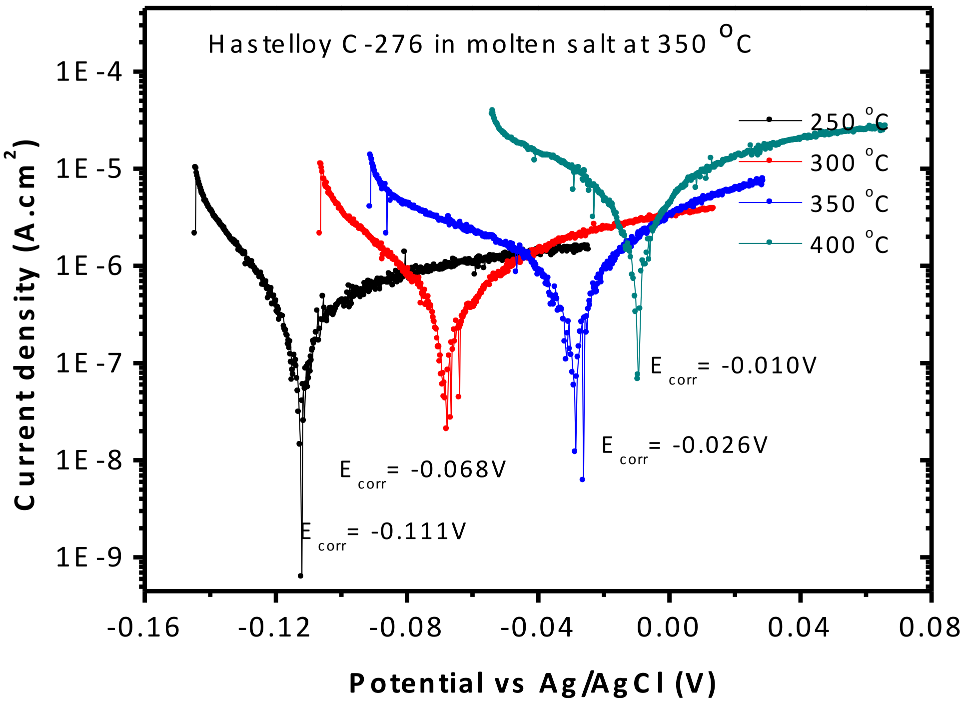


Fig. 4.2 Hastelloy C-276 in molten salt at different temperature

Corrosion rate calculation

$$CR\ (in\ \mu m\ per\ year) = \frac{K_1 \times i_{corr} \times EW}{\rho}$$

250 °C CR = 5.51 µm per year

300 °C CR = 6.09 µm per year

350 °C CR = 8.65 µm per year

400 °C CR = 53.33 µm per year

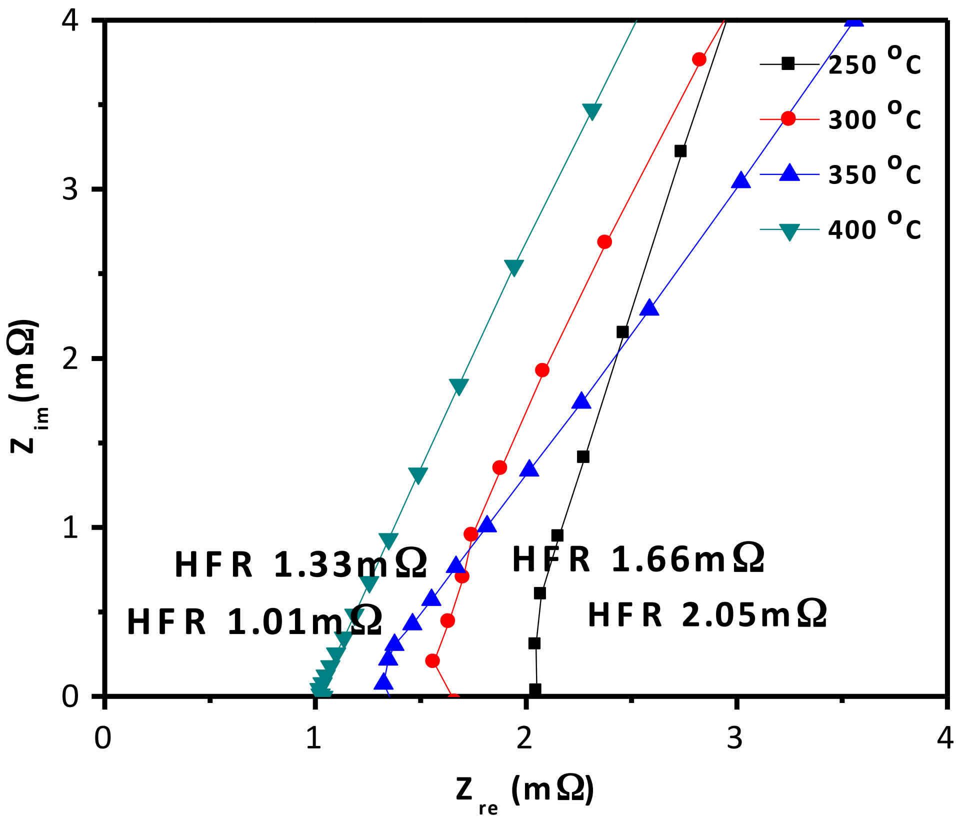


Fig. 4.3 HFR in molten salt at different temperature

It shows that the HFR is higher when the temperature is lower. The reason is higher temperature, lower migration resistance. It suggests that in a battery system, higher temperature might leads to a better performance in a short time. However, higher temperature, higher corrosion rate and other unwanted chemical reaction. If there is a metal material within a pacific heat transfer fluid, higher temperature lower corrosion rate and lower unwanted chemical reaction, it will have good application. Although according to the technology now, it seems impossible, but it might be some materials, higher temperature, there might be film forms on the surface and prevent corrosion, or some chemical reactions can corrode the corrosion product. By unstop imagining, the science being pushed ahead.

Chapter 5

CONCLUSION

In this paper, there are two parts of work. Part one: Test & Evaluation of battery performance. Part two: Test & Evaluation of electrode corrosion.

For the first part, different SOC determination methods have been studied in order to giving evaluation of battery performance and battery conditions. From the experiment, the conclusion is AC impedance method is the better methods compare to another two for supporting a portable battery tester to test SOC for open circuit. It has less limitation. By collecting enough HFR at different SOC, it is accessible to make a look-up chart for the battery tester to determine the SOC of the battery. There are three experiment