

**ELECTROCHEMICAL NOISE INVESTIGATION
OF LITHIUM BASED BATTERIES**

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF SCIENCE
IN
CHEMISTRY

By
Gözde Karaoğlu
September 2021

ELECTROCHEMICAL NOISE INVESTIGATION OF LITHIUM BASED BATTERIES

By Gözde Karaoğlu

September 2021

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Burak Ülgüt (Advisor)

Şefik Süzer

Emrah Özensoy

Kadri Aydınol

Andreas Heyn

Approved for the Graduate School of Engineering and Science:

Ezhan Karaşan

Director of the Graduate School of Engineering and Science

ABSTRACT

ELECTROCHEMICAL NOISE INVESTIGATION OF LITHIUM BASED BATTERIES

Gözde Karaoğlu

M.Sc. in Chemistry

Advisor: Assoc. Prof. Burak Ülgüt

September, 2021

With the widespread use of portable technological devices such as smart phones, laptops, tablets and smart watches, and electric cars in recent years, the need for energy is also increasing. Batteries based on lithium chemistry are the primary choice of the portable technology industry due to their small size, light weight, rechargeability and high energy density, and therefore, the interest in lithium-based batteries has been an important academic research topic.

Electrochemical noise measurements are commonly used measurement methods in the corrosion research. In recent years, electrochemical noise measurements have been employed as a non-destructive testing method, especially in lithium-based batteries, but the measurement methods and analyses methods presented in the literature are insufficient.

In this thesis, electrochemical noise measurement methods and common analyses methods in lithium-based batteries are summarized, a new approach how to make

accurate noise measurement and analysis, and under which conditions lithium-based batteries show noise increase is introduced.

The use of lithium alloy as the anode material in rechargeable batteries causes its energy density to be less than the energy density provided by pure metallic lithium used in non-rechargeable batteries. For this reason, the use of pure metallic lithium in rechargeable batteries is extremely important for industrial development.

The examination of pure metallic lithium batteries with electrochemical noise, which is a non-destructive measurement method during charging and discharging, and imaging with optical microscope in situ and after death with spectroscopic analysis methods are presented.

Key Words: Electrochemical Noise, Rechargeable/Non-Rechargeable Lithium Batteries

ÖZET

LİTYUM BAZLI PİLLERİN ELEKTROKİMYASAL GÜRÜLTÜ İNCELEMELERİ

Gözde Karaoğlu

Kimya, Yüksek Lisans

Tez Danışmanı: Doç. Dr. Burak Ülgüt

Eylül, 2021

Akıllı telefonlar, dizüstü bilgisayarlar, tabletler ve akıllı saatler gibi taşınabilir teknolojik aletlerin ve son yıllarda elektrikli otomobillerin kullanımının dünya çapında yaygınlaşması ile birlikte enerjiye olan gereksinim de artmaktadır. Lityum-iyon pilleri, boyut olarak küçük, hafif, şarj edilebilir ve yüksek enerji yoğunluğuna sahip olması sebebiyle taşınabilir elektronik endüstrisinin birincil tercihi olmaktadır ve dolayısı ile lityum bazlı pillere olan ilgi akademik anlamda önemli bir araştırma konusudur.

Elektrokimyasal gürültü ölçümleri korozyon araştırmalarında yaygın olarak kullanılan bir ölçüm metodudur. Son yıllarda özellikle lityum bazlı pillerde tahribatsız muayene yöntemi olarak elektrokimyasal gürültü ölçümleri yapılmaktadır; fakat literatürün sunduğu ölçüm yöntemleri ve analiz metotları yetersiz kalmaktadır.

Bu tezde, lityum bazlı pillerde elektrokimyasal gürültü ölçüm metotları ve yaygın analiz metotları özetlenmiş, doğru gürültü ölçüm ve analizlerin nasıl yapılması gerektiği, lityum bazlı piller hangi koşullar altında gürültü artışı gösterdiği incelenmiştir.

Şarj edilebilir pillerde anot malzemesi olarak lityum alaşımının kullanılması, sahip olduğu enerji yoğunluğunun, şarj edilemeyen pillerde kullanılan saf metalik lityumun sağladığı enerji yoğunluğundan daha az olmasına sebep olmaktadır. Bu sebeple, şarj edilebilen pillerde saf metalik lityumun kullanılabilmesi endüstriyel gelişim açısından fazlasıyla önem arz etmektedir.

Bu tezde, saf metalik lityum pillerinin şarj ve deşarj sırasında tahribatsız bir ölçüm metodu olan elektrokimyasal gürültü ile incelenmesi, optik mikroskop ile yerinde, spektroskopik analiz yöntemleri ile pilin ölümden sonra görüntülenmesi sunulmaktadır.

Anahtar Sözcükler: Elektrokimyasal Gürültü, Şarj Edilebilir/Edilemeyen Lityum Pilleri

Acknowledgement

I was at the end of the sophomore year when I started working with Assoc. Prof. Burak Ülgüt. Burak Hocam, I learned a lot from you in these 4 years. I learned not to be afraid of making mistakes, not to be afraid of not knowing. I cannot thank you enough for your unwavering support, for patiently answering all my questions over and over again, for teaching me so much. I have had moments where I was afraid, felt inadequate, or thought I could not succeed, but there was one thing you always reminded me of: *What matters most is how you see yourself*. Thanks to you, I stopped being a lion who sees himself as a kitten in the mirror. On the contrary, I am now the lion in the mirror. I feel very lucky to have had the chance to work with you.

I would like to express my thanks to all Profs in the Chemistry department for their patience, help and guidance. Even though I did not have the opportunity to work with him individually, I would like to thank Prof. Şefik Süzer, who contributed a lot to me academically. Over the years, I have learned to conduct research, as well as to question and seek answers thanks to the perspective he has given me.

Besides my professors, I also would like to thank Can Berk Uzundal and Eylül Ergün for their academic contributions to the formation of this thesis.

It was a pleasure to work with Mohammed Zabara, I especially valued and appreciated the teamwork, support, and guidance of him. He made so many conferences, workshops, and group meetings much more interesting and entertaining.

I am appreciative to all my friends and colleagues in the department for entertaining lunch breaks, collegial support, amusing discussions, and often-needed breaks: Beria

Keser, Berrak Soykarafakılı, Salim Can Akyürek, Irmak Karakaya, Işıl Uzunok Ulu, Abel Sika-Nartey, Dilgam Ahmadli, Özgür Şahin, Arca Anıl and many more.

It's time to offer my special thanks to those who are special.

İlke Başara, aka İlkekuş, you have been awarded as the best roommate ever. Without the breakfasts you prepared and the tea and coffee treats that continued throughout the night, I could not have survived these 6 months so well. We spent academically intense, socially entertaining, emotionally exhausting 2 years with you. Pages are not enough to describe what happened at 79. Lojman 25 Numara. Thank you so much for being there; it would not be possible without you.

Can Kap, Eylül Deniz Doğanay, Ahmet Can Varan, Berk Ataç. My lifetime friends. Thank you for filling my university life with unforgettable and unique memories. I learned with you that friendship can become family. You always offered joyful conversation, and much-needed distraction from my research. Berk, you were more than just my friend, thank you for your never-ending love and support. You never let me doubt myself and always be my biggest supporter and make me feel special by believing in my talents. I will always be grateful to you.

I would also like to thank Evrim Haznedaroğlu and Giray İlhan for their help and support.

The closest, but physically farthest, my sister, Gökçe. Unfortunately, I do not have words to thank for the emotional support you have provided me. Even if you are not with me at that moment, knowing that you are always a phone call away and knowing that you will always stand by me no matter what happens has made me stronger. I can never repay you.

Mamam, Babiřim, thank you very much for raising me as a person who can stand on her own feet, for your financial and moral support, for your endless trust and love for me, I am glad to have you.

Last but not least, I would like to take this opportunity to thank *les anciens du lyc e de Galatasaray* Ařkın Altıparmak , Osman Kocaman, G kalp  zdikicioęlu, Mahmut  zl  and Murat Rena who have been great support during my studies at Bilkent University.



Table of Contents

Chapter 1	1
1. Introduction	1
1.1 Electrochemical Noise in Corrosion.....	1
1.2 Electrochemical Noise in Batteries	3
1.3 Electrochemical Noise Measurements	5
1.3.1 Instrumentation	5
1.3.2 Measurement Mode	7
1.4 Electrochemical Noise Analysis	8
1.4.1 Time Domain Analysis.....	9
1.4.2 Frequency Domain Analysis	14
1.4.3 Time-Frequency Domain Analysis.....	15
Chapter 2	17
2. Electrochemical Noise Measurements – How to Measure?	17
Chapter 3	21
3. Why are we NOT using mathematical tools to analyze noise in batteries? 21	
Chapter 4	29
4. Electrochemical Noise Measurements in Lithium Based Batteries.....	29
4.1 Experimental	29
4.1.1 Electrochemical Noise Measurements	29
4.1.2 Battery Disassembly.....	37
4.1.3 Material Characterization.....	39
4.2 Results and Discussions	50
4.3 Summary.....	52
Chapter 5	53
5. Electrochemical Noise and Optical Investigation of Dendrite Formation in Lithium Anode.....	53
5.1 Introduction.....	53

5.2 Experimental	55
5.3 Discussion and Future Work	60
5.4 Summary.....	61
Chapter 6	62
6. Conclusion.....	62
Bibliography	65
Appendix.....	72
A. Instrumentation.....	72
B. Python Codes.....	72



List of Figures

Figure 1.1 Electrode noise output during pit initiation period. Reproduced from [19] with permission from Corrosion Science	2
Figure 1.2 Electrode noise output during crevice attack. Reproduced from [19] with permission from Corrosion Science	2
Figure 1.3 Battery voltage noise measurements. [29]	4
Figure 1.4 Noise patterns of a healthy Gates “J” sealed lead-acid cell while on charge and discharge at 7 A (left) and noisy Gates “J” sealed lead-acid cell while on charge at 0.5 A. (right). Reproduced from [24] with permission from Journal of Power Sources	5
Figure 1.5 Discharge of ICR 18650 Lithium-Ion battery (left) and associated voltage fluctuations. Reproduced from [31] with permission from Journal of Solid State Electrochemistry	10
Figure 1.6 Noise standard deviation of voltage fluctuations obtained using polynomial of order n: 5, 7 and 9 for determining the mean value. Reproduced from [31] with permission from Journal of Solid State Electrochemistry	11
Figure 1.7 Electrochemical potential (bottom line) and current (top line) noise signals and associated appearance of steel surfaces for three types of corrosion (a, d) uniform (b, e) pitting (c, f) passivation. Reproduced from [22] with permission from Corrosion Science	13
Figure 1.8 Recurrence plots for different current data segments of three corrosion types, i.e., uniform (first row), pitting (second row) and passivation (third row). Reproduced from [22] with permission from Corrosion Science	14

Figure 1.9 Wavelets crystals resulting from orthogonal wavelet transform (OWT) analysis of the electrochemical noise measurements signal plotted at the top of this figure. Reproduced from [44] with permission from Electrochimica Acta.....	16
Figure 2.1 Electrochemical noise measurement of non-rechargeable CR2032 coin cell battery. Applied voltage signal (top) and current response (bottom).....	18
Figure 2.2 The switch designed that alternates between parallel and anti-serial connection (top), parallel and anti-serial connection (bottom.) Reproduced from [45] with permission from Journal of The Electrochemical Society	19
Figure 2.3 The noise measurement of CR2032 with 1kHz (black) and 5Hz (red) low pass filters in frequency domain (left) and time domain (right).	20
Figure 3.1 Electrochemical noise data of a resistor and a shorted CR2032 coin cell battery in time and frequency domains with 1kHz and 5Hz sampling frequencies...	23
Figure 3.2 Electrochemical noise data of shorted CR2032 coin cell battery. Raw data (red) and detrended data (red).	24
Figure 3.3 Recurrence quantification analysis results of shorted CR2032 coin cell battery before and after assigned threshold value.	26
Figure 3.4 Wavelet Transform analysis results of shorted CR2032 coin cell battery with width length of 1500 and 150	27
Figure 4.1 Schematic representation of properly discharged batteries and short-circuited batteries	30
Figure 4.2 Electrochemical noise data of pristine non-rechargeable CR2032 battery	31
Figure 4.3 Electrochemical noise data of shorted non-rechargeable CR2032 batteries at various stages of shorted durations (1 day, 3 days, 7 days)	32

Figure 4.4 Electrochemical noise data of properly discharged non-rechargeable CR2032 batteries at different states of charge (75% SOC, 50% SOC, 25% SOC) ...	33
Figure 4.5 Electrochemical noise data comparison of pristine (left), shorted (middle), properly discharged (right) non-rechargeable CR2032 batteries at various stages of shorted durations (1 day, 3 days, 7 days) and different states of charge (75% SOC, 50% SOC, 25% SOC) on the same scale of y-axis.	34
Figure 4.6 Electrochemical noise measurement of non-rechargeable CR2032 batteries after suffering 15 minutes, 30 minutes and 1 hour shorting.	35
Figure 4.7 Electrochemical noise measurement of non-rechargeable and rechargeable CR2032 batteries after suffering 3 days shorting.....	36
Figure 4.8 Schematic and photo of the non-rechargeable CR2032 coin cell battery components. From top to bottom: Metal grid, cathode, separator, and anode.....	37
Figure 4.9 Metallic lithium anode under inert atmosphere (left) and degradation of metallic lithium anode after exposed to air (right).	38
Figure 4.10 Photo of the setup where the batteries are disassembled: Glove bag filled with N ₂ gas.	38
Figure 4.11 The cathode (left) and the anode (right) material of a non-rechargeable CR2032 coin cell battery fixed onto microscope slide and sealed with Kapton tape.	39
Figure 4.12 XRD measurements of anode of non-rechargeable CR2032 coin cell battery exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days) (top), and discharged to different SOC (25% SOC, 50% SOC, 75% SOC) (bottom).	40
Figure 4.13 XRD measurements of cathode of non-rechargeable CR2032 coin cell battery exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days) (top), and discharged to different SOC (25% SOC, 50% SOC, 75% SOC) (bottom).	41

Figure 4.14 The FT-IR measurement of the separator of pristine and shorted for 3 days non-rechargeable CR2032 coin cell battery.	42
Figure 4.15 The XRF measurement of the anode and the cathode of pristine and shorted for 3 days non-rechargeable CR2032 coin cell battery.	43
Figure 4.16 The XRF measurement of the metal grid (current collector) and the separator of pristine and shorted for 3 days non-rechargeable CR2032 coin cell battery.	43
Figure 4.17 SEM image of anode of pristine non-rechargeable CR2032 coin cell battery with the resolutions of 1mm and 500 μ m	44
Figure 4.18 SEM image of anode of shorted non-rechargeable CR2032 coin cell battery at various stages of shorted durations (1 day, 3 days, 7 days) with the resolutions of 500 μ m and 20 μ m; 500 μ m and 300 μ m; 1mm and 300 μ m, respectively.	45
Figure 4.19 SEM image of anode of discharged non-rechargeable CR2032 coin cell battery at different states of charge (75% SOC, 50% SOC, 25% SOC) with the resolutions of 1mm and 1mm; 1mm and 400 μ m; 1mm and 500 μ m, respectively. ...	46
Figure 4.20 EDX Mapping of anode of shorted non-rechargeable CR2032 coin cell battery at various stages of shorted durations (1 day, 3 days, 7 days) with the resolutions of 50 μ m and 100 μ m; 200 μ m and 200 μ m; 1mm and 1mm, respectively.	47
Figure 4.21 EDX mapping of anode of discharged non-rechargeable CR2032 coin cell battery at different states of charge (75% SOC, 50% SOC, 25% SOC) with the resolutions of 1mm, 100 μ m and 50 μ m; 100 μ m; 100 μ m and 100 μ m, respectively. ..	48
Figure 4.22 Photographic images of of anode of non-rechargeable CR2032 coin cell battery discharged to different SOC (Pristine/100% SOC, 75% SOC, 50% SOC, 25%	

SOC) (top) and exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days, 15days) (bottom).....	49
Figure 4.23 Schematic description of a current collector (black) and lithium active material (gray) Pristine battery (a), properly discharged battery (b), 3 days shorted battery (c), 7 days shorted battery (d) (E_{Li} : Open Circuit Potential for the Li Metal, E_{SS} : Open Circuit Potential for the Stainless Steel, V_{meas} : Measured Voltage)	51
Figure 4.24 Short summary of the findings	52
Figure 5.1 Illustration (top) and photograph (bottom) of two electrode setup; Lithium anode as working electrode, graphite rod as counter electrode.	55
Figure 5.2 Electrochemical noise measurement of lithium anode of 25% SOC CR2032 coin cell battery before and after charge	56
Figure 5.3 Electrochemical noise measurement of pristine, charged, and discharged lithium anode of CR2032 coin cell battery.	57
Figure 5.4 SEM images of charged lithium anode of CR2032 coin cell battery.	58
Figure 5.5 Optic microscope setup inside the glove bag (top) and the measurement setup of lithium anode with a steel mesh as a counter electrode on top of it (bottom).	59

List of Tables

Table 1.1 Experimental conditions; three different solutions for three different types of corrosion. Reproduced from [22] with permission from Corrosion Science.....	12
Table 2.1 Noise variance values of shorted and properly discharged non-rechargeable CR2032 batteries at various stages of shorted durations (1 day, 3 days, 7 days) and different states of charge (75% SOC, 50% SOC, 25% SOC)	35



List of Abbreviations

EN	: Electrochemical Noise
EPN	: Electrochemical Potential Noise
ECN	: Electrochemical Current Noise
SOC	: State of Charge
XRD	: X-ray Diffraction
SEM	: Scanning Electron Microscopy
EDX	: Energy Dispersive X-ray Spectroscopy
FT-IR	: Fourier Transform Infrared Spectroscopy
XRF	: X-Ray Fluorescence
WE	: Working Electrode
RE	: Reference Electrode
CE	: Counter Electrode
CA	: Chronoamperometry
CP	: Chronopotentiometry
PSD	: Power Spectral Density

Chapter 1

1.Introduction

1.1 Electrochemical Noise in Corrosion

Electrochemical noise (EN) is based on measurement and analysis of stochastic voltage or current fluctuations of a given system as a function of time at a rest condition. It is a well-known and powerful technique preferred for the early detection of corrosion processes, especially those with stochastic nature. Due to the fact that corrosion has a very important place in the industry for planning the lifetime of structures, various studies have been carried out for the formation and prevention of corrosion; pitting corrosion[1]–[4], CO₂ induced corrosion [5][6], microbiologically induced corrosion [7][8], organic coatings [9]–[12], inhibitors [13]–[15] etc. and electrochemical noise measurement have emerged as a remarkable method that enables these studies. The earliest reported studies on this subject were published by Tyagai and Iverson in the 1960s. [16], [17] Electrochemical noise studies on various metals revealed that corrosion on the metal surface causes voltage oscillations in the microvolt range, and this first study put the electrochemical noise technique to an important place

in the corrosion science. [16], [18] In the work of Hladky and Dawson in the early 1980s, stochastic corrosion modes such as pit initiation and crevice attack, were monitored by sensitive measurements of the electrode potential. [19] Voltage fluctuations on naturally corroding electrodes were monitored with respect to two platinum reference electrodes using a two-channel high gain amplifier system. Figure 1.1 and Figure 1.2 show electrode noise output during pit initiation and crevice attack, respectively.

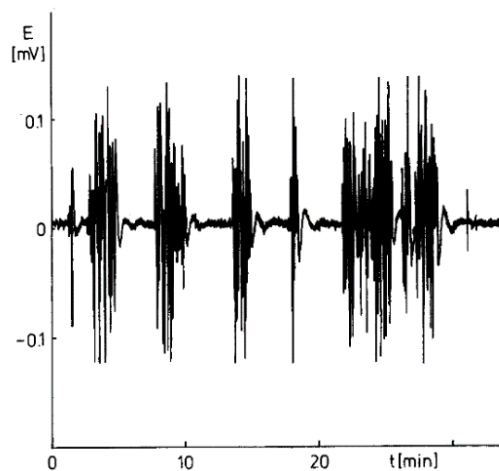


Figure 1.1 Electrode noise output during pit initiation period. Reproduced from [19] with permission from Corrosion Science

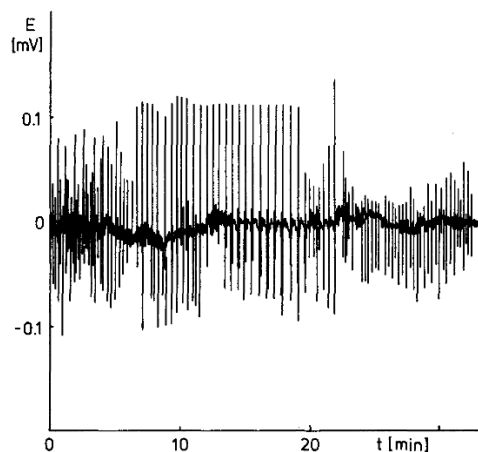


Figure 1.2 Electrode noise output during crevice attack. Reproduced from [19] with permission from Corrosion Science

It has been observed that the patterns of voltage oscillations, even if they occur randomly, are different from each other, and these findings are supported by post-mortem analysis results. In this way, it is thought that information that can be obtained from electrochemical noise measurements is not only limited to early corrosion detection, but also features such as the type, character and rate of corrosion can be determined with accurate measurement and analyses methods. Ultimately, this led to an increase in research around this topic. More recently, interpretation of noise data by various mathematical analyses methods for early detection and characterization of corrosion modes are employed and these studies will be mentioned in further detail in upcoming chapters. [5], [20]–[23]

1.2 Electrochemical Noise in Batteries

Batteries are used as low noise voltage sources in electronics. In fact, they are thought as no noise voltage sources. In reality, there is always some noise even at low amplitudes. As mentioned before, electrochemical noise technique is well-known in corrosion science. Nowadays, electrochemical noise measurement technique, which examines voltage oscillations in batteries, apart from known methods that provide information about the condition, life and health of batteries, has gained popularity. Electrochemical noise measurement is a non-invasive diagnosis tool and there are reports in the literature on electrochemical noise measurements of batteries with different chemistries. [24]–[27] One of the examples of electrochemical noise measurement on batteries was published by Knott and the aim of the research was to determine the lowest noise power supply for noise sensitive electronic devices. [28] Similarly, in 1995 Boggs et al. published a paper that aimed to detect an ultra-low noise power source for use in electronic devices and electrochemical noise technique

was used during the measurements (reproduced in Figure 1.3). [29] After these studies, the aim of noise studies on batteries was not only to determine the low noise power source, but also to find the answer to the question, whether information about batteries could be obtained from the noise signals, just like in corrosion studies.

