

IMPEDANCE BASED MODELING OF BATTERY PARAMETERS AND BEHAVIOR

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IMPEDANCE BASED MODELING OF BATTERY PARAMETERS AND BEHAVIOR

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July 2017

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ABSTRACT

IMPEDANCE BASED MODELING OF BATTERY PARAMETERS AND BEHAVIOR

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Modeling battery performance under arbitrary load has gained importance in recent years with the increasing demand on batteries in various fields from automotive industry to consumer electronic devices. Due to numerous application areas of electrochemical energy storage (EES) systems, researchers have tried to predict the battery performance and the voltage using extensive calculations. Unfortunately, in order to achieve high levels of accuracy, the model has to be algebraically and computationally complex. Models with decreased computational and algebraic complexity suffer from loss of accuracy.

In this thesis, we offer a new modeling approach to predict the voltage responses of batteries and supercapacitors which is both algebraically straightforward and yielding more accurate results. Our approach is valid using any discharge profile including published by regulatory bodies such as Environmental Protection Agency (EPA).

Our method is based on Electrochemical Impedance Spectroscopy (EIS) measurements done on the system to be predicted and slow DC discharge. EIS data is used directly to predict the fast moving portion of the voltage response to the profiles. The EIS data is used as is, namely, in frequency domain without any modeling. The slow DC discharge data provides DC response and is added in through a straightforward lookup table. This widely applicable approach can predict the voltage with less than 1% error, without any adjustable parameters to a large variety of discharge profiles.

Keywords: Electrochemical Impedance Spectroscopy, Battery Modeling, Battery, Supercapacitor

ÖZET

BATARYA KARAKTERİSTİK ÖZELLİK VE DAVRANIŞLARININ EMPEDANS TEMEL ALINARAK MODELLENMESİ

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Otomotiv endüstrisinden tüketici elektroniğine kadar çeşitli alanlarda pillere olan talebin artması ile pil performansının herhangi bir yük altında modellenmesi son yıllarda önem kazandı. Elektrokimyasal enerji depolama (EES) sistemlerinin çok sayıda uygulama alanı nedeniyle, araştırmacılar kapsamlı hesaplamaları kullanarak pil performansını ve voltajını tahmin etmeye çalışıyorlar. Ne yazık ki, yüksek düzeyde doğruluk elde etmek için modelin cebirsel ve hesaplama açısından karmaşık olması gerekir. Azalan hesaplama ve cebirsel karmaşıklığı olan modellerde doğruluk kaybı yaşanır.

Bu tezde hem piller hem de süperkapasitlerdeki gerilim tepkilerini öngörmek için cebirsel açıdan basit ve daha doğru sonuçlar veren yeni bir modelleme yaklaşımı

sunuyoruz. Yaklaşımımız, Çevre Koruma Ajansı (EPA) gibi düzenleyici kurumlar tarafından yayınlanan herhangi bir deşarj profili için geçerlidir.

Yöntemimiz, tahmin edilecek sistem üzerinde yapılan Elektrokimyasal Empedans Spektroskopisi (EIS) ölçümlerine ve yavaş DC deşarjına dayanmaktadır. EIS verileri, profillere voltaj tepkisinin hızlı hareket eden bölümünü tahmin etmek için doğrudan kullanılır. EIS verileri olduğu gibi, yani herhangi bir modelleme olmaksızın frekans alanında kullanılır. Yavaş DC deşarj verileri DC yanıtı sağlar ve basit bir arama tablosu aracılığıyla eklenir. Bu yaygın uygulanabilir yaklaşım, büyük bir aralıktaki deşarj profilleri için herhangi bir ayarlanabilir parametre olmaksızın, % 1'den daha az hatayla gerilimi öngörebilir.