have been designed to characterize the aging, temperature and C rate affects to the battery performance, battery life. The conclusions are: At higher temperature, the rate is higher and will have an obvious increase in impedance. At room temperature, the rate is higher and impedance will have a slight increase.

For the second part, Hastelloy C-276 corrosion rate has been studied at different temperature in the chlorides salts. Hastelloy C-276 corrosion rate is 5.51 μm per year at 250 ^{o}C while jumps up to 53.33 μm per year when the temperature reached 400 ^{o}C in the NaCl, KCl, $ZnCl_2$ mixture. The conclusion from the experiment is higher temperature the corrosion rate is higher.

There are four recommendations from the experiment:

First, there should be more research to make the evaluation of other battery system, such as lithium-ion batteries and NiMH batteries.

Second, collect more data about HFR values of different SOC and make a look up chart to support a portable battery tester.

Third, explore other types of fluids which are cheap and stable in high temperature can act as the heat transfer fluids in concentrated solar thermal power system. Different ratio of different chlorides salts should be studied.

Forth, test different metal materials corrosion rate in different molten salts for different temperature, also includes HFR (high frequency resistance) into consideration. Search the heat transfer fluids at the same time do study with metal materials to find the best match up.

REFERENCES

[1] Pop, V. (2005). State-of-the-art of battery state-of-charge determination.*Measurement Science & Technology*, *16*(12), R93; R93; R01-R110; R110.

[2] Pop, V., Bergveld, H. J., Notten, P. H. L., Op het Veld, J. H. G., & Regtien, P. P. L. (2009). Accuracy analysis of the state-of-charge and remaining run-time determination for lithium-ion batteries. Measurement, 42(8), 1131-1138.