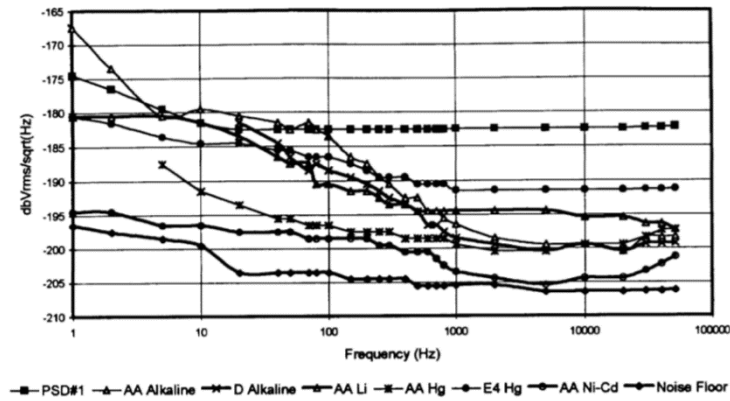


Figure 1.3 Battery voltage noise measurements. [29]

Electrochemical noise measurements carried out on sealed lead-acid batteries by Roberge et al. revealed that the noise levels of healthy and fresh batteries are almost non-existent, but the noise level increases with the use of batteries. [24] Although, there is not a well-established connection between the decrease in battery performance and the observed increase in voltage noise with the use of the battery, the necessity of more advanced measurement and analysis methods is emphasized to determine the source of the problems inside the battery. Figure 1.4 shows the comparison of the noise data obtained after charging and discharging of a healthy and fresh battery (left), with the noise data after recharging (right) of a battery exposed to a short circuit for 20 hours at the end of discharge. As can be seen, while a healthy and fresh battery does not show any significant noise increase, the recharged battery exhibits serious voltage oscillations.

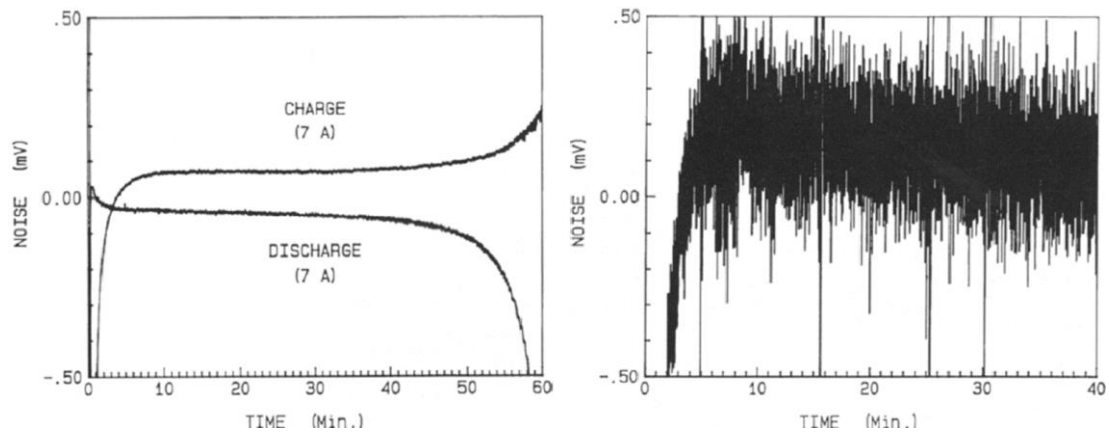


Figure 1.4 Noise patterns of a healthy Gates “J” sealed lead-acid cell while on charge and discharge at 7 A (left) and noisy Gates “J” sealed lead-acid cell while on charge at 0.5 A. (right). Reproduced from [24] with permission from Journal of Power Sources

The fact that portable electronic devices have become one of the most important parts of our daily lives, and electric vehicles have become important with the developing technology has led to increase in the popularity of studies on batteries. Therefore, it is important to research and develop non-destructive testing methods such as electrochemical noise measurements, especially for economic reasons. Considering the studies conducted since the early 2000s, it is seen that studies on noise of batteries are channeled towards lithium-based batteries mostly in order to determine state-of charge of a battery, to detect overcharge process or other battery characterizations. [27], [30]–[34]

1.3 Electrochemical Noise Measurements

1.3.1 Instrumentation

One of the advantages of electrochemical noise measurement is that no external signal is required to collect experimental data. By monitoring voltage changes without any

excitation, it enables a completely passive measurement that is neither invasive, nor perturbing. This allows for real-time monitoring of devices in their commercial form without any modifications.

Obtained stochastic voltage oscillations are generally seen at very low amplitudes, requiring the measurement to be sensitive and accurate.

Therefore, it is important to consider some possible sources of error when considering noise measurements such as thermal noise, utility frequency, shot noise, flicker noise, aliasing in the analog to digital (A/D) conversion and quantization.

Thermal Noise – Thermal noise or Johnson-Nyquist noise is associated with random motion of free electrons in the conductor occurring with thermal agitation and it is directly proportional to noise bandwidth (B_w) and temperature. The amount of thermal noise can be calculated by using Equation (1.1) where k is the Boltzmann's constant, T is the absolute temperature, B_w is the noise bandwidth and R is the resistance value.

$$V_n = \sqrt{4kTBR} \quad (1.1)$$

Shot Noise – The fluctuations in the current due to the discrete nature of the charges carried by charge carriers create a noise signal which is called as shot noise and its magnitude is proportional to the square root of the current.

1/f noise – Flicker noise or 1/f noise, similar to shot noise, can be associated with a DC current flow and is present in all active and some passive devices at low frequencies. Random trapping and releasing of charge carriers between the interfaces of two materials causes the flicker noise which is generally observed in semiconductors that are used in amplifiers. Further, any source of drift in voltage or

current also manifests itself as a $1/f$ noise. The coincidence that both drift and stochastic flickers yield signal that looks similar in the frequency domain is a major reason that frequency domain analysis is troublesome in battery noise studies.

Aliasing in the A/D conversion – Such errors occur during the conversion of an analog signal to a digital signal, and often result in low-frequency features that are not present in the analog signal, appearing in the digital signal because of the high-frequency components. According to the Nyquist theorem, the sampling frequency (i.e. digitization process) must be at least twice as much as the frequency of the highest frequency signal. Any higher superfluous frequency signal has to be filtered, otherwise the signals at the frequencies higher than the sampling frequency manifest themselves as signals at lower frequencies.

Quantization – Quantization noise is a type of error which occurs during the signal processing and causes variations between actual analog signal and discrete digital signal due to either rounding or truncation process.

1.3.2 Measurement Mode

Zero-resistance ammeter (ZRA) is typically employed in corrosion noise measurements where electrochemical potential noise (EPN) and electrochemical current noise (ECN) can be measured. In this mode, the voltage measured is the voltage of a corroding couple of metals shorted together with respect to some reference electrode and current is the current flowing across the couple of the shorted metals. On the flip side, ECN can be measured in potentiostatic mode (at an applied potential) by using potentiostat or EPN can be measured in galvanostatic mode (at an applied current) by using galvanostat.

Zero resistance ammeter (ZRA) mode – In ZRA mode, EPN measurement is performed by measuring the oscillations in the potential of the coupled working electrodes with respect to the reference electrode. Similarly, galvanic coupling current can be measured between two identical working electrodes. In order to ensure that the two identical working electrodes exhibit the same electrochemical potential, current must be measured by using a ZRA.

Potentiostatic/Galvanostatic mode – No matter whether galvanostatic or potentiostatic, noise measurements include three electrode experiments and voltage noise is measured as a function of time. In potentiostatic mode, constant potential is applied to the system to obtain ECN whereas in galvanostatic mode, constant current is applied to the system to obtain EPN. In any of the above three modes, a signal in the form of a potential or a current has to be applied to the system. The application process and the electronics is not noise free and care has to be taken in order to decouple the intrinsic noise from the system and the noise caused as a response to the noise in the applied signal.

Open Circuit Noise – In this measurement mode, no signal is applied, simply a voltage is measured between a working and a reference electrode. In the case of batteries, these are simply the two electrodes of the battery.

1.4 Electrochemical Noise Analysis

Although a superficial correlation can be obtained between the noise data obtained and early corrosion detection, attempts at quantitative interpretation of electrochemical noise to determine the corrosion mechanism, rate, initiation, and propagation over time

has led to the use of mathematical analysis methods in corrosion science. There are many mathematical methods and parameters needed to be identified but they can be classified into three groups: the time domain, the frequency domain and the joint time-frequency domain.

1.4.1 Time Domain Analysis

Time domain analysis of electrochemical noise is a well-known technique where the intensity of the corrosion is believed to be related to the amplitude of noise fluctuations; the amplitude of the noise fluctuations increases as the severeness of the corrosion increases. [20], [21] Moreover, information about the type of corrosion can be obtained from the shape of the noise; If the data show a symmetrical distribution around the average value, it is determined that the corrosion occurring on the surface is uniform corrosion, and if the data points show continuous sudden changes, it is pitting corrosion. [35]

Standard deviation can also be used to quantify the amount of noise. From the standard deviation, information about the rate of corrosion can be extracted; potential standard deviation has tendency to decrease when corrosion rate is high, whereas current standard deviation increases when the corrosion rate is high, according to Lv. et. al. [36] A similar approach was used by Martemianov et al, for electrochemical noise analysis of Li-ion batteries. [31] The main purpose of the study was to utilize electrochemical noise analysis for in-situ diagnosis during discharging and charging processes on ICR 18650 commercial lithium-ion batteries. By using high-order polynomials for fitting the mean signal value in small time windows they measure the noise standard deviation versus state of charge. Discharge of Li-ion battery from its

open circuit potential, 3.98V to 1.2V and associated voltage fluctuations with the amplitude of microvolts which is approximately 1000 times higher than the instrumental noise shown in Figure 1.5.

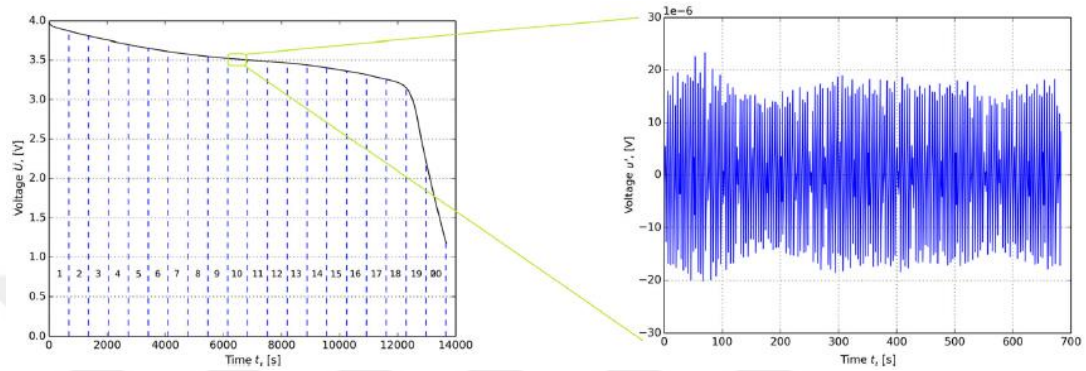


Figure 1.5 Discharge of ICR 18650 Lithium-Ion battery (left) and associated voltage fluctuations. Reproduced from [31] with permission from Journal of Solid State Electrochemistry

In Figure 1.6, it is shown that the mean signal value is fitted with higher order polynomials (n: 5, 7, 9).

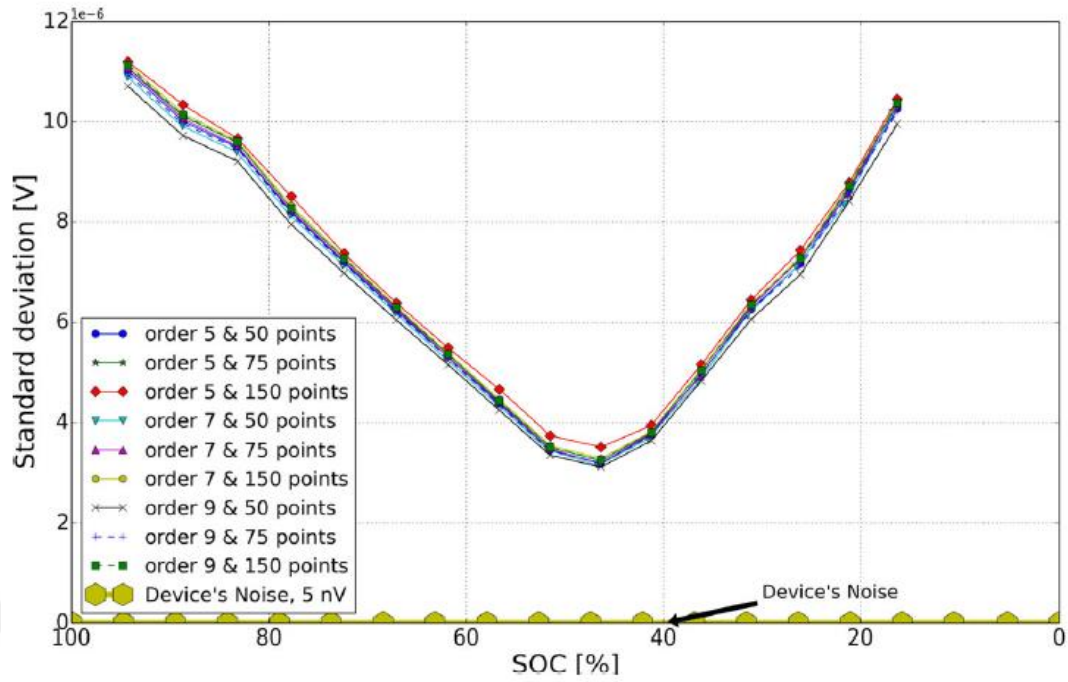


Figure 1.6 Noise standard deviation of voltage fluctuations obtained using polynomial of order n : 5, 7 and 9 for determining the mean value. Reproduced from [31] with permission from Journal of Solid State Electrochemistry

According to the conclusion of the study, which is questionable, electrochemical kinetics of the electrodes are dominant at high SOC values, whereas transport properties are dominant at low SOC values. The main issue is the fact that a drifting signal would also increase the standard deviation, just as fluctuations would. The reported standard deviation in the manuscript very closely follows the slope of the voltage curve. As the slope of the curve changes the standard deviation changes accordingly.

Another mathematical approach to analyze electrochemical noise data in time domain is Recurrence Quantification Analysis (RQA) method. RQA is used to investigate dynamical systems by analyzing nonlinear data. Rhythmic structure of a dynamical system can be quantified by converting the number and the duration of recurrences into recurrence plots (RPs).

Recurrence plot is a visualization of an $N \times N$ matrix. Each element in the matrix represents those times of recurrence of a state in a dynamical system in the phase space.

In one particular study, Kinsella et al. proposed using RQA as a way of analyzing electrochemical noise, as the basis for an automated monitoring scheme for aqueous corrosion systems. [22] During the study, corrosion tests with carbon steel in three different conditions (uniform corrosion, pitting and passivation) in aqueous media were done. Different types of corrosion were set up by using three different solutions as shown in Table 1.1.

Corrosion Type	Solution	pH	Test Duration
Uniform	0.1 M NaCl	6.6	18 h
Pitting	0.45 M NaHCO ₃ +0.1 M NaCl	8.6	19 h
Passivation	0.5 M NaHCO ₃	8.4	2.5 h

Table 1.1 Experimental conditions; three different solutions for three different types of corrosion. Reproduced from [22] with permission from Corrosion Science

Electrochemical noise measurements were recorded continuously and different behaviors of electrochemical current and potential signals for different corrosion systems can be seen from Figure 1.7 and Recurrence plots of the electrochemical current and potential signals are generated and shown in Figure 1.8. The study indicated that the use of RQA appears to be a promising approach for continuous corrosion monitoring. However, monitoring map could not distinguish between pitting and passivation therefore improvements are needed, such of additional recurrence quantification variable. Aside from these minor issues, the method Kinsella et al. proposed provides a new approach to automated corrosion monitoring.

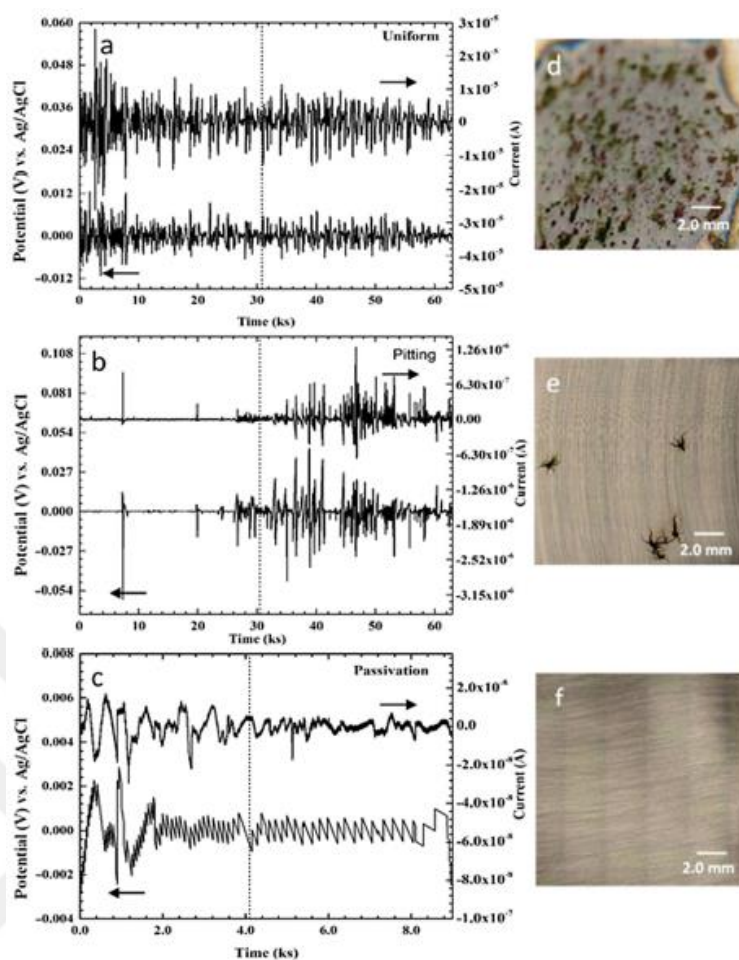


Figure 1.7 Electrochemical potential (bottom line) and current (top line) noise signals and associated appearance of steel surfaces for three types of corrosion (a, d) uniform (b, e) pitting (c, f) passivation. Reproduced from [22] with permission from Corrosion Science

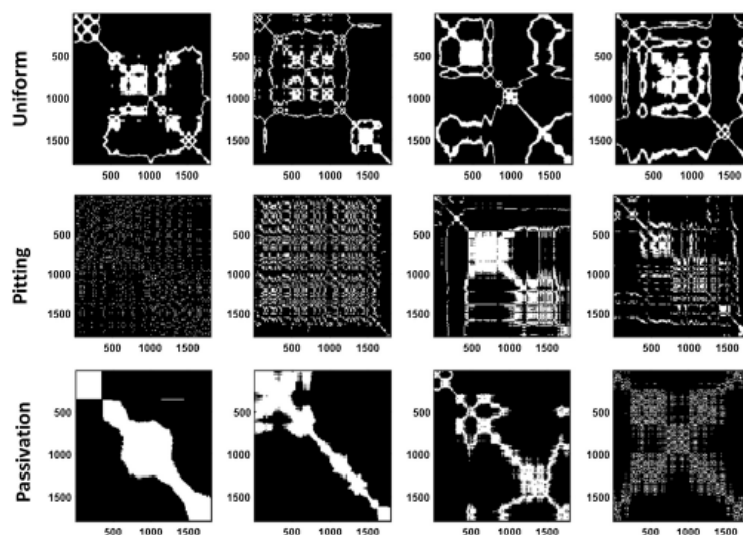


Figure 1.8 Recurrence plots for different current data segments of three corrosion types, i.e., uniform (first row), pitting (second row) and passivation (third row). Reproduced from [22] with permission from Corrosion Science

1.4.2 Frequency Domain Analysis

Frequency domain analysis is a common technique in electrochemical noise analysis to obtain the power spectrum.

PSD curves can be very powerful in terms of identifying important parameters such as the white noise level W (the height of the horizontal part of the frequency domain spectrum), the corner frequency f_r (the frequency of curve turning point), the cut-off frequency f_c (the frequency at which the curve was submerged into the base level), and the linear slope k of the curves in the high frequency region and association of these terms with appropriate post-mortem results, especially for corrosion studies, is necessary according to Lv. et. al. [36] It is indicated that, even though the time-domain provides all the information regarding to the electrochemical reactivity of the system, PSD is important in terms of providing kinetic information about the corrosion formation. Utilization of PSD in corrosion literature is very common. [37]–[40] The

extension of such an application to batteries, however, is non-trivial due to the aforementioned overlap of drift and oscillatory behavior. Since batteries are more prone to drifting signals, decoupling of drift and oscillations has to be diligently performed. Astafev et. al. conducted electrochemical noise investigation upon lithium based primary batteries and the noise analysis is based on PSD. [32]–[34], [41] In these studies, the drift compensation is carried out with a high pass filter, which is shown to be ineffective in most cases. [42]

1.4.3 Time-Frequency Domain Analysis

Electrochemical noise signals can also be analyzed in time-frequency domain, which is simultaneous analysis in both time and frequency domain where the time-frequency representations are utilized. Wavelet transform technique is one particular example of time-frequency domain analysis. [23], [43]–[45] Fourier transform captures global frequency information which is a signal decomposition for frequencies that lasts over the entire signal. Wavelet Transform is an alternative to this approach, which is decomposition of a function into a set or sets of wavelets. Wavelets are oscillations which are localized in time. Two main properties of wavelets are scale and location. Where the wavelet is positioned in time, is the Location. How much squeezed or stretched the wavelet is defined by the Scale. Local spectral and temporal information can be extracted by using Wavelet Transform simultaneously.