Anahtar Sözcükler: Elektrokimyasal Empedans Spektroskopisi, Batarya Modellemesi, Batarya, Süperkapasit

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List of Abbreviations

350F: Supercapacitor (having 350 F capacitance)

A.C.: Alternating Current

CAFE: Corporate Average Fuel Economy

Cdl: Double layer capacitor

D.C.: Direct Current

EDLC: Electrical Double Layer Capacitor

EIS: Electrochemical Impedance Spectroscopy

EPA: Environmental Protection Agency

ESS: Energy Storage System

FFT: Fast Fourier Transform

FUDS: Federal Urban Driving Schedule

HDDUDS: Heavy-Duty Dynamometer Urban Driving Schedule

Highway-FET: Highway Fuel Economy Test

iFFT: inverse Fast Fourier Transform

IHP: Inner Helmholtz Plane

KK: Kramers-Kronig

LFP: Lithium Iron Phosphate (LiFePO_4)

NiCd: Nickel Cadmium

NiMH: Nickel Metal Hydride

OCP: Open Circuit Potential

OHP: Outer Helmholtz Plane

R_{ct}: Charge-transfer resistance

R_S: Uncompensated Solution Resistance

SEI: Solid Electrolyte Interface

SOC: State-of-charge

SVD: Singular Value Decomposition

ZW: Warburg impedance

Chapter 1

1. Introduction

1.1. Energy Storage Systems

The main question of any energy related discussion is how the continuously rising global energy need will be fulfilled. It is a clear fact that in the 21st century the energy demand is much more increased with new improvements in technology [1]. From industry to households, large amount of power is used in almost every point of daily life for extended periods of time. Since the industrial revolution, the highest portion of the pie chart that indicates the distribution of the energy supply by different energy sources belongs to fossil fuels. The major fossil fuels are petroleum, coal, and natural gas. According to Key World Energy Statistics published by the International Energy Agency (an autonomous body within the OECD) in 2016, fossil fuels are responsible for supplying about 81 % of the world's energy demand [2]. Certainly, the benefits of fossil fuels like being easy-to-find, efficient, easier-to-transport, and easy-set-up are

why they have been dominant sources for energy supply. However, the drawbacks such as environmental degradation (i.e. global warming due to released carbon dioxide resulting from the burning of fossil fuels), finite energy sources, and a threat to public health due to pollution are the main reasons why new energy sources are sought after today for meeting world's energy demand. Besides, its fluctuating cost as a consequence of either physical conditions or political reasons in the world hinders that countries all over the world to evenly access it. This is another important reason that boosts the search of new energy sources.

As alternatives to fossil fuels, renewable energy sources such as sunlight, wind and hydro power has been indicated since they are only as finite as the sun and they mitigate carbon emissions. Nonetheless, they possess their own shortcomings. Their energy production and efficiency are controlled by external, natural and unpredictable factors [3]. Specifically, climate occurrences such as slow wind and abundant rain cause the energy production to decrease. Since renewable energy sources are not available in all locations in the world and their energy output is generally lower than comparable sized fossil fuel installations, energy generated by renewable sources tends to be stored for later use (i.e. when energy sources are in less productive time). This is where Energy Storage Systems (ESS), along with Energy Conversion Systems (ECS) are of utmost importance. Energy storage means storing produced energy to use when needed whereas energy conversion is the process of converting the energy produced from one form to another. Since energy storage systems are limited and variable in terms of their reliability, stability and reproducibility, converting the form of energy that is produced into a form that is storable with greater efficiency and lower losses is desirable.

ESS are classified according to form of energy that is stored. Some examples are mechanical, electrochemical, chemical, and electrical [4]. The ESS that are related to the present work are electrical and electrochemical energy storage systems. Basically, in the latter one electrochemical processes and interfaces such as redox reactions or electrochemical double layer are used in order to store energy whereas in the former one energy storage is done electrically without a chemical reaction. Batteries are one of the members of electrochemical energy storage systems while an example of electrical energy storage is supercapacitors [4].