[3] Mastali, M. (2013). Battery state of the charge estimation using kalman filtering. *Journal of Power Sources*, 239, 294; 294-307; 307.

[4] Bhangu, B. S., Bentley, P., Stone, D. A., & Bingham, C. M. (2005). Observer techniques for estimating the state-of-charge and state-of-health of VRLABs for hybrid electric vehicles. *Vehicle Power and Propulsion, 2005 IEEE Conference,* 10 pp.

[5] Pop, V., Bergveld, H. J., Notten, P. H. L., Op het Veld, J. H. G., & Regtien, P. P. L. (2009). Accuracy analysis of the state-of-charge and remaining run-time determination for lithium-ion batteries. *Measurement, 42*(8), 1131-1138.

[6] Kim, S. K., Shin, B., Kim, J. H., Ahn, S., & Lee, S. (2008). Nano-encapsulation of graphite-based anodes by a novel polymer electrolyte and its influence on C-rate performances of li-ion batteries. *Electrochemistry Communications, 10*(10), 1625-1628.

[7] Pavlov, D., Ruevski, S., Naidenov, V., & Sheytanov, G. (2000). Influence of temperature, current and number of cycles on the efficiency of the closed oxygen cycle in VRLA batteries. *Journal of Power Sources, 85*(1), 164-171.

[8] Coleman, M., Hurley, W. G., & Chin Kwan Lee. (2008). An improved battery characterization method using a two-pulse load test. *Energy Conversion, IEEE Transactions on, 23*(2), 708-713.

[9] Guo, Y. (2005). A sensor of sulfuric acid specific gravity for lead-acid batteries. *Sensors and Actuators B: Chemical, 105*(2), 194-198.

[10] Lin, C. H., & Duh, J. G. (2009). Electrochemical impedance spectroscopy (EIS) study on corrosion performance of CrAlSiN coated steels in 3.5 wt.% NaCl solution. Surface and Coatings *Technology, 204*(6–7), 784-787.

[11] Zaversky, F. (2013). Transient molten salt two-tank thermal storage modeling for CSP performance simulations. *Solar Energy, 93*, 294; 294-311; 311.

[12] *Molten Salt Corrosion*, Chapter 15 in “High-Temperature Corrosion and Materials Applications”, George Y. Lai, editor (2007) 409-421.

[13] L.L. Wang, S.I. Martin, R.B. Rebak, Methods to calculate corrosion rates for alloy 22 from polarization resistance experiments, *Proceedings of ASME Pressure Vessels and Piping Division Conference*, *July 23-27, 2006*, Vancouver, BC, Canada.

[14] Haynes International, Inc. HASTELLOY® C-276 alloy Information*, 2001. Available:http://www.haynesintl.com/HASTELLOYC276Alloy/HASTELLOYC276AlloyPF.htm

[15] ASTM International, Volume 03.02, Standards G 5, G 48, G 59, G 61 and G 102 (ASTM International, 2003: West Conshohocken, PA).

[16] Salkind, A. J., Singh, P., Cannone, A., Atwater, T., Wang, X., & Reisner, D. (2003). Impedance modeling of intermediate size lead–acid batteries. *Journal of Power Sources, 116*(1–2), 174-184.

[17] Pascoe, P. E., & Anbuky, A. H. (2002). The behaviour of the coup de fouet of valve-regulated lead–acid batteries. *Journal of Power Sources, 111*(2), 304-319.

[18] Pavlov, D.*Lead-acid batteries - science and technology - A handbook of lead-acid battery technology and its influence on the product* Elsevier.

[19] Sequeira, C. A. C. (2013). Role of solid state chemistry in high temperature corrosion. *Chemical Engineering Research and Design, 91*(2), 318-324.

[20] Dunn, R. I., Hearps, P. J., & Wright, M. N. (2012). Molten-salt power towers: Newly commercial concentrating solar storage. *Proceedings of the IEEE, 100*(2), 504-515.