In corrosion literature, the wavelet transform method is also used for analysis of noise data. [23], [43]–[45] One particular example can be given to a publication by Marcos et al., where wavelet transform technique was utilized for identification of onset of the corrosion. [44]

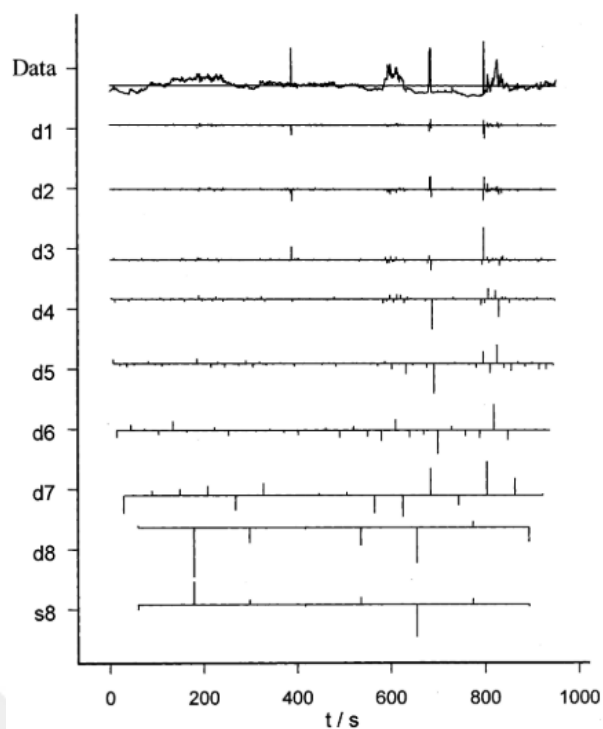


Figure 1.9 Wavelets crystals resulting from orthogonal wavelet transform (OWT) analysis of the electrochemical noise measurements signal plotted at the top of this figure. Reproduced from [44] with permission from Electrochimica Acta

Electrochemical noise data indicates the composition of distinct type of events, and they are classified according to their time constants and these time constants are associated with scale coefficients according to their length which are indicated as crystals.

Chapter 2

2. Electrochemical Noise Measurements – How to Measure?

(This part is also described in Gözde Karaoğlu, Can Berk Uzundal, Burak Ulgut, “Uneven Discharge of Metallic Lithium Causes Increased Voltage Noise in Li/MnO₂ Primary Batteries upon Shorting”, Journal of Electrochemical Society, 2020, 167, 130534. Reproduced from [45] with permission from Journal of Electrochemical Society)

In corrosion literature, both voltage and current noise are commonly measured, however, in batteries where the noise levels are very low, noise in the applied potential dominates the current noise measurement. Thus, it is more convenient to focus on voltage noise in order to perform electrochemical noise measurements without any applied signal under open circuit. As a proof, potentiostatic electrochemical noise measurements were done and applied voltage signal and current noise response are shown in Figure 2.1. The data clearly shows that the current noise obtained progresses following the trends of the potential applied. There is undoubtedly some information

in the current noise pertaining to the battery. However, it is practically impossible to extract the part of the current noise that is not related to the voltage control circuitry.

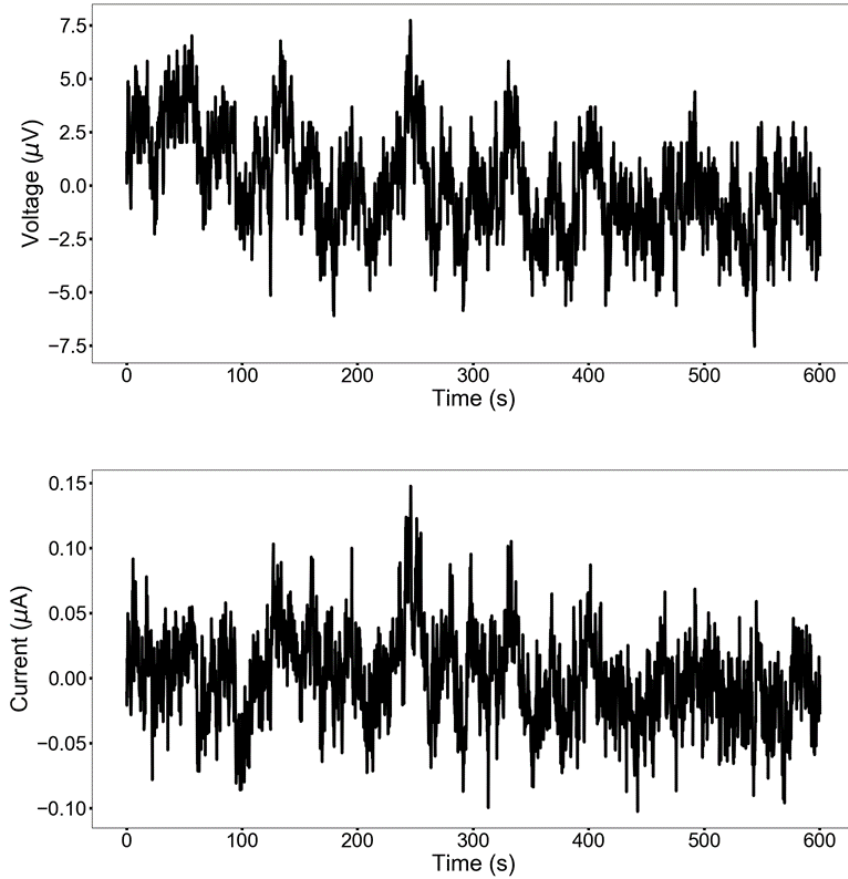


Figure 2.1 Electrochemical noise measurement of non-rechargeable CR2032 coin cell battery. Applied voltage signal (top) and current response (bottom).

Making electrochemical noise measurements on batteries requires resolving noise data in the μV range over their DC voltages. For this reason, it is important to remove the DC voltage of the battery from the equation in order to get a much higher resolution measurement. Most commercial voltage measurement instruments have the ability to subtract DC voltage during noise measurements, but the data is likely to be subject to distortions during this process. In a study published by Uzundal et al, a switch that can

quickly alternate between parallel and anti-series connection was designed to eliminate the DC voltage of the battery. [46] After two batteries with the same physical and chemical properties are connected in parallel, and after allocating enough time for equilibrium, two batteries with the same voltage in the microvolt range are obtained. Then, when the anti-series connection is established, the DC voltage of these two batteries is eliminated and any measurement to be made on them is made over 0V. as depicted in Figure 2.2.

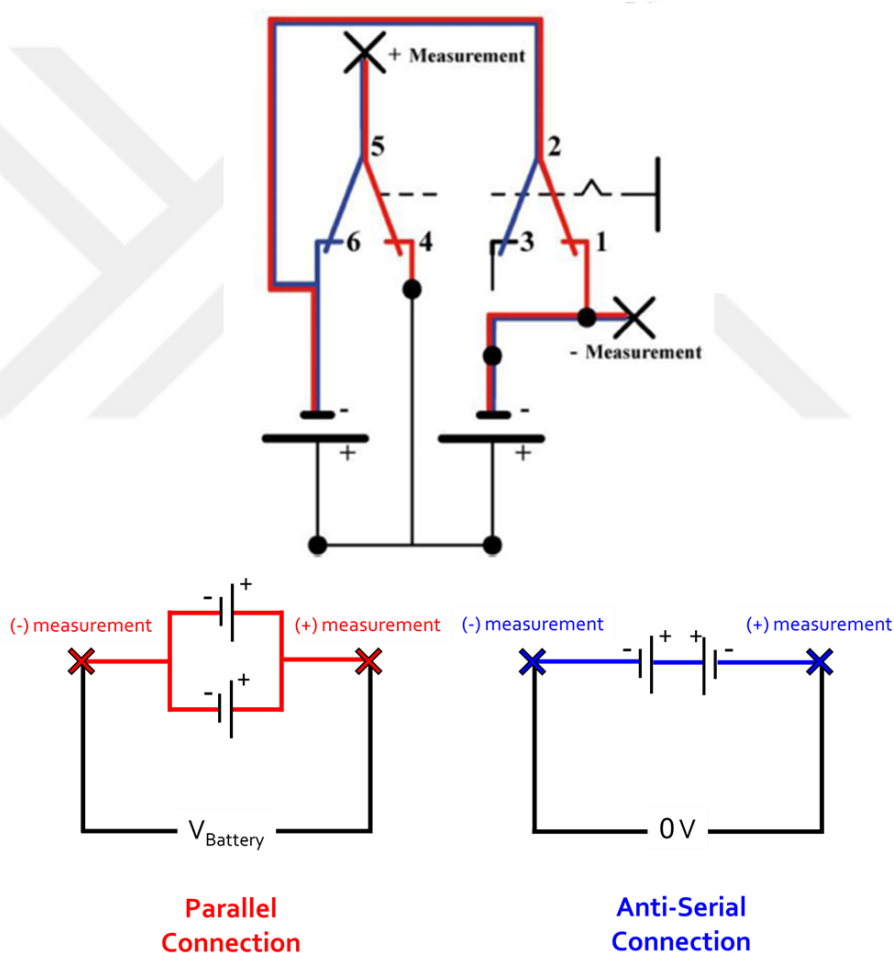


Figure 2.2 The switch designed that alternates between parallel and anti-series connection (top), parallel and anti-series connection (bottom.) Reproduced from [45] with permission from Journal of The Electrochemical Society

Noise measurements were carried out using a Gamry Interface 5000 potentiostat after comparing different instruments as was outlined in the article published by Uzundal et al. [46] Electrochemical Signal Analyzer (ESA 410) version 7.0.4 software from Gamry Instruments was used to adjust analog parameters of the instrument. The cut-off frequency of the measurement, the sampling rate and low pass filters were all set to 5 Hz.¹ Since the time domain will provide the necessary information (whether the battery is shorted or not) it is important to filter the output and subsequently choose the suitable low pass filter. The bandwidth was selected based on our previous experiments on the same battery regarding where most of the electrochemical information resides in the noise spectrum. [47] Figure 2.3 clearly indicates that important features can be extracted from the measurement that has been done with 5 Hz. When the sampling frequency were set to be 1kHz important features are suppressed. An acquisition time of 10 min was used. To reduce the effects of voltage drift on our measurements, a voltage stability criterion of $\sim 100 \mu\text{V min}^{-1}$ was selected, meaning over a 10-min period the change in voltage never exceeded 1 mV. In cases of severely abused batteries, this criterion was relaxed as the noise profile is easily distinguished from drift by visual inspection.

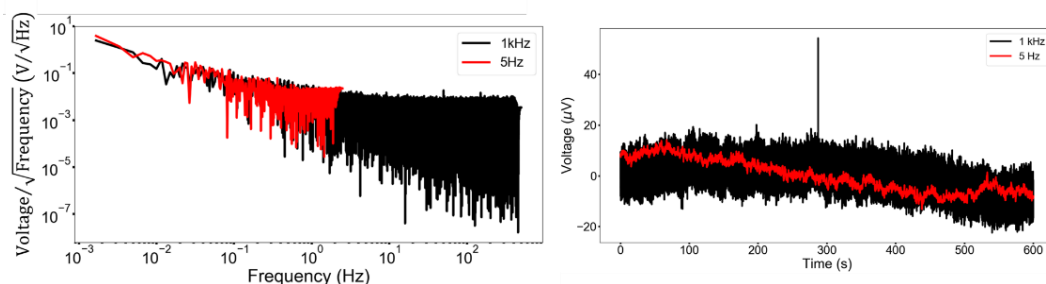


Figure 2.3 The noise measurement of CR2032 with 1kHz (black) and 5Hz (red) low pass filters in frequency domain (left) and time domain (right).

¹ Though the filter is specified as a low pass 5Hz, it is not a brickwall at 5Hz. This effectively filters at 10Hz and beyond, therefore sampling at 5Hz does not violate the Nyquist criterion. [53]

Chapter 3

3. Why are we NOT using the mathematical tools to analyze noise in batteries?

Since electrochemical noise is a widely used measurement method in the corrosion literature for the detection and characterization of corrosion, similar measurement and analysis methods have also been used for electrochemical noise measurements in batteries. [27], [30]–[34], [41] Considering the monitoring of corrosion with the electrochemical noise method, it should be noticed that there are controllable parameters such as at what point, in which form or at what speed the corrosion will occur. In this way, noise measurements made over controllable parameters can provide a true correlation between noise data and corrosion and this correlation can be aided by mathematical analysis methods. On the other hand, considering the electrochemical noise measurements made on batteries, it is considered as hypothetical study to try to make mathematical analyses with externally allocated parameters. This is because the noise data obtained and source of the noise increase are both uncharacterized in batteries.

Hence, the first question that needs to be asked is; How can the voltage signature of a given electrochemical phenomenon be determined? In the corrosion literature, the postmortem analyses of the samples are the answer, since signals can be associated with various forms of corrosion after the noise measurements carried out through physical examination of samples. A similar approach is described in an article published by Karaoglu et al. [48] In that report, one source of the noise increase was found to be uneven discharge of metallic lithium. (See Chapter 4). Therefore, it is important to expand these kinds of studies in order to identify more sources for the fluctuations in the signal. Then, and only then, the appropriate mathematical analysis methods can be chosen that will reveal the relevant information out of the data. Mathematical tools alone cannot be used to identify the characteristics of the signal which are directly related to the electrochemistry without further investigation of the origin of the signals.

Analyzing electrochemical noise signals in frequency domain via Fourier Transform is a common technique in corrosion literature, however, it is important to emphasize that it can be a useful in cases where periodic signals of specific frequency are present. On the other hand, frequency domain analysis can be tricky in the absence of such well-defined periodic signals. In order to demonstrate the extent of use of frequency domain in batteries a simple comparison between two different samples, 3 k Ω resistor and a shorted battery which is known to exhibit noisy signals, is illustrated in Figure 3.1, sampled with two different frequencies.

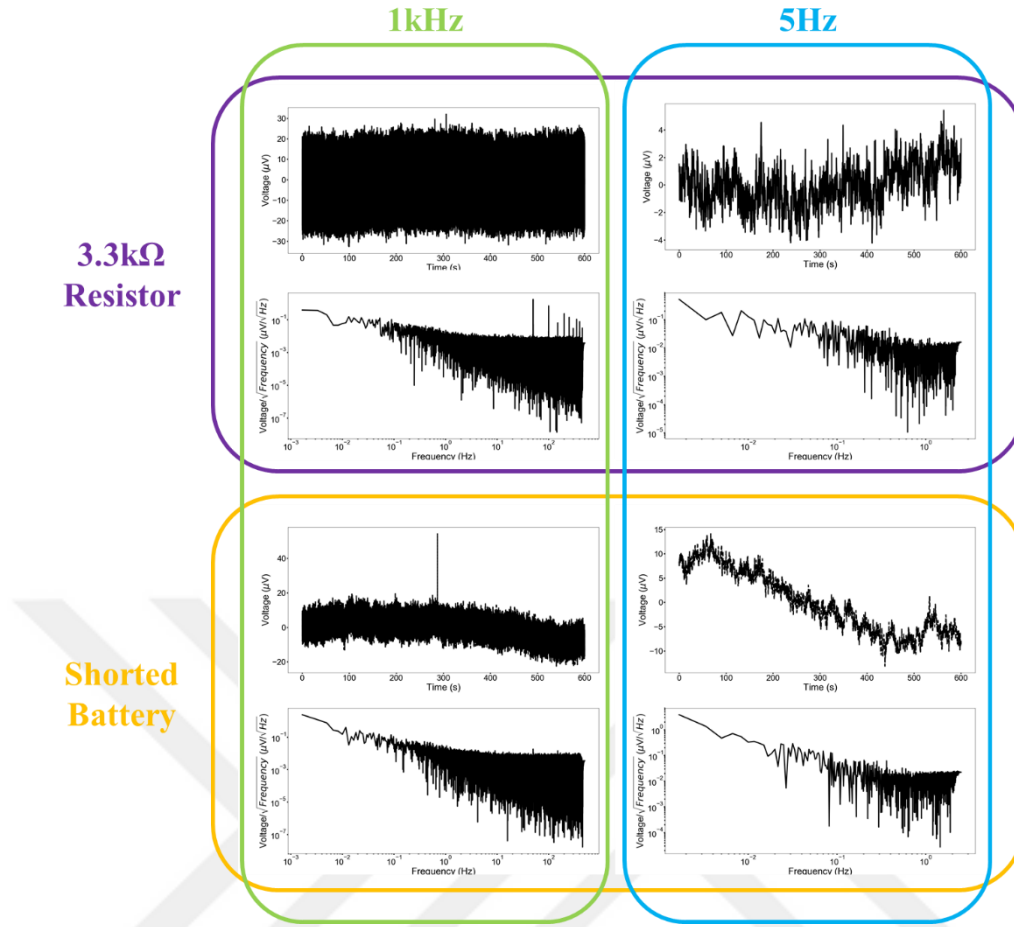


Figure 3.1 Electrochemical noise data of a resistor and a shorted CR2032 coin cell battery in time and frequency domains with 1kHz and 5Hz sampling frequencies

When the sampling frequency is set at 1kHz, the original signal can be interfered by power line signal (which is 50Hz) and its potential overtones. On the other hand, when the sampling frequency is set at 5Hz the signal becomes much clearer in both time and frequency domain. When the battery is compared to the resistor, it can be seen that battery has many ripples and drastic changes in voltage and this difference is almost indistinguishable in frequency domain. However, when the low frequency region is considered the increase in the noise level in the battery is higher compared to the resistor, and it is hard to deduce that this is due to ripples and drastic changes in battery or drift.

This brings up the second question to consider; how to distinguish the drift seen in the signal from the actual signal and how to get rid of the drift? All of the algorithms are driven from some user input in order to determine the details of the compensation algorithm. One of the challenges is being able to identify the parts of the signal that are to be compensated.

1 hour of noise data from a short-circuited battery known to show electrochemical noise signal and its detrended version is illustrated in Figure 3.2 for clearer explanation of drift.

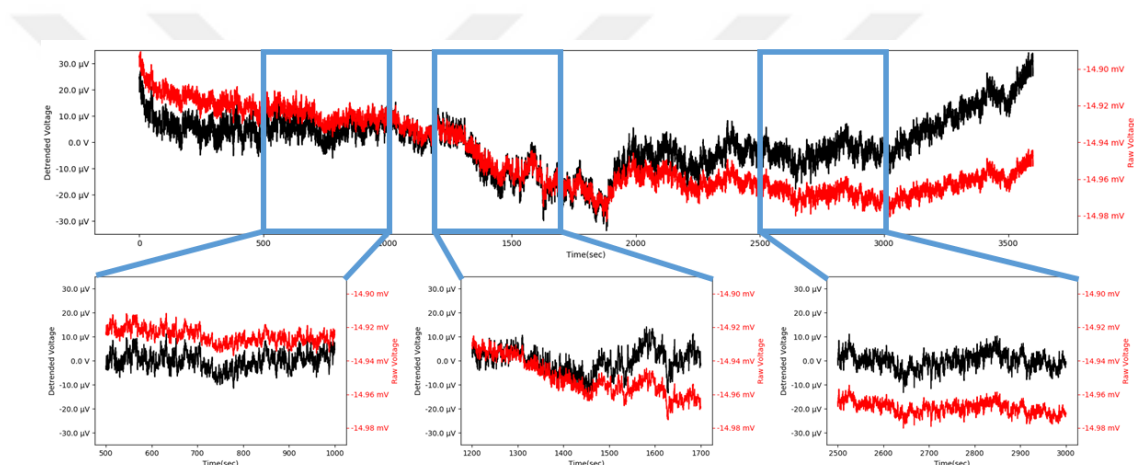


Figure 3.2 Electrochemical noise data of shorted CR2032 coin cell battery. Raw data (red) and detrended data (red).

The top panel shows the entire 1-hour noise measurement, with the original signal in red (using the right y-axis) and the detrended version in black (using the left y-axis). Detrending process was done by fitting a line through the entire dataset. In the lower panel, 500 second portions taken from three different regions of the original signal are shown. Just like in the top panel, the original signals are drawn together in their detrended form in the panels below. It is important to emphasize that this detrending was performed within the 500s section. Especially when the middle panel is considered, it becomes clear how important and relative it is to separate the drift from

the actual signal. If only 500 second portions were considered, it seems that there is a negative going overall drift there and it needs to be removed, however, considering the entire data, it seems to be the global minimum of the original data independent of drift. Thus, it is important to understand the origin of such features before manipulating it.

Methods such as Recurrence Quantification Analysis [5], [22], [49], Wavelet analysis [23], [40], [43], [44], Stochastic Process Detector [50] are useful mathematical tools that are widely used in corrosion literature. As mentioned earlier, these analysis methods can reveal useful information as long as they can be compared with correct post-mortem analysis under specific conditions yet the applicability of these methods for the analysis of noise measurements of batteries is yet to be proven.

Recurrence Quantification Analysis is one of the time domain analysis methods for dynamic systems and it is also a common method that is used in corrosion science for noise analysis. [5], [22] Every width up to half the length of the data is extracted. Then, the correlation is calculated with various shift levels. This is illustrated by a 2-D contour plot which shows how often the data presenting recurring sections. These sections manifest themselves as persistent regions in the recurrence plots. Yet again, electrochemical noise data of the shorted battery was utilized in order to illustrate the application of RQA to the batteries. RQA applied to noise data taken with sampling frequencies of 1kHz and 5Hz with and without assigning 1 μ V threshold value. The RQA results are shown in Figure 3.3.

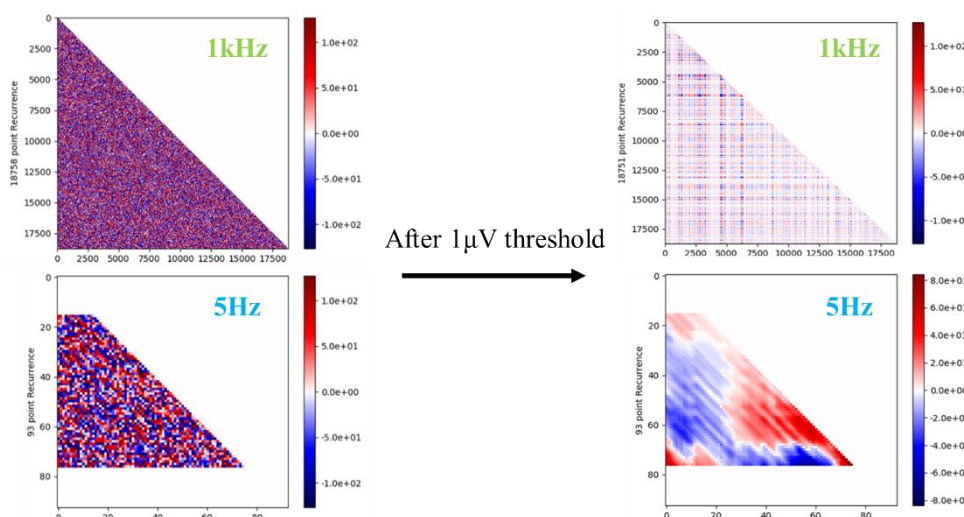


Figure 3.3 Recurrence quantification analysis results of shorted CR2032 coin cell battery before and after assigned threshold value.