1.2. Batteries

Battery is the main electrochemical energy storage system that is a series or parallel connection of electrochemical cells containing a positive and a negative electrode separated by an electrolyte. It can store electrical energy in the form of chemical energy during charge and transform that chemical energy back into electricity during discharge. Battery electrodes comprise of an active material and a current collector. Designation of battery electrodes can often cause confusion. In conventional way of battery design, the negative electrode is named as anode and the positive electrode is called cathode. Considering the electrochemical reactions, of course, these nomenclatures are only valid for discharge process. Fig. 1.1 indicates the traditional way of battery and electrodes nomenclature during discharge (supplying load) and charge (connected to a power supply) [5].

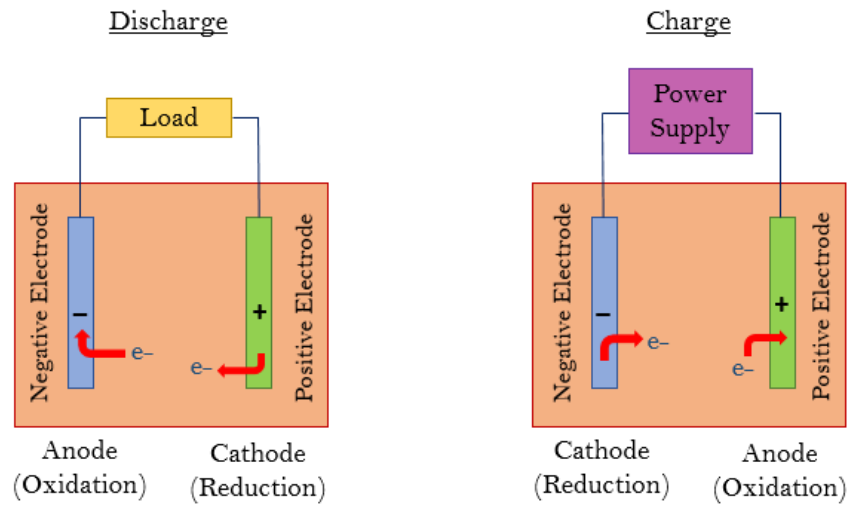


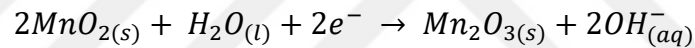
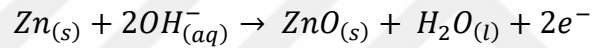
Fig. 1. 1: Conventional way of battery and electrodes nomenclature.

During discharge, oxidation which is an anodic process takes place at the negative electrode while reduction which is a cathodic process occurring at the positive electrode. During charge the electrochemical reactions are reversed: reduction occurs at the negative electrode and oxidation at the positive electrode. Thus, it is clearer and more accurate to use negative and positive electrode terms instead of naming electrodes as the anode and cathode.

The active layer of the battery electrode takes the main part in the reactions. The active layer is coated on the current collector and oxidized or reduced during the discharge and charge processes. Since the reactions for both sides of the battery electrodes occur at the interface of the electrode and the electrolyte, high surface areas are of great benefit. Therefore, porous materials are used as active ingredients as well as conductive matrices. These porous materials have to be connected to the external circuit through a wire. This connection is generally achieved using a current collector. Current collector is generally a metal that carries current efficiently in and out of the

electrode. Another function of the current collector is to serve as the mechanical support for the active material mixture.

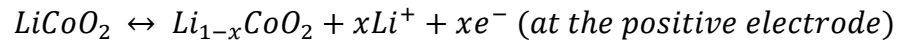
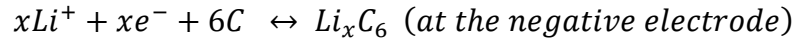
Batteries can be classified as primary and secondary batteries. This classification is based on the ability of the battery to be recharged. Primary batteries are non-rechargeable batteries. These batteries work in only one direction, which is discharge. They can be used once until they totally discharge. An example of the primary batteries is commonly used alkaline batteries (Zinc/Manganese dioxide). In the alkaline battery, the negative electrode is Zn and the positive electrode is MnO₂ and the electrolyte of the cell is potassium hydroxide (KOH). The reactions taking place in the cell:



Applying current in reverse direction, namely, trying to charge the battery can result in several problems in the alkaline battery such as irrecoverable changes in the reactants, gas formation in the electrolyte and damaging the separator. When the alkaline battery discharges, Zn is dissolved, however, the current in reverse direction cannot deposit Zn back onto the negative electrode evenly. Besides, electrolyzing the electrolyte, gas formation, which can damage the separator and the whole process, can be observed. Thus, these problems cause the reactions not to be reversible, and Zn/MnO₂ cell is considered to be a primary cell, namely a non-rechargeable cell.