These kind of mathematical tools require the user to assign parameters externally such as threshold value in this case. No feature is observed as a result of RQA of a signal known to be noisy before assigning any threshold value. However, assigning a threshold value while performing the analysis reveals features that are open to interpretation. For this reason, determining the parameters suitable for the system under consideration complicates the analysis.

Another common method that is used to analyze electrochemical noise data is Wavelet Transform technique where the wavelet is used to analyze signals through basis sets other than sinewaves. It is proposed that Ricker wavelet is the appropriate function for the analysis of stochastic corrosion events that involves spikes due to the peak type of signal nature of the function. [45] Yet again, similar to the aforementioned analysis method external parameter are needed to be selected such as width for the peak shape for further associations.

Wavelets are functions that are localized in time. Therefore, they are much better to identify non-periodic events. The overall calculation typically computes the correlation of a peak-like function (i.e. wavelet) to the overall data while shifting it. The points where the correlation function shows maxima are the points where an event of given width occurs. To highlight the importance of the selected width value when wavelet transform analysis is used to analyze the electrochemical noise measurement data of a battery, the shortened battery is used, and the results are shown in Figure 3.4. Electrochemical noise data of shorted battery taken with sampling frequencies of 1kHz and 5Hz are analyzed with width length of 1500 and 150 which is defined to be unitless parameter. The detailed analysis presented in figure 3.4 below is the result of applying the method to the data.

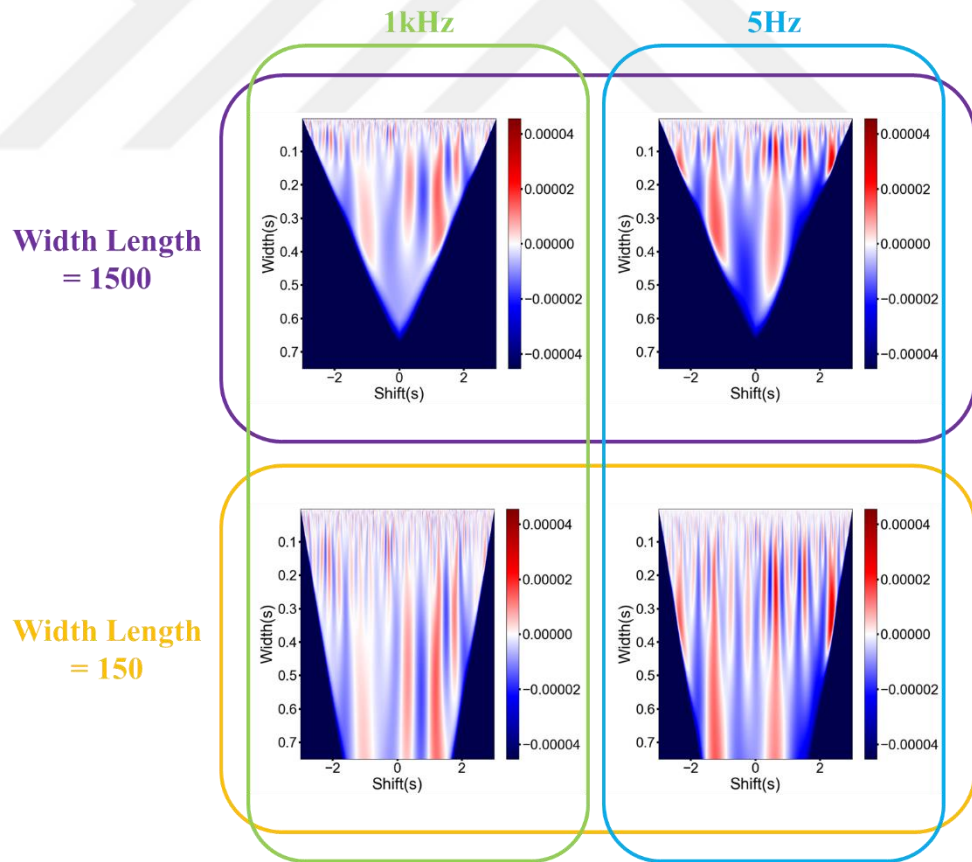


Figure 3.4 Wavelet Transform analysis results of shorted CR2032 coin cell battery with width length of 1500 and 150

Despite the fact that there are ways to quantify this further, the first point to make is that they are different, especially when the wavelet width is high. There are, however, parameters to consider when calculating these results, which clearly influence the quantification of the wavelet transform.

All the examples shown above emphasize that the use of mathematical analysis methods alone is deeply subjective and does not lead to trustworthy results. For this reason, the mathematical methods to characterize certain properties of the signal should be used together with post-mortem analysis methods to make correct analyses.



Chapter 4

4. Electrochemical Noise Measurements in Lithium Based Batteries

(This part is also described in Gözde Karaoğlu, Can Berk Uzundal, Burak Ulgut, “Uneven Discharge of Metallic Lithium Causes Increased Voltage Noise in Li/MnO₂ Primary Batteries upon Shorting”, Journal of Electrochemical Society, 2020, 167, 130534. Reproduced from [45] with permission from Journal of Electrochemical Society)

4.1 Experimental

4.1.1 Electrochemical Noise Measurements

Non-rechargeable CR2032 coin cell batteries with nominal voltage of 3.0V were subjected to electrochemical noise measurements and divided into two sets as properly-discharged and short-circuited. For the properly-discharged batteries, product datasheet² provided the information that typical current drain is 0.19 mA when 15 k

² Energizer, “ENERGIZER CR2032”, 2032NA0618 Product Datasheet (<https://data.energizer.com/pdfs/cr2032.pdf>)

ohms resistance is connected. Consequently, it takes approximately 1225 hours (51 days) to fully discharge a single coin cell battery and thereafter this information was used to calculate how long the battery had to be connected to the resistor to reach the desired state of charge (SOC) values. On the other hand, for the short-circuited batteries, the positive and negative ends of the battery are directly connected to each other with the help of a crocodile to ensure short-circuiting. Schematic representation of connections are shown in Figure 4.1.

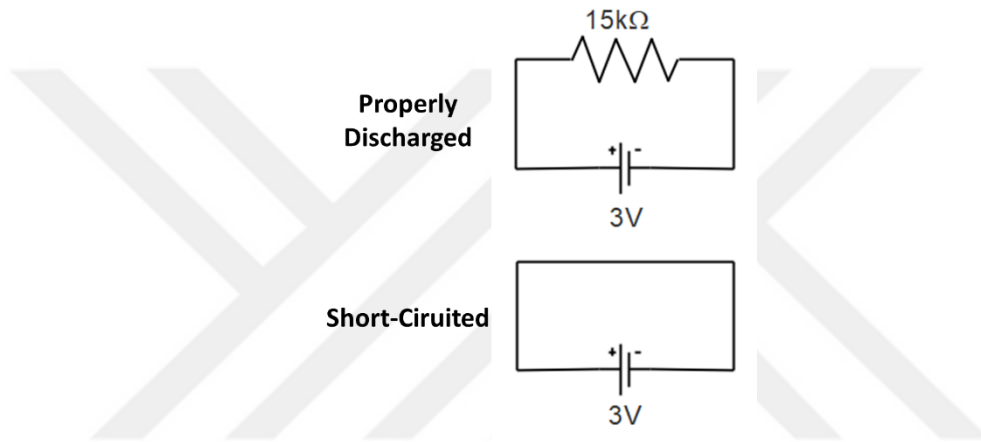


Figure 4.1 Schematic representation of properly discharged batteries and short-circuited batteries

Electrochemical noise measurements were done as it is described in Chapter 2. The noise measurements of the batteries, after waiting for about 2-3 hours to reach equilibrium in parallel, were measured in an anti-serial connection and 10-minute measurements were recorded. All data are presented with a global line fitted to the original signal that gets subtracted for trend removal.

First, noise measurement of the pristine CR2032 battery was conducted as a reference to further experiments. Noise data of a pristine battery is shown in Figure 4.2 with a maximum amplitude of approximately 7μV.

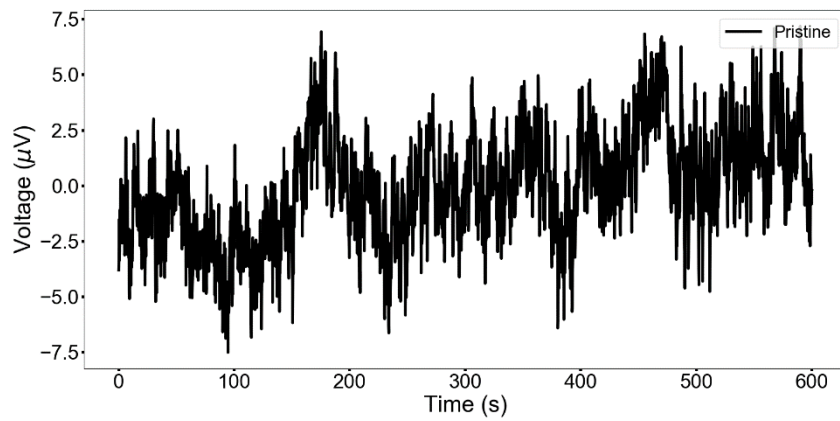


Figure 4.2 Electrochemical noise data of pristine non-rechargeable CR2032 battery

Then, noise measurements of batteries exposed to short circuit with different time durations and batteries properly discharged to different SOC were taken. The batteries were short-circuited for 1 day, 3 days and 7 days and properly discharged to 75%, 50% and 25% SOC. The noise data of the short-circuited and the discharged batteries are shown in Figure 4.3 and Figure 4.4, respectively. As the data shows, batteries exposed to short circuits show amplitudes around 100 μV , where 3 days shorting of a battery provides highest noise values, while discharged batteries have potential oscillations at low amplitudes as in pristine batteries.

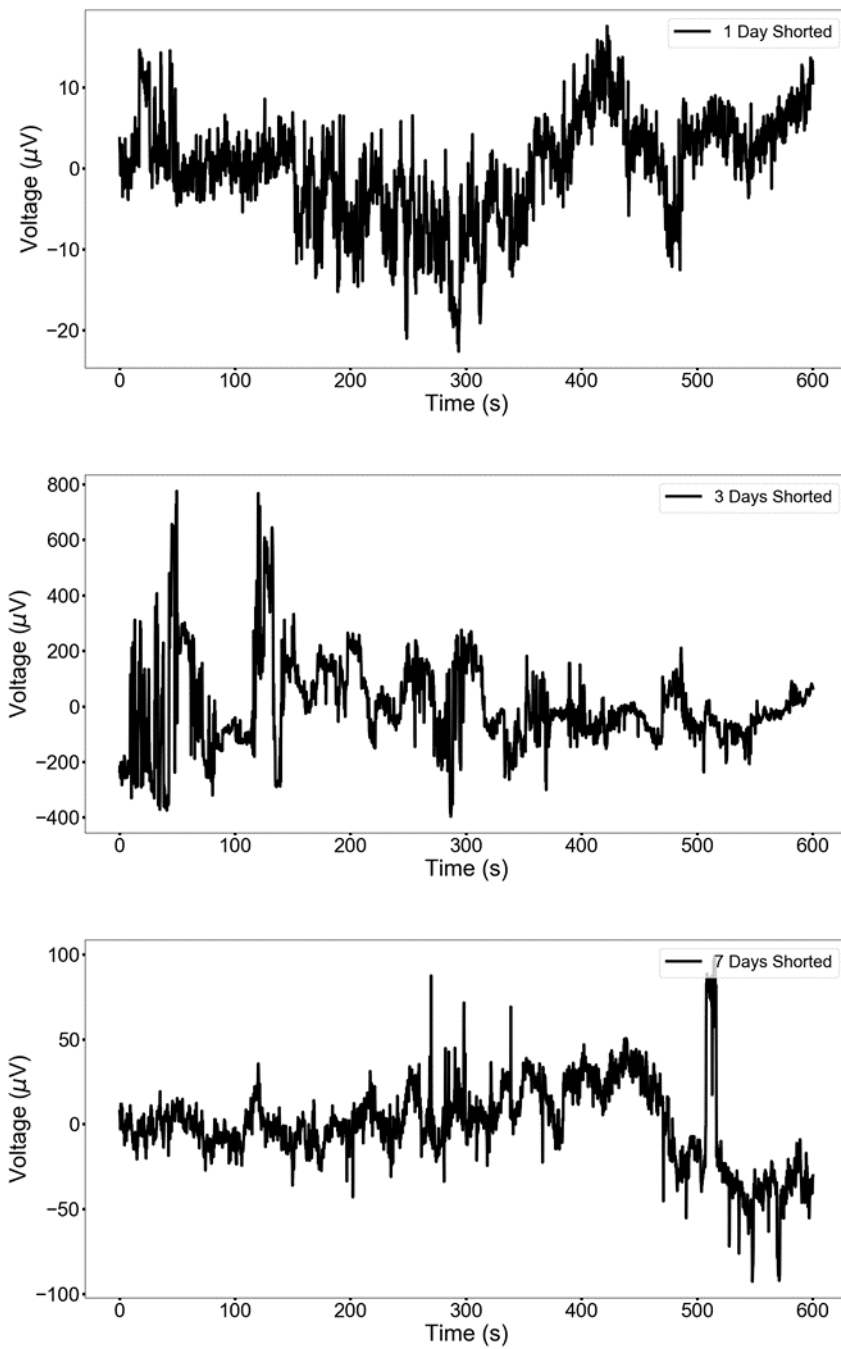


Figure 4.3 Electrochemical noise data of shorted non-rechargeable CR2032 batteries at various stages of shorted durations (1 day, 3 days, 7 days)

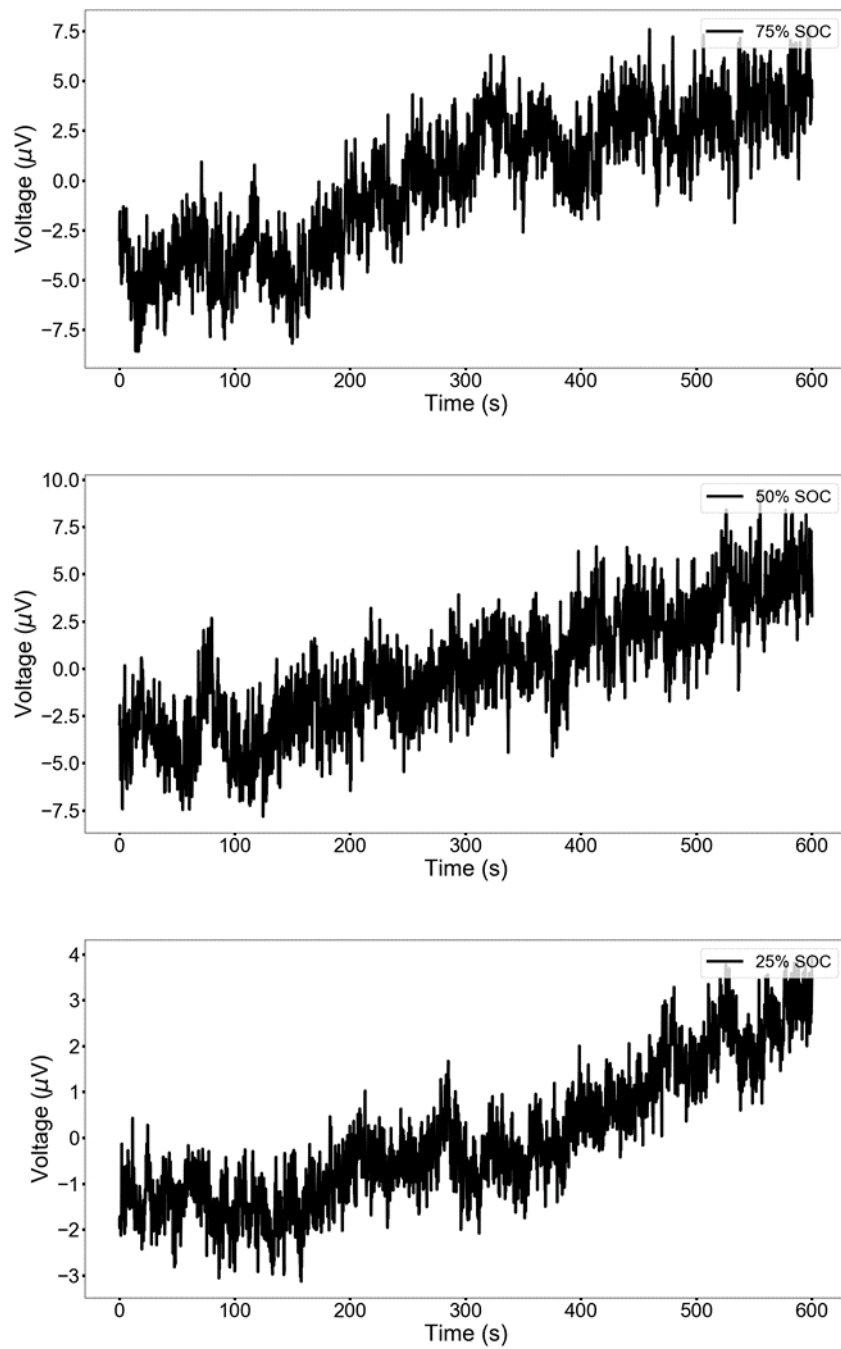


Figure 4.4 Electrochemical noise data of properly discharged non-rechargeable CR2032 batteries at different states of charge (75% SOC, 50% SOC, 25% SOC)

Although in Figure 4.3 and Figure 4.44, it is seen that there are serious differences in the noise levels of the batteries exposed to short circuits and the noise levels of batteries that are properly discharged. It can be emphasized how obvious the difference is by keeping the scales of the y-axis of the graphs the same as demonstrated in Figure 4.5.

For further emphasis (and at the persistent request of reviewer 2) noise variances were calculated for every noise measurement and values were shown in Table 2.1.

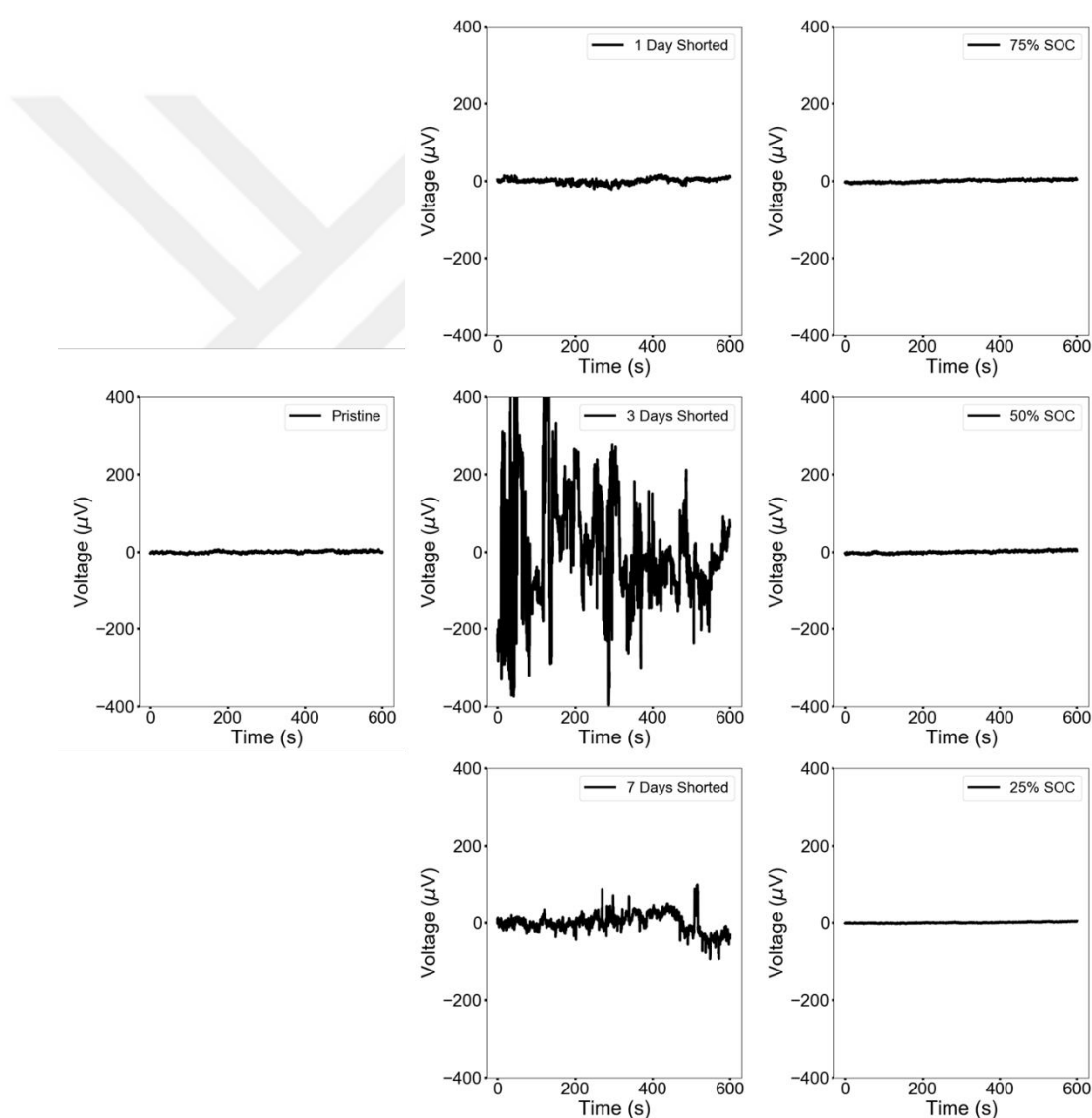


Figure 4.5 Electrochemical noise data comparison of pristine (left), shorted (middle), properly discharged (right) non-rechargeable CR2032 batteries at various stages of shorted durations (1 day, 3 days, 7 days) and different states of charge (75% SOC, 50% SOC, 25% SOC) on the same scale of y-axis.

	Noise Variance (σ^2)		Noise Variance (σ^2)
1 Day Shorted	44 μV^2	75% SOC	12 μV^2
3 Days Shorted	24200 μV^2	50% SOC	12 μV^2
7 Days Shorted	592 μV^2	25% SOC	2.21 μV^2

Tablo 2.1 Noise variance values of shorted and properly discharged non-rechargeable CR2032 batteries at various stages of shorted durations (1 day, 3 days, 7 days) and different states of charge (75% SOC, 50% SOC, 25% SOC)

After observing an increase in the noise levels of the batteries exposed to short circuit, measurements were made to determine the minimum short-circuit duration that can be determined by noise measurements and the data obtained are shown in Figure 4.6 and the data shows that the noise levels of the batteries start to increase after they exposed to the short circuit for 1 hour.

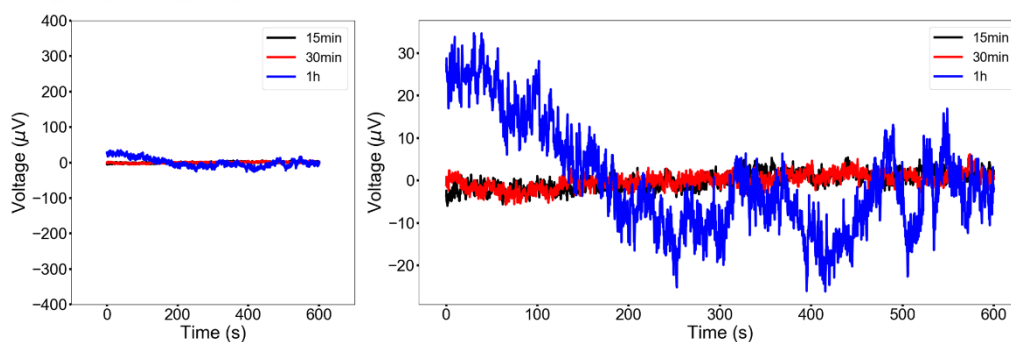


Figure 4.6 Electrochemical noise measurement of non-rechargeable CR2032 batteries after suffering 15 minutes, 30 minutes and 1 hour shorting.

Finally, a comparison of noise measurements of non-rechargeable and rechargeable batteries is shown in Figure 4.7. Aforementioned experiments have shown that batteries exposed to a short circuit for 3 days showed the highest noise levels. For this reason, both non-rechargeable and rechargeable CR2032 batteries were exposed to a short circuit for 3 days and their noises were compared for an accurate comparison. According to the data obtained, the noise levels of rechargeable batteries do not increase by exposure to short circuits like those of non-rechargeable batteries.

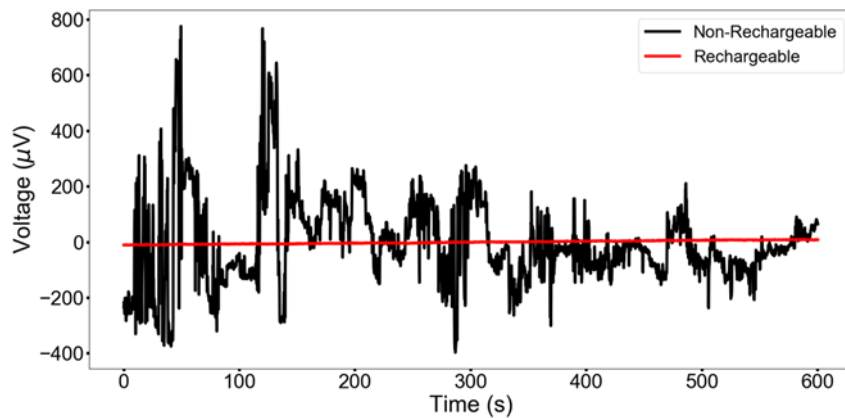


Figure 4.7 Electrochemical noise measurement of non-rechargeable and rechargeable CR2032 batteries after suffering 3 days shorting.

Further investigations have revealed that the difference between non-rechargeable and rechargeable CR2032 batteries is the anode material. Every single component of the batteries are identical except that the anode material of the non-rechargeable CR2032 battery is pure metallic lithium whereas rechargeable CR2032 batteries exhibit lithium-aluminum alloy as an anode material. [51]

4.1.2 Battery Disassembly

In order to further locate the source for the increase in noise levels requires post-mortem analysis and therefore batteries were disassembled. CR2032 coin cell batteries with Li/MnO₂ chemistry have components of metal grid, cathode, separator, and anode from positive end to negative end with an electrolyte. Representative schematic and photo of coin cell is given in Figure 4.8. Further, to separate each component of the coin cell with minimal deformations, the cells were held with medical pliers with the tips wrapped by cloth. Small cuts were performed along the perimeter of the positive terminal. Once the full perimeter of the positive terminal was cut, the cell can simply be pulled apart revealing all the components of the battery with minimal deformations.

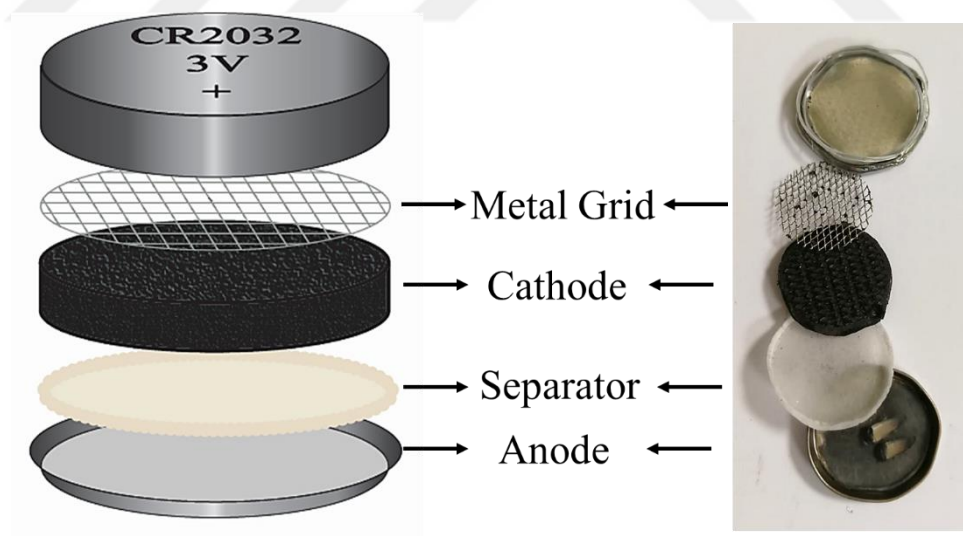


Figure 4.8 Schematic and photo of the non-rechargeable CR2032 coin cell battery components. From top to bottom: Metal grid, cathode, separator, and anode.

Battery components are highly reactive, especially the anode material, which is metallic lithium, and in order to prevent degradation due to the presence of O_2 and H_2O batteries were disassembled under inert atmosphere. Degradation of lithium anode under air is shown in Figure 4.9. To prevent the degradation batteries were disassembled in a glove bag filled with N_2 gas as shown in Figure 4.10.



Figure 4.9 Metallic lithium anode under inert atmosphere (left) and degradation of metallic lithium anode after exposed to air (right).



Figure 4.10 Photo of the setup where the batteries are disassembled: Glove bag filled with N_2 gas.

4.1.3 Material Characterization

CR2032 coin cell batteries were disassembled under inert atmosphere and thereafter all components were analyzed by various analyses methods such as X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and photographic imaging. For technical specifications please see the Appendix.

XRD Analysis – Once the battery is disassembled, the battery components, the anode and the cathode material are fixed onto a microscope slide and sealed with Kapton tape which is X-Ray transparent and suitable for XRD measurements. Figure 4.11 shows the sealed anode and cathode material.



Figure 4.11 The cathode (left) and the anode (right) material of a non-rechargeable CR2032 coin cell battery fixed onto microscope slide and sealed with Kapton tape.

The anode and the cathode materials of batteries exposed to short circuit and discharged properly were investigated by XRD in order to locate the source of increased observed in our noise measurements, due to short circuit exposure, is due to the change in the crystal structure of the anode or cathode material.

Therefore, both the anode and the cathode materials of batteries exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days) and discharged to different SOC (25% SOC, 50% SOC, 75% SOC) were examined by XRD, however, no significant change was observed in their crystal structures. XRD measurements for anode and cathode are shown in Figure 4.12 and Figure 4.13, respectively.

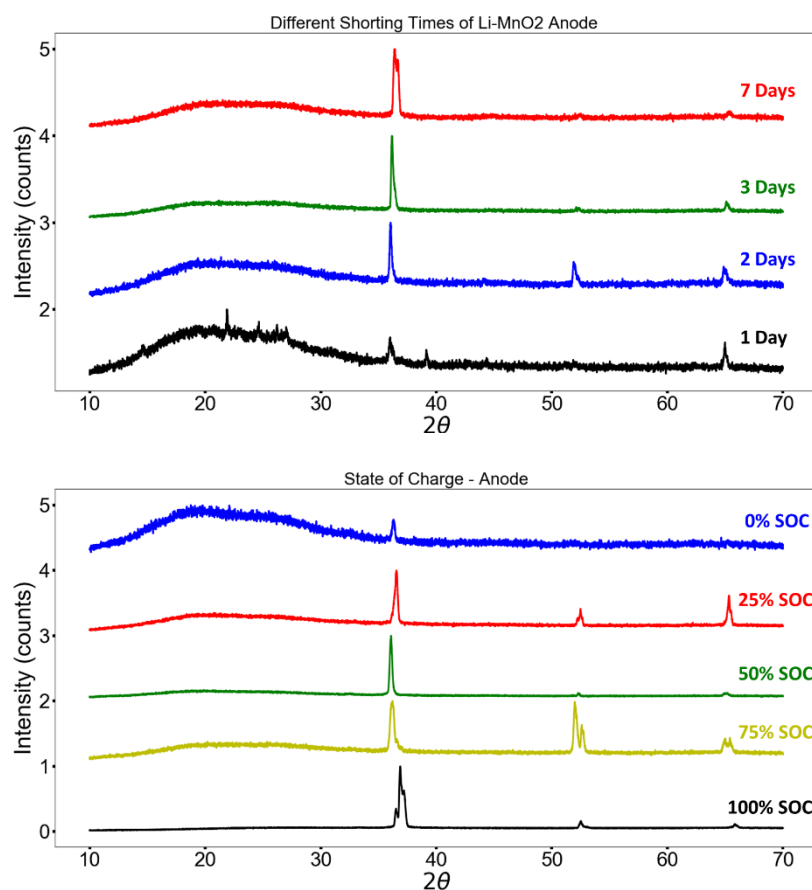


Figure 4.12 XRD measurements of anode of non-rechargeable CR2032 coin cell battery exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days) (top), and discharged to different SOC (25% SOC, 50% SOC, 75% SOC) (bottom).

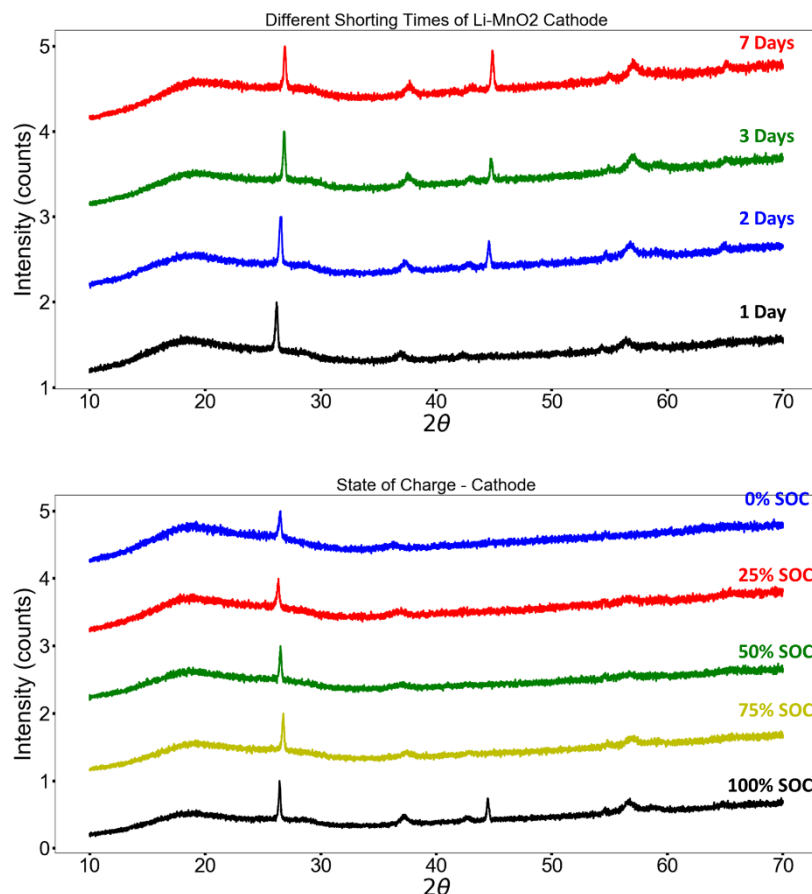


Figure 4.13 XRD measurements of cathode of non-rechargeable CR2032 coin cell battery exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days) (top), and discharged to different SOC (25% SOC, 50% SOC, 75% SOC) (bottom).

Within experimental reproducibility, there is no significant difference in the diffraction patterns of the materials collected from the shorted batteries and the pristine ones. Similar analyses were performed for other parts of the cell, as well as the properly discharged ones to confirm that there were no significant differences.

FT-IR Analysis – Once the battery is disassembled, FT-IR was used for compositional analysis of the separator. The separator of pristine battery and the battery shorted for 3 days were compared in Figure 4.14, which indicated that the separator is polypropylene, as expected. The differences in the ATR-FTIR from sample to sample was very large. Therefore, the differences in the data shown before

and after shorting is hard to interpret. More analysis is required on whether the large sample-to-sample variation is due to measurement method or due to actual inconsistencies of the separators.

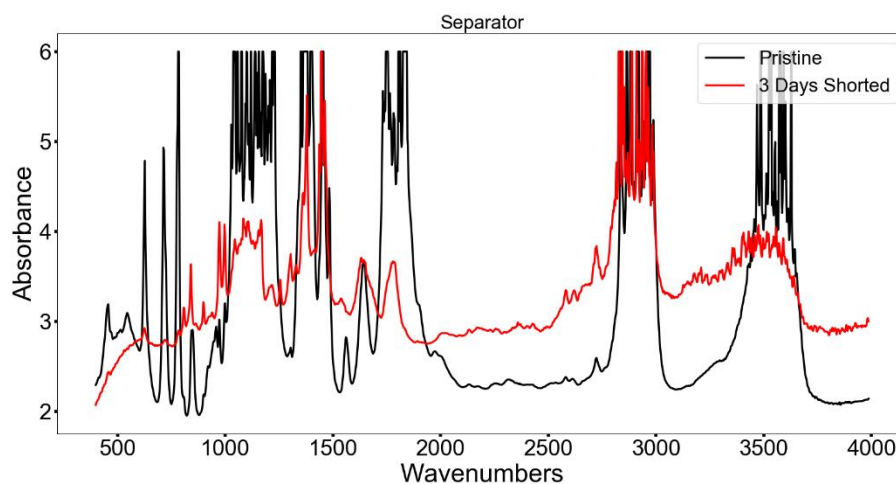


Figure 4.14 The FT-IR measurement of the separator of pristine and shorted for 3 days non-rechargeable CR2032 coin cell battery.

XRF Analysis – Once the battery is disassembled, all the components of the battery (anode, cathode, separator, and metal grid current collector) were subjected to XRF analysis for elemental composition determination. Both components of the pristine battery were examined in order to figure out the elemental composition and the components of the 3 days shorted battery to see if there is any difference upon shorting. The XRF results of the anode and the cathode are shown in Figure 4.15 where the XRF results of the metal grid (current collector) and the separator were shown in Figure 4.16.

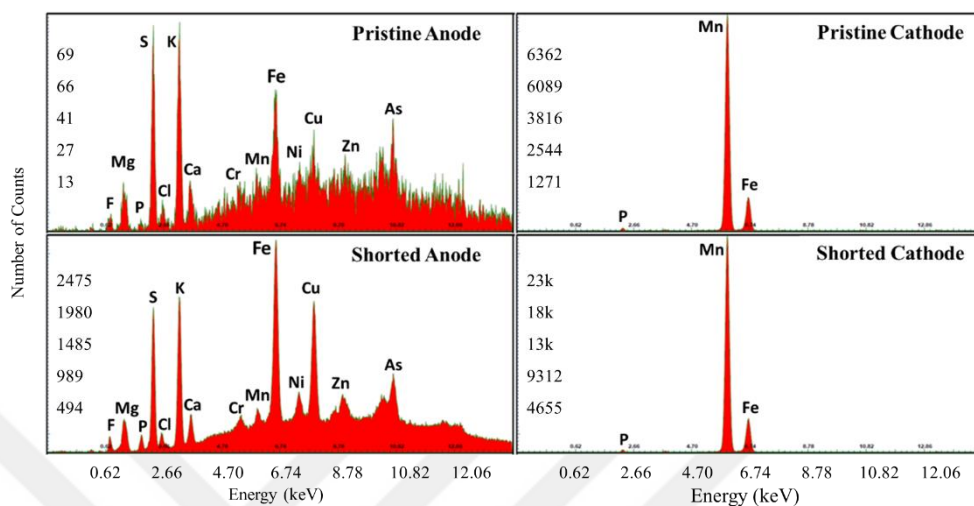


Figure 4.15 The XRF measurement of the anode and the cathode of pristine and shorted for 3 days non-rechargeable CR2032 coin cell battery.

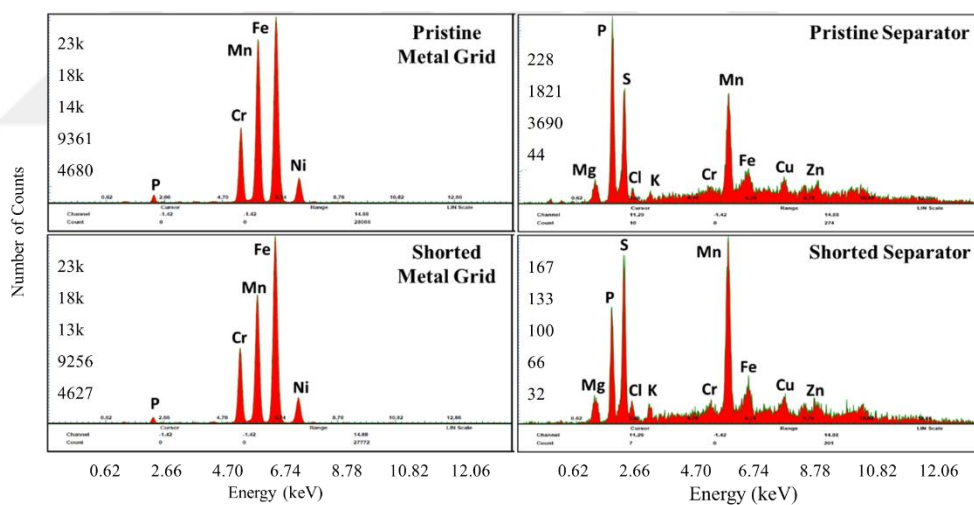


Figure 4.16 The XRF measurement of the metal grid (current collector) and the separator of pristine and shorted for 3 days non-rechargeable CR2032 coin cell battery.

SEM and EDX Mapping Analysis – In order to investigate surface morphology and to identify elemental composition of anode material (lithium and manganese dioxide) SEM and EDX analyses were utilized yet again the pristine version of

components were compared with shorted and discharged versions with different shorting durations (1 days, 3 days and 7 days) and different SOC values (25% SOC, 50% SOC and 75% SOC). In Figure 4.17, the SEM image of anode of the pristine battery where the pure metallic lithium is monitored with the resolutions of 1mm and 500 μ m.

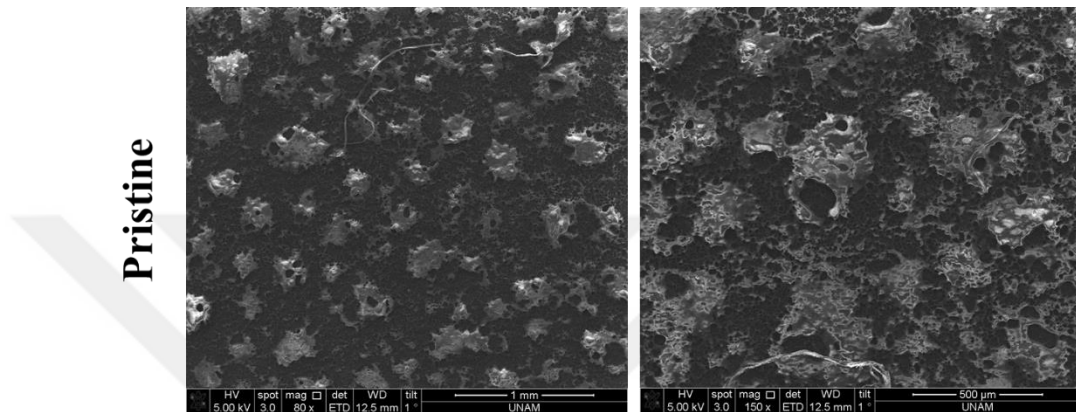


Figure 4.17 SEM image of anode of pristine non-rechargeable CR2032 coin cell battery with the resolutions of 1mm and 500 μ m

Subsequently, the anode of the short-circuited and discharged batteries was investigated by SEM. It seems that the anode of the short-circuited batteries is damaged by exposure to short-circuit, and deterioration occurs on the anode surface. Moreover, as the short-circuit exposure time increases, the severity of the deterioration on the lithium surface also increases. On the other hand, no deterioration is observed in the anode of the batteries that are left to be properly discharged. As the discharge time increases, the anode material lithium decreases, but this happens in a homogeneous manner. SEM images of the anode of short-circuited batteries are shown in Figure 4.18, and SEM images of the anode of discharged batteries are shown in Figure 4.19.

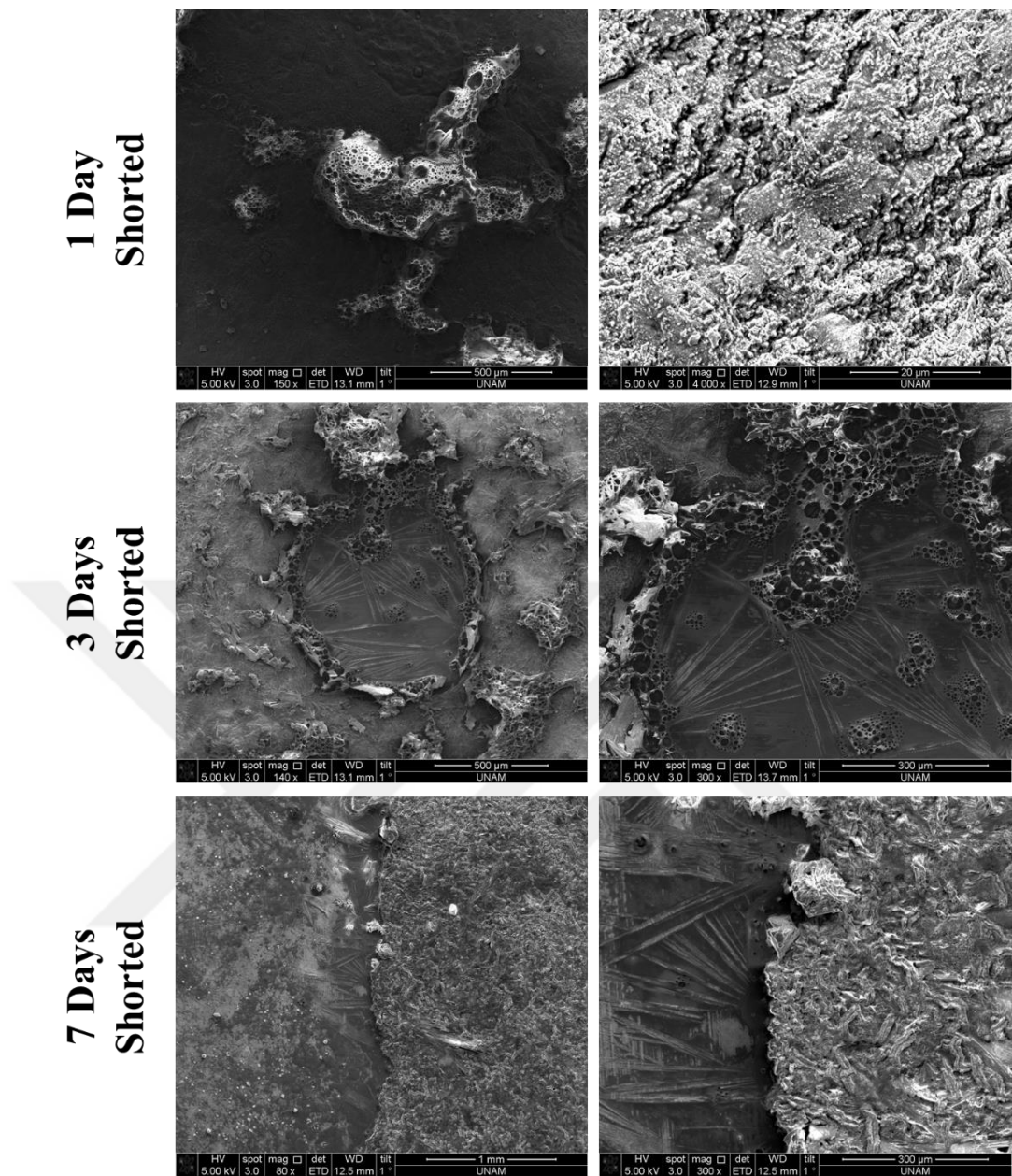


Figure 4.18 SEM image of anode of shorted non-rechargeable CR2032 coin cell battery at various stages of shorted durations (1 day, 3 days, 7 days) with the resolutions of 500µm and 20µm; 500µm and 300µm; 1mm and 300µm, respectively.

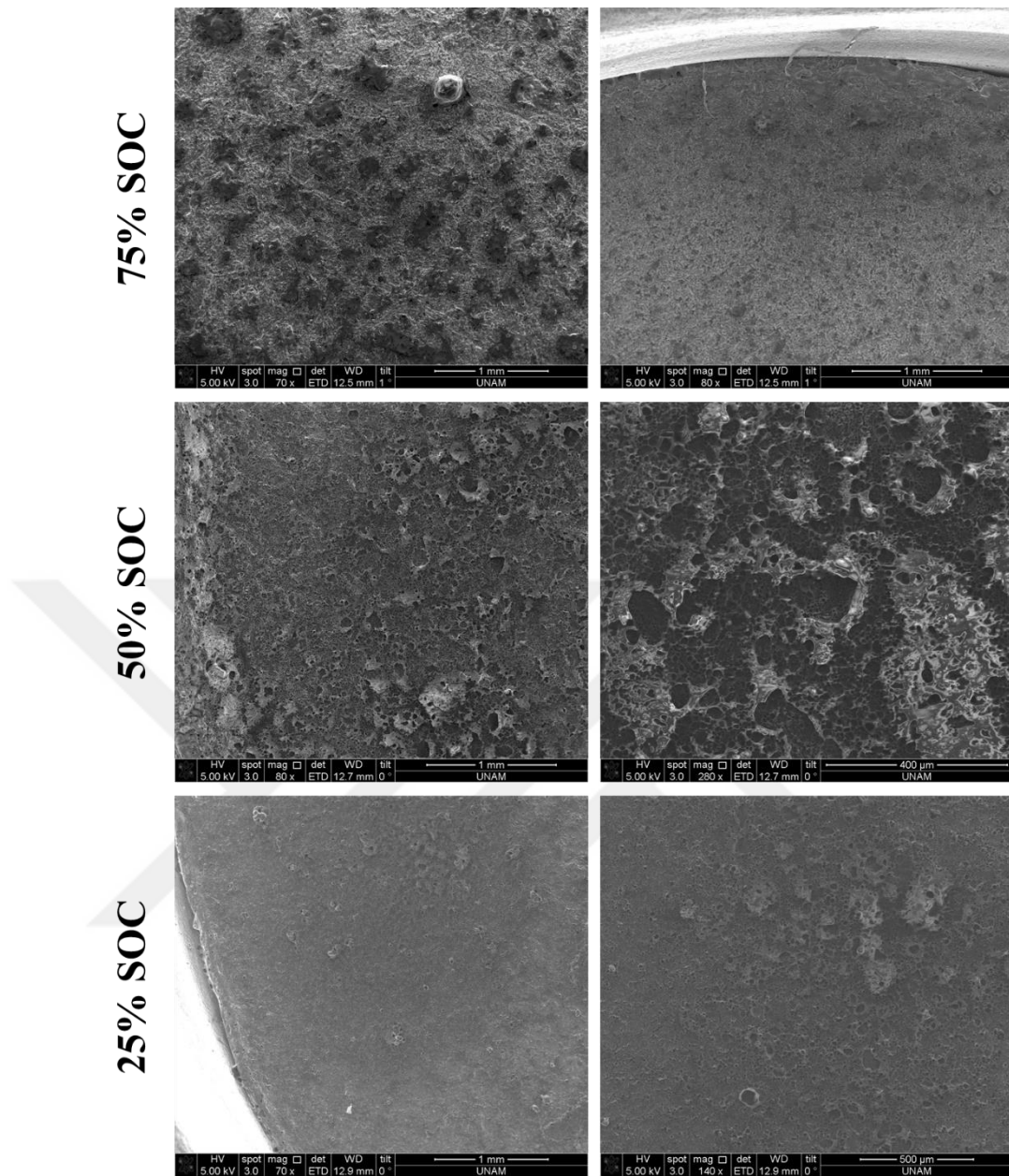


Figure 4.19 SEM image of anode of discharged non-rechargeable CR2032 coin cell battery at different states of charge (75% SOC, 50% SOC, 25% SOC) with the resolutions of 1mm and 1mm; 1mm and 400µm; 1mm and 500µm, respectively.

After obtaining high resolution images with SEM, EDX measurements were also made on the same samples for elemental identification and quantitative compositional information. EDX maps of the anode of short-circuited batteries are shown in Figure 4.20, and EDX maps of the anode of discharged batteries are shown in Figure 4.21.

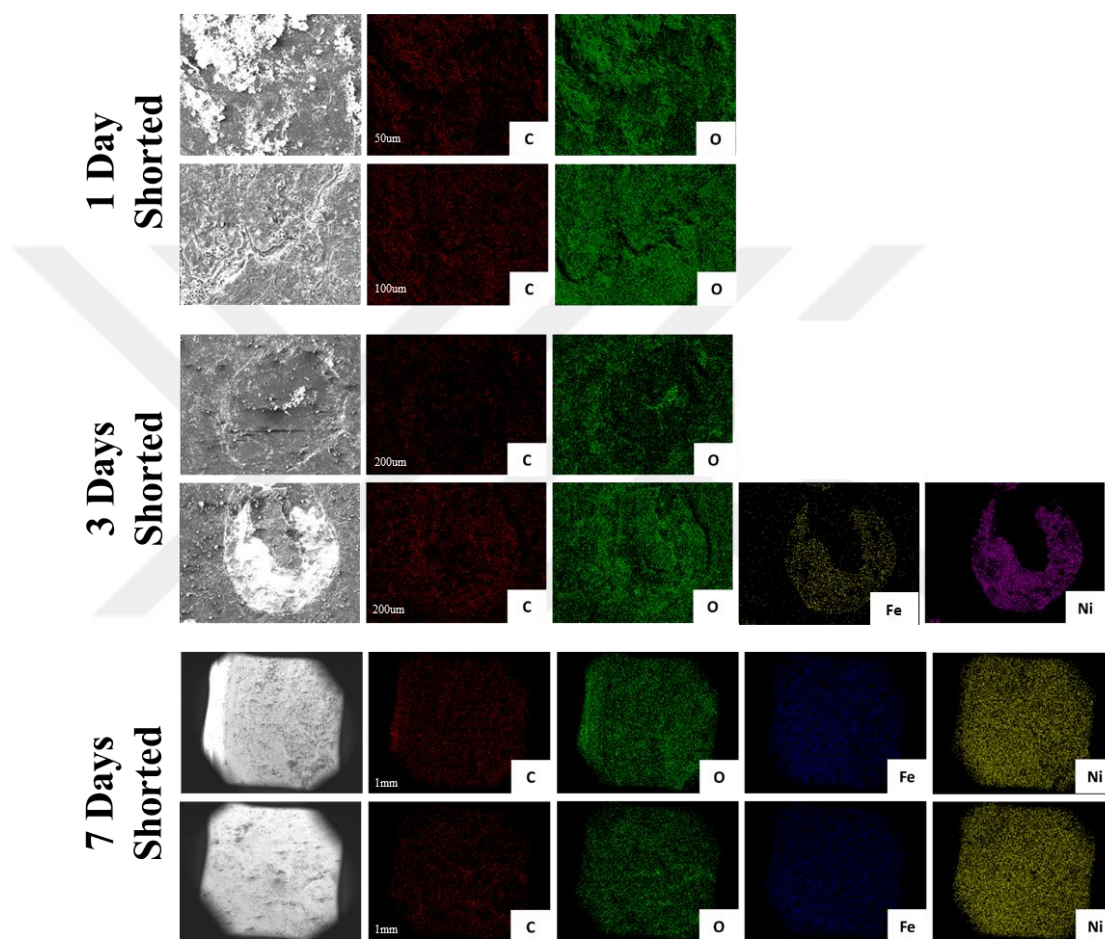


Figure 4.20 EDX Mapping of anode of shorted non-rechargeable CR2032 coin cell battery at various stages of shorted durations (1 day, 3 days, 7 days) with the resolutions of 50μm and 100μm; 200μm and 200μm; 1mm and 1mm, respectively.

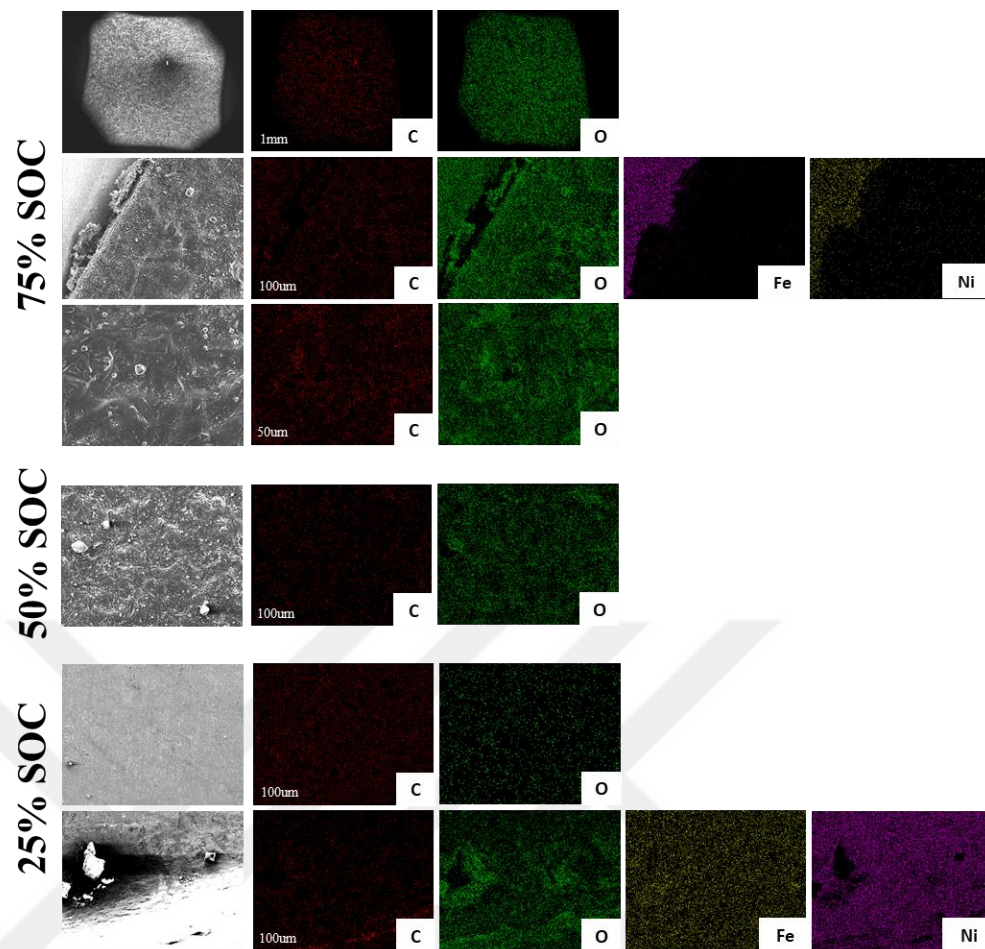


Figure 4.21 EDX mapping of anode of discharged non-rechargeable CR2032 coin cell battery at different states of charge (75% SOC, 50% SOC, 25% SOC) with the resolutions of 1mm,100μm and 50μm; 100μm; 100μm and 100μm, respectively.

Finally, after the batteries are disassembled inside the glove bag, all the components were subjected to photographic imaging especially the anode since SEM images revealed that short circuit destroys the anode of the battery, but discharge does not. For this reason, photos of the anode were taken as soon as the batteries were disassembled, and the anode of the short-circuited batteries was compared with the anode of the discharged batteries. It seems that the anode, metallic lithium, is visibly damaged due to short-circuit exposure where the anode of discharged batteries remained undamaged. The comparison is shown in Figure 4.22.

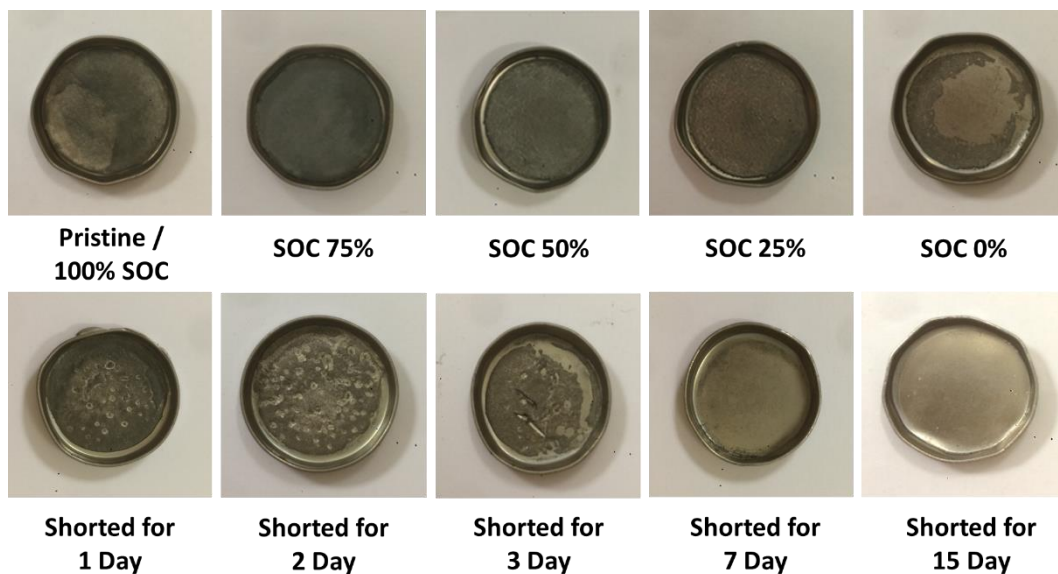


Figure 4.22 Photographic images of of anode of non-rechargeable CR2032 coin cell battery discharged to different SOC (Pristine/100% SOC, 75% SOC, 50% SOC, 25% SOC) (top) and exposed to different short-circuit durations (1 day, 2 days, 3 days, 7 days, 15days) (bottom).

4.2 Results and Discussions

In the previous published work by Uzundal et. al. [47], it was shown that the voltage noise of the CR2032 coin cells with the primary $\text{Li}\backslash\text{MnO}_2$ chemistry was increased when the cells were shorted for set periods of time. Drawing inspirations from electrochemical noise studies in corrosion, visual inspection and chemical and physical analyses on the components of the battery were carried out to identify the phenomenological reason behind the increased noise.

In order to investigate the differences in a controlled manner, two major experimental routes were followed to systematically study the effects of abuse on the outlined battery components. These involved comparisons between shorted and properly-discharged batteries both in terms of their noise profiles and their chemical properties.

Another interesting observation can be made on the voltage noise level of primary batteries as the length of shorting increases. The voltage noise level increases when the battery first suffers a short that lasts 1 days or 3 days. However, when the battery is shorted for a full week, the measured voltage noise decreases drastically back to levels that are still above the pristine battery (limited by the instrument) yet much lower compared to a battery that is shorted for three days. This result sheds some more light into the phenomenon behind the voltage oscillations. It appears that the measured voltage noise is larger when the exposed surfaces of stainless steel and lithium are comparable in area. In contrast, the signal is quieter when only the lithium metal, or only the stainless steel is exposed. We speculate that the noise measured is fundamentally due to the voltage measurement mechanism choosing the dominant surface when one exists and is effectively bi-stable when both surfaces are roughly equally available. Measurement of voltage by definition is done via a small DC current

passing through the device under test. Irrespective of the method used, there is a small current, either the current on the needle, or the input bias current on the comparator. This current will pass through the path of the least resistance, in the case where multiple paths exist. As illustrated on Figure 4.23, the only time voltage would be noisier is when the electrode surface has two widely different options for the current as shown on Figure 4.23 (c).

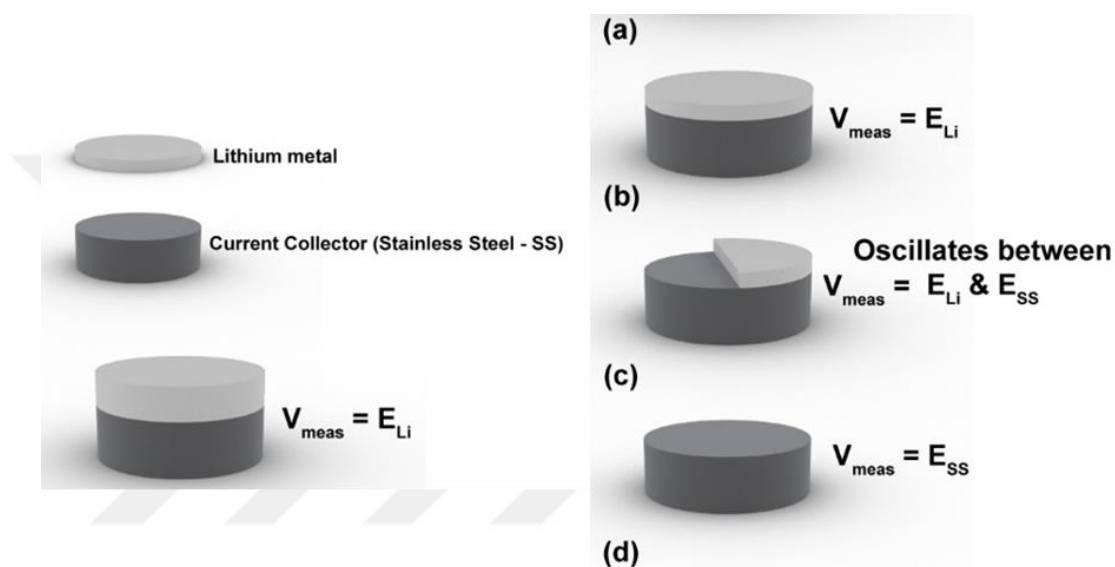


Figure 4.23 Schematic description of a current collector (black) and lithium active material (gray) Pristine battery (a), properly discharged battery (b), 3 days shorted battery (c), 7 days shorted battery (d) (E_{Li} : Open Circuit Potential for the Li Metal, E_{SS} : Open Circuit Potential for the Stainless Steel, V_{meas} : Measured Voltage)

In summary, we have shown that increased noise of primary lithium batteries is due to the heterogeneous oxidative dissolution of the lithium anode. We have two significant experiments that lead to this conclusion. First, when the shorting experiment is repeated using a rechargeable battery with almost the same composition (except the anode material), the noise is not present. Second, when the discharge is carried out with a low current (homogeneous dissolution), the noise is not present. This is summarized in Figure 4.24.

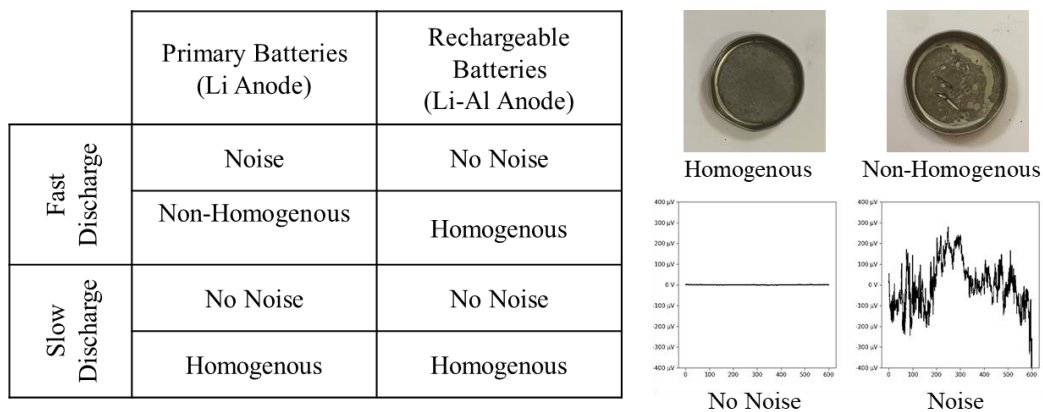


Figure 4.24 Short summary of the findings

This noise is similar in nature to pitting corrosion where electrochemical noise measurements are routinely used to identify. Localized oxidative discharge of the anode eventually exposes parts of the underlying stainless-steel substrate. This causes the open circuit to be noisier, akin to the voltage noise increasing when pitting corrosion occurs. Increased noise can be attributed to various competing electrochemical processes on different parts of the electrode surface.

4.3 Summary

Voltage noise in LiMnO_2 primary batteries was shown to be due to the localized discharge of metallic lithium anode. In nonchargeable batteries, if the battery is properly discharged lithium depletion occurs homogeneously thus no noise is observed at significant levels. On the other hand, shorting causes non-homogeneous depletion which can be observed by electrochemical noise measurements. The localized discharge eventually exposing the underlying stainless-steel substrate causes the open circuit to be noisier, akin to the voltage noise increasing when pitting corrosion occurs. The increased noise can be attributed to the various competing electrochemical processes on different parts of the electrode surface.

Chapter 5

5. Electrochemical Noise and Optical Investigation of Dendrite Formation in Lithium Anode

5.1 Introduction

Electrochemical energy storage systems in general and battery systems in particular emerge as one of the most important subjects of academic and industrial research. Compared to other batteries, batteries with lithium chemistry can be charged faster, provide higher power density for a longer period of time and are lightweight at the portable level. This has increased the popularity of lithium batteries in electric vehicles, storage systems or portable electrical appliances such as phones and computers.

The most important reason why non-rechargeable lithium-based chemistries generally have a much higher capacity than rechargeable chemistries is the metallic pure lithium used at the anode side of non-rechargeable batteries, as opposed to the use of lithium-aluminum alloy in rechargeable chemistries. As explained in detail in the lithium-ion

Batteries for Mobile and Stationary Storage Applications (European Union 2017) report prepared by the Joint Research Commission of the European Union, in the medium and long term, lithium-ion battery systems have to use metallic lithium as the anode. [52] Increasing energy densities and the increase in demand in this regard can only be answered by using metallic lithium. The use of metallic lithium will increase both the total load capacity in the cell and the energy and power density due to the voltage increase. In this way, the range, lifetime, etc. are extended by the battery systems.

The dendrite formation on the lithium during charging of the batteries containing pure lithium metal on the anode side is the main cause for not using the pure lithium metal in rechargeable chemistries. Dendrite formation in lithium metal can cause a decrease in battery capacity and burning or destruction of the battery during charging. Lithium dendrite formation has been the subject of intense research in recent years, but lithium dendrite formation during the charge and discharge cycles of the battery has not yet been definitively prevented. Although its industrial applicability is not yet clear, the metallic lithium Solid-State batteries that resist dendrite formation put forward by the company QuantumScape may hold promise.³

For this reason, the pre-detection of any dendrite formation that may occur in the anode of the battery is important both academically and industrially. As explained in the previous Chapter, noise measurements made on non-rechargeable lithium chemistry batteries exposed to short circuits have shown that it causes deformation in the anode of the battery and also causes an increase in the electrochemical noise of the battery. Simultaneous noise measurements were taken while charging and discharging cycles

³ <https://www.quantumscape.com/blog/solid-state-battery-landscape/>

were carried out on the anode of lithium batteries, which are prone to dendrite formation, and at the same time, simultaneous noise measurements were made using an optical microscope.

5.2 Experimental

Non-rechargeable CR2032 coin cell batteries were disassembled in glove bag which have an inert atmosphere in order to prevent the degradation of lithium due to O_2 and H_2O . Subsequently, inside the glove bag two electrode setup were constructed where lithium anode acts as the working electrode. As a counter electrode a graphite rod was used. Lithium hexafluorophosphate ($LiPF_6$) dissolved in EC/DEC used as an electrolyte in the system. The schematic representation of the setup is demonstrated in Figure 5.1 and the photograph of the setup is shown in Figure 5.1.

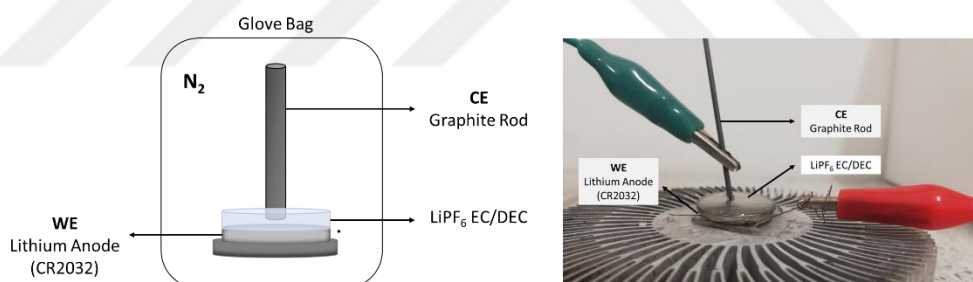


Figure 5.1 Illustration (top) and photograph (bottom) of two electrode setup; Lithium anode as working electrode, graphite rod as counter electrode.

Electrochemical Noise Measurements – Firstly, the anode of non-rechargeable CR2032 coin cell battery, which was properly discharged to 25% SOC, was used. By chronoamperometry, 3.5V of potential was applied to the working electrode, Lithium anode, in order to charge the system. At the end of the charging process electrochemical noise measurements were done as described in Chapter 2. According to the data, the anode of a battery properly discharged to 25% SOC shows noise at very low orders, a few μV , as expected. On the other hand, there is an increase in the noise levels of the anode exposed to charging for 1 hour. The electrochemical noise data taken before and after charging are shown in Figure 5.2.

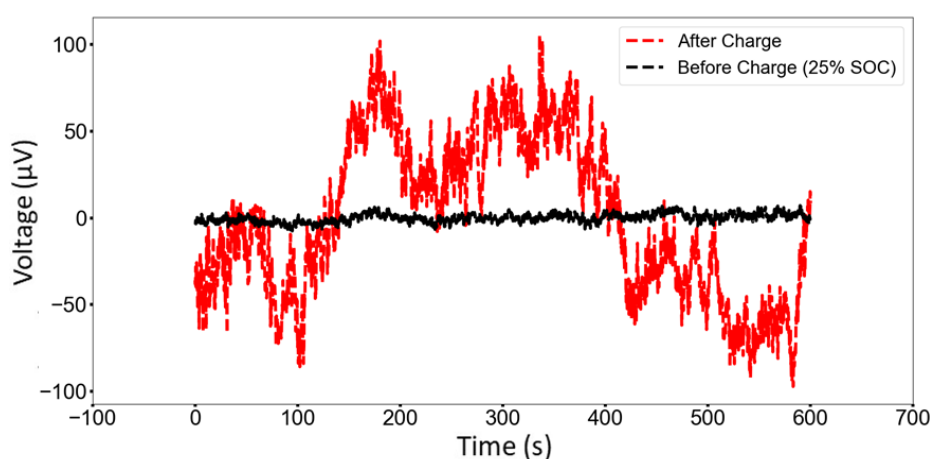


Figure 5.2 Electrochemical noise measurement of lithium anode of 25% SOC CR2032 coin cell battery before and after charge

In the second place, the anode of pristine non-rechargeable CR2032 coin cell battery was used and again by chronoamperometry, 0V of potential was applied to the working electrode, Lithium anode, for 1 hour in order to discharge the system. Then again, by chronoamperometry, 3.5V of potential which is the open circuit potential of the CR2032 coin cell battery was applied to the working electrode for 1 hour in order to charge the system. At the end of each discharging and charging processes

electrochemical noise measurements were done as described in Chapter 2. Although there is some noise increase after discharge, the most significant increase is seen after charging the anode. Electrochemical noise data taken before and after discharging and charging are shown in Figure 5.3.

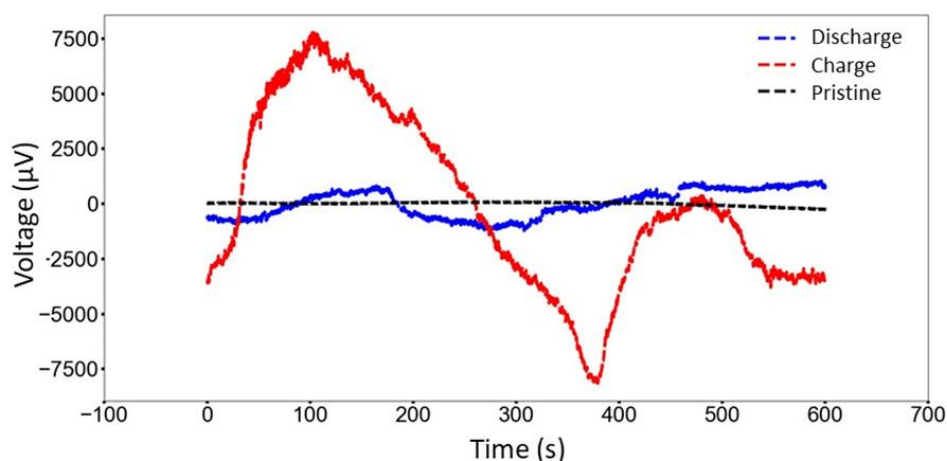


Figure 5.3 Electrochemical noise measurement of pristine, charged, and discharged lithium anode of CR2032 coin cell battery.

SEM Analysis – Lithium anodes with increased noise level after charging were examined by SEM for further analysis. (For technical details see Appendix). It is seen in SEM images that the lithium anode, which is known to have a homogeneous appearance of a pristine battery, is seriously damaged after charging. It is observed that there are occasional cracks and breaks in the SEM images taken with different resolutions and the SEM images are shown in Figure 5.4.

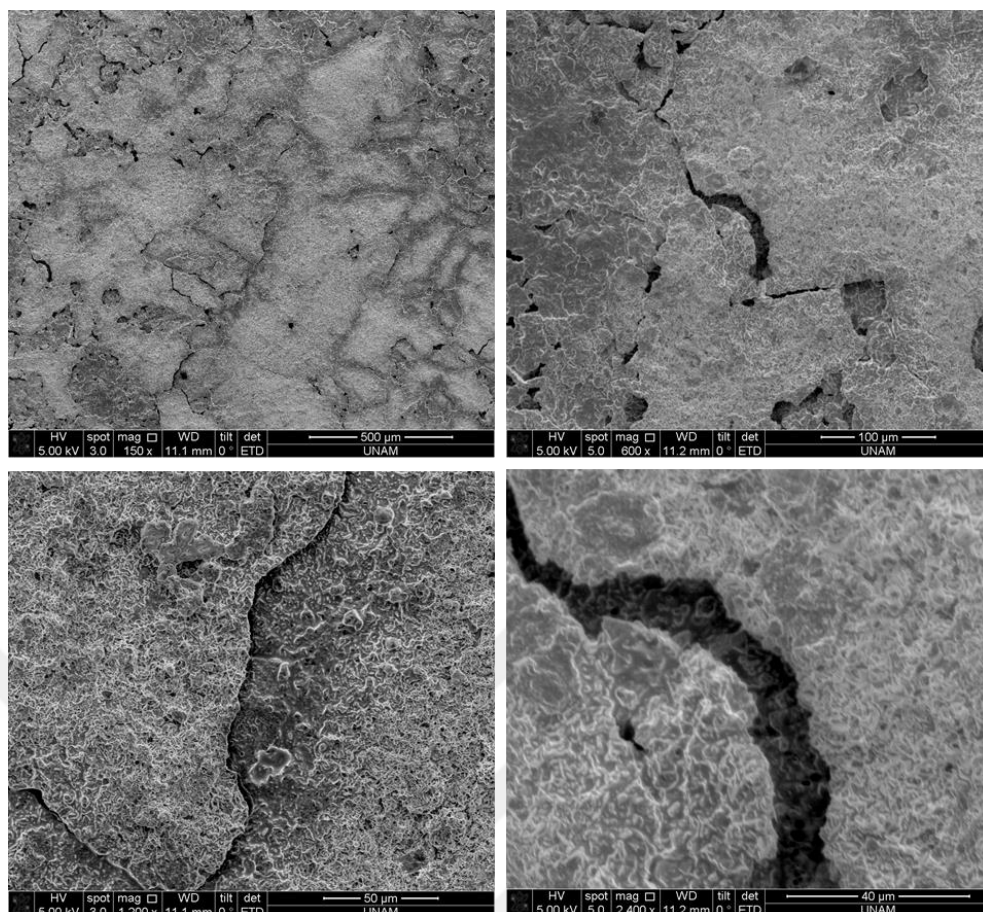


Figure 5.4 SEM images of charged lithium anode of CR2032 coin cell battery.

Optical Microscope Imaging – After the deterioration of the lithium anode after charging is shown with SEM images, an optical microscope was (for technical details see Appendix) placed in the glove bag in order to monitor the changes in the lithium anode simultaneously with the charging process, and videos were recorded during the experiment. In this case, in order for the applied current to affect the anode surface equally and for the convenience of imaging, a stainless-steel grid with a hole in the middle was used as the counter electrode instead of graphite rod. Photograph of the optic microscope and setup placed in the glove bag is shown in Figure 5.5.

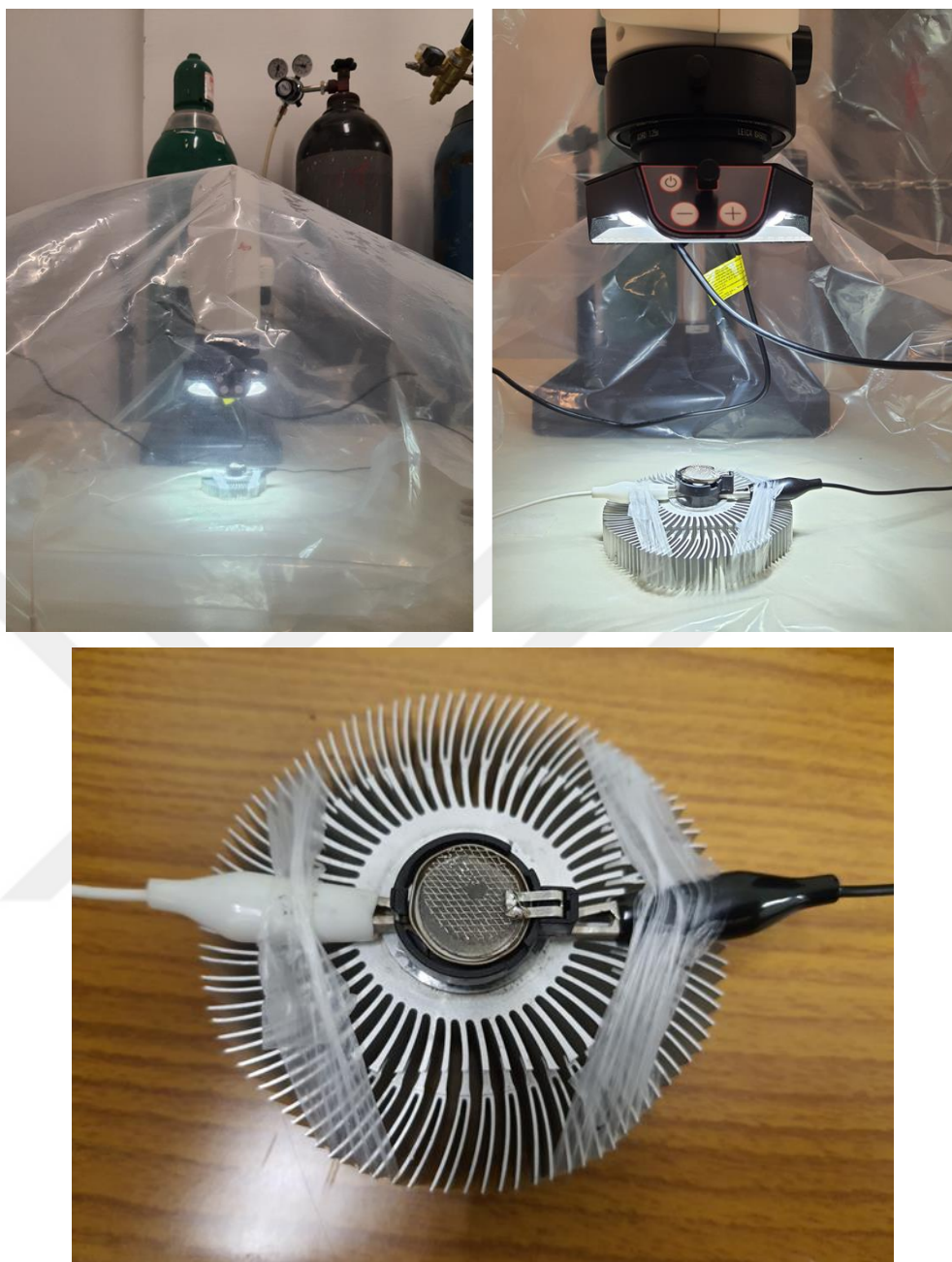


Figure 5.5 Optic microscope setup inside the glove bag (top) and the measurement setup of lithium anode with a steel mesh as a counter electrode on top of it (bottom).

5.3 Discussion and Future Work

As a result of the electrochemical noise measurements made on the anode of the non-rechargeable cr2032 batteries, it was observed that the application of the charging process in the follow-up of the discharge caused serious increases in the noise levels. While the noise levels of a pristine battery or a properly discharged battery were around a few μV , the noise levels after rapid discharge (1-hour discharge) with chronoamperometry increased to the order of 100 μV , followed by rapid charge (1-hour charge) with chronoamperometry, the noise levels increased to the order of mV. It is known that when non-rechargeable lithium batteries are charged, dendritic structures form on the lithium surface. In order to understand whether the increase in the electrochemical noise of the non-rechargeable battery after charging is due to the formation of a similar structure, the lithium surface was then examined by SEM analysis. It seems that there is serious damage to the surface of lithium, as observed in experiments on closed batteries. (See Chapter 4) Although, as anticipated, dendritic structures could not be observed in SEM images, it was shown that the change in the lithium surface was accompanied by noise increase. An optical microscope placed in the glove bag was used to view this change on the lithium surface simultaneously with the charging process. A battery holder was used to place the lithium anode in the setup created to facilitate viewing with an optical microscope. At the same time, steel mesh was preferred instead of graphite rod as counter electrode as it does not block imaging. Due to reasons such as insufficient maximum resolution of the optical microscope and contact problems caused by the battery holder, it is not possible to view the morphological changes that occur during the charging and discharging of the battery.

For this reason, a new cell is being designed in which both electrochemical measurements and simultaneous imaging can be made on the lithium anode.

5.4 Summary

After it was seen that the increase in electrochemical noise levels of lithium anode batteries exposed to short circuit was due to the morphological deterioration in the lithium anode, the electrochemical noise measurement of the lithium anode was studied. It aimed to perform both post-mortem and operando imaging, as well as electrochemical noise measurements of metallic lithium anodes, which cannot be used due to dendrite formation in rechargeable batteries despite having higher energy density. Using the anode of non-rechargeable CR2032 coin cell batteries opened in a glove bag with an inert atmosphere, the anode was first discharged and then charged, and noise measurements were recorded before and after each stage. Preliminary results indicate that upon charging significant increases in electrochemical noise can be observed, however, the monitoring via optical microscope requires further optimization and cell designing for better resolution and improved contact.

Chapter 6

6. Conclusion

Electrochemical noise measurements are widely used in the corrosion literature and noise studies have been carried out on batteries in recent years. However, it seems that noise studies on batteries are insufficient in terms of measurement methods and analysis. Therefore, in this thesis, electrochemical noise measurements of lithium-based non-rechargeable batteries are examined.

In the corrosion literature, noise is measured as current noise or potential noise, and sometimes a combination of both. More specific information about corrosion is attempted to be extracted with use of different mathematical analysis methods, which are often associated with post-mortem analyses. In addition, corrosion measurements are usually made on systems with an open circuit potential of 0V, making it easy to distinguish noise in the microvolt range. On the other hand, when considering batteries, it should first be taken into account that the battery has parameters that are difficult or impossible to predict due to its chemical and physical properties. Moreover, the presence of a DC voltage of the battery significantly complicates the detection of noise in the microvolt range and the lack of necessary parameters for post-mortem

analysis significantly reduces the number of mathematical analysis methods that can be used. Therefore, for batteries, it is important to approach with the correct measurement method and search for the source of the noise recorded before resorting to mathematical tools.

Electrochemical noise investigation of non-rechargeable CR2032 coin cell batteries were carried out under open circuit conditions with appropriate parameters. In order to eliminate the DC voltage of a battery, two batteries were connected in parallel to each other to let them equilibrate in terms of voltages and then connected in anti-serial fashion to obtain 0V. Therefore, noise measurements were done in anti-serial connection. When compared, shorted batteries show significantly higher noise levels than properly discharged ones. Before utilizing any mathematical analysis method, post-mortem analysis was used to locate the main source of the noise and disassembled batteries were analyzed by SEM and optical imaging. It has been found that, non-homogeneous depletion Lithium metal in the anode side might be associated with the increase in the noise levels.

As a control experiment, identical experiments were performed with rechargeable CR2032 batteries, and no noise increase was observed. The only difference between rechargeable CR2032 batteries and non-rechargeable CR2032 batteries is that lithium alloy is used instead of lithium metal in the anode part. The use of lithium metal creates certain morphological formations that damage the battery, such as dendrite formation during the charging of the battery. Thus, electrochemical noise measurements were done on lithium anode inside a glove bag. The main purpose was to see if there is an increase in noise after the charge of the battery. The preliminary results indicate that the charging of the Lithium anode might be the cause of significant increase noise levels and SEM images support the morphological changes on the surface of the

Lithium. Although it was aimed to capture the morphological changes occurring during the charging of the anode simultaneously with the optical microscope, it was not successful due to the electrical contact and imaging problems.



Bibliography

- [1] K. H. Na and S. Il Pyun, “Effect of sulphate and molybdate ions on pitting corrosion of aluminium by using electrochemical noise analysis,” *J. Electroanal. Chem.*, vol. 596, no. 1, pp. 7–12, 2006.
- [2] H. S. Klapper, J. Goellner, A. Burkert, and A. Heyn, “Environmental factors affecting pitting corrosion of type 304 stainless steel investigated by electrochemical noise measurements under potentiostatic control,” *Corros. Sci.*, vol. 75, pp. 239–247, 2013.
- [3] K. Sasaki and H. S. Isaacs, “Origins of Electrochemical Noise during Pitting Corrosion of Aluminum,” *J. Electrochem. Soc.*, vol. 151, no. 3, p. B124, 2004.
- [4] M. Kiwilszo and J. Smulko, “Pitting corrosion characterization by electrochemical noise measurements on asymmetric electrodes,” *J. Solid State Electrochem.*, vol. 13, no. 11, pp. 1681–1686, 2009.
- [5] Y. Hou, C. Aldrich, K. Lepkova, and B. Kinsella, “Detection of under deposit corrosion in a CO₂ environment by using electrochemical noise and recurrence quantification analysis,” *Electrochim. Acta*, vol. 274, pp. 160–169, 2018.
- [6] M. Zeidabadinejad, M. Shahidi-Zandi, M. M. Foroughi, and H. Asadollahzadeh, “Advantages of asymmetrical over symmetrical cells for detection of under deposit CO₂ corrosion using electrochemical noise,” *Mater. Corros.*, vol. 70, no. 11, pp. 1999–2008, 2019.
- [7] H. Men, J. Zhang, L. Zhang, S. Yang, and Z. Xu, “Study on Srb Induced

- Corrosion Based on Electrochemical Noise Analysis and Signal Processing,” vol. 2011, pp. 407–413, 2011.
- [8] A. M. Homborg, C. F. Leon Morales, T. Tinga, J. H. W. De Wit, and J. M. C. Mol, “Detection of microbiologically influenced corrosion by electrochemical noise transients,” *Electrochim. Acta*, vol. 136, pp. 223–232, 2014.
- [9] H. Ashassi-Sorkhabi, D. Seifzadeh, and M. Raghibi-Boroujeni, “Analysis of electrochemical noise data in both time and frequency domains to evaluate the effect of ZnO nanopowder addition on the corrosion protection performance of epoxy coatings,” *Arab. J. Chem.*, vol. 9, pp. S1320–S1327, 2016.
- [10] M. Gong, W. Zhou, MC. Tsai, J. Zhou, M. Guan, MC. Lin, B. Zhang, Y. Hu, D.Y. Wang, J. Yang and S.J. Pennycook, “Nanoscale nickel oxide/nickel heterostructures for active hydrogen evolution electrocatalysis,” *Nat. Commun.*, vol. 5, pp. 1–6, 2014.
- [11] Y. Puget, K. Trethewey, and R. J. K. Wood, “Electrochemical noise analysis of polyurethane-coated steel subjected to erosion-corrosion,” *Wear*, vol. 233–235, pp. 552–567, 1999.
- [12] D. J. Mills and S. Mabbutt, “Investigation of defects in organic anti-corrosive coatings using electrochemical noise measurement,” *Prog. Org. Coatings*, vol. 39, no. 1, pp. 41–48, 2000.
- [13] P. Kannan, T. S. Rao, and N. Rajendran, “Anti-corrosion behavior of benzimidazoliumtetrafluoroborate ionic liquid in acid medium using electrochemical noise technique,” *J. Mol. Liq.*, vol. 222, pp. 586–595, 2016.
- [14] A. Ehsani, M. G. Mahjani, M. Hosseini, R. Safari, R. Moshrefi, and H.

- Mohammad Shiri, "Evaluation of *Thymus vulgaris* plant extract as an eco-friendly corrosion inhibitor for stainless steel 304 in acidic solution by means of electrochemical impedance spectroscopy, electrochemical noise analysis and density functional theory," *J. Colloid Interface Sci.*, vol. 490, pp. 444–451, 2017.
- [15] G. Golestani, M. Shahidi, and D. Ghazanfari, "Electrochemical evaluation of antibacterial drugs as environment-friendly inhibitors for corrosion of carbon steel in HCl solution," *Appl. Surf. Sci.*, vol. 308, pp. 347–362, 2014.
- [16] V. A. Tyagai, "Faradaic noise of complex electrochemical reactions," *Electrochim. Acta*, vol. 16, no. 10, pp. 1647–1654, 1971.
- [17] W. P. Iverson, "Transient Voltage Changes Produced in Corroding Metals and Alloys," *J. Electrochem. Soc.*, vol. 115, no. 6, p. 617, 1968.
- [18] P. Iverson and F. Detrick, "Gonmuncas," pp. 617–618, 1968.
- [19] K. Hladky and J. L. Dawson, "The measurement of localized corrosion using electrochemical noise," *Corros. Sci.*, 1981.
- [20] R. A. Cottis, "Interpretation of electrochemical noise data," *Corrosion*, vol. 57, no. 3, pp. 265–284, 2001.
- [21] D.-H. Xia *et al.*, "Review—Electrochemical Noise Applied in Corrosion Science: Theoretical and Mathematical Models towards Quantitative Analysis," *J. Electrochem. Soc.*, vol. 167, no. 8, p. 081507, 2020.
- [22] Y. Hou, C. Aldrich, K. Lepkova, L. L. Machuca, and B. Kinsella, "Monitoring of carbon steel corrosion by use of electrochemical noise and recurrence quantification analysis," *Corros. Sci.*, vol. 112, pp. 63–72, 2016.

- [23] A. Aballe, M. Bethencourt, F. J. Botana, and M. Marcos, "Wavelet transform-based analysis for electrochemical noise," *Electrochem. commun.*, vol. 1, no. 7, pp. 266–270, 1999.
- [24] P. R. Roberge, R. Beaudoin, G. Verville, and J. Smit, "Voltage noise measurements on sealed leadacid batteries," *J. Power Sources*, vol. 27, no. 2, pp. 177–186, 1989.
- [25] S. Martinet, R. Durand, P. Ozil, P. Leblanc, and P. Blanchard, "Application of electrochemical noise analysis to the study of batteries: State-of-charge determination and overcharge detection," *J. Power Sources*, 1999.
- [26] D. H. J. Baert and A. A. K. Vervaet, "Small bandwidth measurement of the noise voltage of batteries," *J. Power Sources*, vol. 114, no. 2, pp. 357–365, 2003.
- [27] E. Astafev, "Electrochemical noise of a Li-ion battery during the charging process," *Instrum. Sci. Technol.*, vol. 48, no. 2, pp. 162–172, 2020.
- [28] K. F. Knott, "Measurement of battery noise and resistor-current noise at subaudio frequencies," *Electron. Lett.*, vol. 1, no. 5, p. 132, 1965.
- [29] C. K. Boggs, A. D. Doak, and F. L. Walls, "Measurement of Chemical Battery Noise," *1995 Ieee Int. Freq. Control Symp.*, 1995.
- [30] S. Martinet, R. Durand, P. Ozil, P. Leblanc, and P. Blanchard, "Application of electrochemical noise analysis to the study of batteries: State-of-charge determination and overcharge detection," *J. Power Sources*, vol. 83, no. 1–2, pp. 93–99, 1999.
- [31] S. Martemianov, N. Adiutantov, Y. K. Evdokimov, L. Madier, F. Maillard,

- and A. Thomas, “New methodology of electrochemical noise analysis and applications for commercial Li-ion batteries,” *J. Solid State Electrochem.*, vol. 19, no. 9, pp. 2803–2810, 2015.
- [32] E. A. Astafev, “Electrochemical noise measurement of a Li/SOCl₂ primary battery,” *J. Solid State Electrochem.*, vol. 22, no. 11, pp. 3569–3577, 2018.
- [33] E. A. Astafev, A. E. Ukshe, and Y. A. Dobrovolsky, “Measurement of electrochemical noise of a Li/MnO₂ primary lithium battery,” *J. Solid State Electrochem.*, vol. 22, no. 11, pp. 3597–3606, 2018.
- [34] E. A. Astafev, “Wide-frequency band measurement and analysis of electrochemical noise of Li/MnO₂ primary battery,” *J. Solid State Electrochem.*, vol. 23, no. 6, pp. 1705–1713, 2019.
- [35] A. M. Homborg *et al.*, “Transient analysis through Hilbert spectra of electrochemical noise signals for the identification of localized corrosion of stainless steel,” *Electrochim. Acta*, vol. 104, pp. 84–93, 2013.
- [36] J. Lv, Q. xian Yue, R. Ding, X. Wang, T. jiang Gui, and X. dong Zhao, “The Application of Electrochemical Noise for the Study of Metal Corrosion and Organic Anticorrosion Coatings: A Review,” *ChemElectroChem*, vol. 8, no. 2, pp. 337–351, 2021.
- [37] S. Girija, U. K. Mudali, V. R. Raju, R. K. Dayal, H. S. Khatak, and B. Raj, “Determination of corrosion types for AISI type 304L stainless steel using electrochemical noise method,” *Mater. Sci. Eng. A*, vol. 407, no. 1–2, pp. 188–195, 2005.
- [38] T. Haruna, Y. Morikawa, S. Fujimoto, and T. Shibata, “Electrochemical noise

- analysis for estimation of corrosion rate of carbon steel in bicarbonate solution,” *Corros. Sci.*, vol. 45, no. 9, pp. 2093–2104, 2003.
- [39] C. J. Park and H. S. Kwon, “Electrochemical noise analysis of localized corrosion of duplex stainless steel aged at 475°C,” *Mater. Chem. Phys.*, vol. 91, no. 2–3, pp. 355–360, 2005.
- [40] D. H. Xia *et al.*, “Identifying defect levels in organic coatings with electrochemical noise (EN) measured in Single Cell (SC) mode,” *Prog. Org. Coatings*, vol. 126, no. October 2018, pp. 53–61, 2019.
- [41] E. Astafev, “Electrochemical noise of a Li-ion battery during the charging process,” *Instrum. Sci. Technol.*, vol. 48, no. 2, pp. 162–172, 2020.
- [42] G. Karaoğlu, G. Hatipoğlu, and B. Ulgut, “Electrochemical Noise Analysis in Batteries.”
- [43] Y. Hoshi, N. Yakabe, K. Isobe, T. Saito, I. Shitanda, and M. Itagaki, “Wavelet transformation to determine impedance spectra of lithium-ion rechargeable battery,” *J. Power Sources*, vol. 315, pp. 351–358, 2016.
- [44] A. Aballe, M. Bethencourt, F. J. Botana, and M. Marcos, “Using wavelets transform in the analysis of electrochemical noise data,” *Electrochim. Acta*, vol. 44, no. 26, pp. 4805–4816, 1999.
- [45] R. A. Cottis, A. M. Homborg, and J. M. C. Mol, “The relationship between spectral and wavelet techniques for noise analysis,” *Electrochim. Acta*, vol. 202, pp. 277–287, 2016.
- [46] C. B. Uzundal and B. Ulgut, “A Method for Voltage Noise Measurement and Its Application to Primary Batteries,” *J. Electrochem. Soc.*, vol. 165, no. 11,

- pp. A2557–A2562, 2018.
- [47] C. B. Uzundal and B. Ulgut, “A method for voltage noise measurement and its application to primary batteries,” *J. Electrochem. Soc.*, vol. 165, no. 11, pp. A2557–A2562, 2018.
- [48] G. Karaoğlu, C. B. Uzundal, and B. Ulgut, “Uneven Discharge of Metallic Lithium Causes Increased Voltage Noise in Li/MnO₂ Primary Batteries upon Shorting ,” *J. Electrochem. Soc.*, vol. 167, no. 13, p. 130534, 2020.
- [49] W. Liu, D. Wang, X. Chen, C. Wang, and H. Liu, “Recurrence plot-based dynamic analysis on electrochemical noise of the evolutive corrosion process,” *Corros. Sci.*, vol. 124, no. 8, pp. 93–102, 2017.
- [50] P. R. Roberge, “Analysis of electrochemical noise by the stochastic process detector method,” *Corrosion*, vol. 50, no. 7, pp. 502–512, 1994.
- [51] J. O. Besenhard, *Handbook of Battery Materials*, 1st ed. Wiley-VCH, 1999.
- [52] I. Tsiropoulos, D. Tarvydas, and N. Lebedeva, *Li-ion batteries for mobility and stationary storage applications, JRC Science for Policy Report, EU Commission*. 2018.
- [53] G. Instruments, “Interface 5000 Potentiostat/Galvanostat/ZRA Operator’s Manual,” *ReVision*, 2015.

Appendix

A. Instrumentation

X-Ray Diffraction (XRD) – XRD characterization of samples were done by Rigaku Miniflex diffractometer, which uses a high-power Cu-K α source operating at 30 kV/15 mA and a wavelength of 1.5405 Å. Samples were placed on glass slides and sealed with Kapton tape.

Fourier Transform Infrared Spectroscopy (FT-IR) – FT-IR characterization of samples was done by Bruker Tenson 27 spectrometer. Samples were placed onto the holder of the FT-IR directly. The spectrums were taken with scan time of 64 scans and 4 cm⁻¹ resolution.

X-Ray Fluorescence (XRF) – XRF characterization of samples were done by AMPTEK EXP-1 XRF Experimenter's Kit. Samples were placed onto sample chamber directly.

Scanning Electron Microscopy (SEM) – For SEM images FEI Quanta 200 F scanning electron microscope were used. Samples were placed on aluminum sample holders.

B. Python Codes

Noise Analysis in Frequency Domain

```
import numpy as np
import scipy
from scipy import fftpack
from scipy import optimize
import glob as glob
import matplotlib.pyplot as plt
import os
```

```

import matplotlib as mpl

plt.rcParams['ytick.labelsize']=28
plt.rcParams['ytick.major.width']=4
plt.rcParams['ytick.minor.width']=4.5
plt.rcParams['xtick.labelsize']=28
plt.rcParams['xtick.major.width']=4
plt.rcParams['xtick.minor.width']=4.5
plt.rcParams['text.latex.preamble']=[r"\usepackage{amsmath}"]
mpl.rc('font', family='Arial')

def func(x,m,b):
    return m*x + b

def fft(voltage,time):
    var_fftV = {}
    var_fftFreq = {}
    for key in voltage:
        voltage_array = voltage[key]
        sampletime = time[key][2]-time[key][1]
        freqlength = int(len(voltage_array)/2)
        fftfreq_ =
    scipy.fftpack.fftfreq(len(voltage_array),sampletime)[:freqlength]
        fft_voltage =
    abs(scipy.fft(voltage_array))[:freqlength]/len(voltage_array)
        var_fftV[key] = fft_voltage[1:]
        var_fftFreq[key] = fftfreq_[1:]
    return(var_fftV,var_fftFreq)

def import_gamry(filename):
    os.chdir(filename)
    a = glob.glob('.*.DTA')
    print(a)
    var_GamryV = {}
    var_GamryT = {}
    j = 0
    for files in a:
        arrays = np.genfromtxt(files, dtype = [('T', 'f8'), ('V',
'f8'), ('I', 'f8')])
        var_GamryV[j] = arrays['V']
        var_GamryT[j] = arrays['T']
        j = j + 1
    os.chdir('..')
    return(var_GamryV, var_GamryT)

def plotting_function(var_GamryV,var_GamryT, labels,
colors,background_subtract = True):
    i = 0

    for key in var_GamryV:
        voltage = var_GamryV[key]
        time = var_GamryT[key]
        if background_subtract:
            voltage = voltage - np.mean(voltage)

        plt.loglog(time,abs(voltage*1e6), color = colors[i], label =
labels[i], lw = 4)

```

```

plt.ylabel(r'Voltage ( $\mu$ V)', fontsize = 32)
plt.xlabel('Frequency (Hz)', fontsize = 32)
plt.legend(loc = 1, fontsize= 24)
plt.tight_layout()

i = i + 1
plt.show(True)
return()

filename = ''
var_GamryV, var_GamryT = import_gamry(filename)
var_fftV, var_fftFreq = fft (var_GamryV, var_GamryT)
labels= []
colors = []

plotting_function(var_fftV, var_fftFreq, labels, colors,
background_subtract = True)

```

Noise Analysis in Time Domain

```

import numpy as np
import scipy
import glob as glob
import matplotlib.pyplot as plt
import os
import matplotlib as mpl
from matplotlib.offsetbox import AnchoredText

plt.rcParams['ytick.labelsize']=28
plt.rcParams['ytick.major.width']=4
plt.rcParams['ytick.minor.width']=4.5
plt.rcParams['xtick.labelsize']=28
plt.rcParams['xtick.major.width']=4
plt.rcParams['xtick.minor.width']=4.5
plt.rcParams['text.latex.preamble']=[r"\usepackage{amsmath}"]
mpl.rc('font', family='Arial')

global_array=[]

def func(x,m,b):
    return m*x + b

def import_gamry(filename):
    os.chdir(filename)
    a = glob.glob('.*.DTA')
    print(a)
    var_GamryV = {}
    var_GamryT = {}
    j = 0
    for files in a:
        arrays = np.genfromtxt(files, dtype = [('T', 'f8'), ('V',
'f8'), ('I', 'f8')])
        var_GamryV[j] = arrays['V']

```

```

        var_GamryT[j] = arrays['T']
        j = j + 1
    os.chdir('.')

    return(var_GamryV, var_GamryT)

def final_Voltage(var_GamryV, background_subtract = True):
    global global_array
    for key in var_GamryV:
        voltage = var_GamryV[key]

        if background_subtract:
            voltage = voltage - np.mean(voltage)
            global_array.append(voltage)

def plotting_function(var_GamryV, var_GamryT, labels,
                    colors, background_subtract = True):
    i = 0
    global global_array
    for key in var_GamryV:
        voltage = var_GamryV[key]
        time = var_GamryT[key]
        if background_subtract:
            voltage = voltage - np.mean(voltage)
            sigma_2 = np.var(voltage * 1E6)
            sigma_2 = "{:1.2e}".format(sigma_2)

        f, ax = plt.subplots(1, 1)
        plt.plot(time, voltage * 1e6, color = colors[i], label =
labels[i], lw = 4)

        plt.ylabel(r'Voltage ( $\mu V$ )', fontsize = 32)
        plt.xlabel('Time (s)', fontsize = 32)
        i = i + 1
        plt.show(True)

    return()

filename = 'Noise'
var_GamryV, var_GamryT = import_gamry(filename)

labels = []
colors = []

print(global_array)
final_Voltage(var_GamryV, background_subtract = True)
plotting_function(var_GamryV, var_GamryT, labels, colors,
background_subtract = True)

```

Recurrence Quantification Analysis (RQA)

```

import numpy as np
import pylab
import scipy.signal as signal

```

```
"""RQA Analysis"""
```

```
def integRQA(time_series, patternsiz=1):
    if len(time_series.shape)==1:
        n_time=len(time_series)
    else:
        print('multidimensional array')
        recurrence=np.zeros([n_time,n_time],dtype=np.int8)
        for j in range(n_time-patternsiz)[patternsiz:]:
            k=1
            while k<j:
                #recurrence[k-1][j]=recurrence[j][k-1]
                1]=np.dot(time_series[(k-1):(k-1+patternsiz)],time_series[j:(j+patternsiz)])
                recurrence[j][k-1]=np.dot(time_series[(k-1):(k-1+patternsiz)],time_series[j:(j+patternsiz)])
                k=k+1
            print ('creating image')
            fig= pylab.figure()

            plot=pylab.imshow(recurrence,cmap='seismic',vmax=recurrence.max(),
vmin=-1.0*recurrence.max())
            fig.colorbar(plot, format='%.1e')
            pylab.ylabel('%s point Recurrence' % str(len(time_series)))
            pylab.show()
            return (recurrence)

segmentlength = 3000
thresh = 0.5E-6
decimationfactor = 32
patternsiz=16
debug = False

for filename in glob.glob("*.dta"):
    inputfile = filename
    print (inputfile)

    inputarray = np.genfromtxt(inputfile, dtype =
[('T','f8'),('V','f8'),('I','f8')])

    if(debug):
        pylab.plot(inputarray['V'])
        pylab.show()

    downsampledinputarray =
np.zeros(int(len(inputarray['V'])/decimationfactor))

    for i in range(int(len(inputarray['V'])/decimationfactor)):
        downsampledinputarray[i] =
np.average(inputarray['V'][i*decimationfactor:(i+1)*decimationfactor
])

    if(debug):
```

```

pylab.plot(downsampledinputarray[1:],label=len(downsampledinputarray))
    pylab.legend()
    pylab.show()

    detrendedinputarray =
signal.detrend(downsampledinputarray,bp=np.arange(0,len(downsampledi
nputarray),segmentlength))

    if(debug):

pylab.plot(detrendedinputarray,label=len(detrendedinputarray))
    pylab.legend()
    pylab.show()

    RobergeArray = np.zeros(len(detrendedinputarray),dtype =
np.int8)
    for j in range(len(detrendedinputarray)):
        RobergeArray[j] = int(detrendedinputarray[j]/thresh)

    if(debug):
        pylab.plot(RobergeArray,label=len(RobergeArray))
        pylab.legend()
        pylab.show()

    recurrenceRate=integRQA(RobergeArray,patternsize)

```

Wavelet Transform

```

def func(x,m,b):
    return m*x + b

import numpy as np
from scipy.optimize import curve_fit
from scipy import signal
import pylab
import datetime
import matplotlib.pylab as plt
import matplotlib as mpl

plt.rcParams['ytick.labelsize']=28
plt.rcParams['ytick.major.width']=4
plt.rcParams['ytick.minor.width']=4.5
plt.rcParams['xtick.labelsize']=28
plt.rcParams['xtick.major.width']=4
plt.rcParams['xtick.minor.width']=4.5
plt.rcParams['text.latex.preamble']=[r"\usepackage{amsmath}"]
mpl.rc('font',family='Arial')

datalength = 3000
widthlength = 1500
widthplotlength = 375

```

```

noiseShort = np.genfromtxt('.dta', dtype =
[('T', 'f8'), ('V', 'f8'), ('I', 'f8')])
noisebat_t = np.genfromtxt(r'.dta', dtype =
[('T', 'f8'), ('V', 'f8'), ('I', 'f8')])

popt, pcov = curve_fit(func, noisebat_t['T'], noisebat_t['V'])
noisebat_subtracted = np.zeros(len(noisebat_t))
for i in range(len(noisebat_t)):
    noisebat_subtracted[i] = noisebat_t['V'][i] -
popt[0]*noisebat_t['T'][i] - popt[1]

print (datetime.datetime.now())
batCWT = signal.cwt(noisebat_subtracted[:datalength], signal.ricker,
np.arange(1, 1+widthlength))
print (datetime.datetime.now())
backgCWT = signal.cwt(noiseShort['V'][:datalength], signal.ricker,
np.arange(1, 1+widthlength))
print (datetime.datetime.now())

pylab.subplot(121)
plot = pylab.imshow(backgCWT[:widthplotlength, :], extent=[-
(1/500.0)*datalength/2.0, (1/500.0)*datalength/2.0,
(1/500.0)*widthplotlength, (1/500.0)], cmap='seismic', interpolation
= 'None', aspect='auto', vmax=batCWT[:widthplotlength, :].max(),
vmin=batCWT[:widthplotlength, :].min())
pylab.xlabel('Shift(sec)', fontsize=32)
pylab.ylabel('Width(sec)', fontsize=32)
pylab.colorbar()

pylab.show()

```