On the other hand, secondary batteries are called rechargeable batteries and they can be utilized multiple times through external charging even if they get discharged. Lithium-ion and Nickel-Metal Hydride batteries are two examples of the secondary batteries. In Li-ion batteries, the negative electrode is a graphitic carbon and its current

collector is aluminum while the positive electrode is a Li-intercalation compound (i.e. LiCoO_2) and its current collector is copper [6]. The chemical reactions that occur at the electrodes during charge and discharge are shown below:



Here, the products of the reactions are deposited back onto electrodes, and the original reagents are obtained during the charging process. Thus, the reactions are reversible and the Li-ion batteries are considered to be secondary batteries.

1.3. Supercapacitors

Supercapacitors are an example of electrical energy storage systems. Supercapacitors are electrical storage devices that can store and release large amount of electrical charge quickly. They are the latest generation capacitors which build upon electrostatic and electrolytic capacitors. Capacitors can be categorized based on the mechanisms used to store electrical charge [7]. First generation capacitors, which are electrostatic capacitors, comprise two parallel metal electrodes and a dielectric that separates electrodes as in Fig. 1.2.

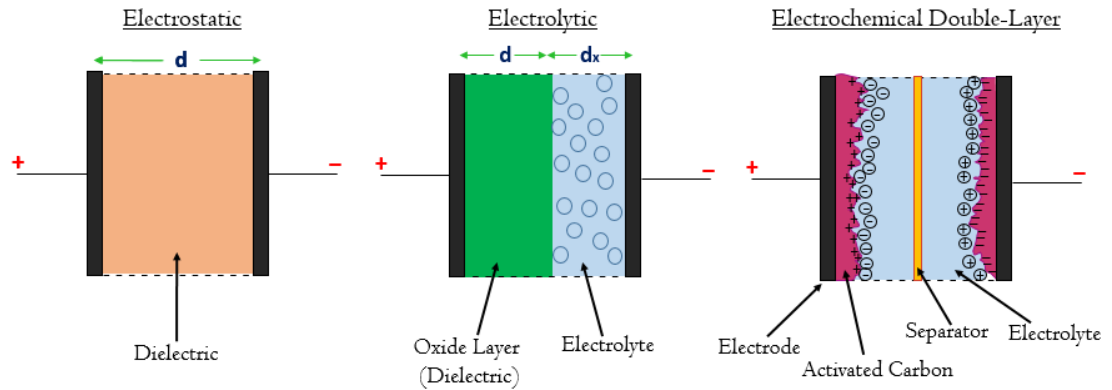


Fig. 1. 2: Schematic representation of electrostatic capacitor, electrolytic capacitor and electrochemical double-layer capacitor.

The dielectric is a non-conducting material interpolated between the parallel metal electrodes and boosts the overall capacitance, namely the ability to store electric charge [7]. The electrolytic capacitors have similar structure except possessing a conducting electrolyte between the electrodes (see Fig. 1.2) and very thin oxide layer coated on the electrodes acts as a dielectric and enables to have a higher capacitance per unit volume [7].

Supercapacitors or electrochemical double-layer capacitors have capacitances that are much higher compared to conventional capacitors (electrostatic and electrolytic capacitors) and hold out much higher power density than batteries [8]. As a construction they consist of parallel electrodes, electrolyte and a separator as in Fig. 1.2. The electrodes have activated carbon coated on them. This porous layer offers the electrodes to get a higher surface area that enables them to store much more electric charge. An ion-permeable membrane separates the two electrodes and makes ionic charge transfer possible. One more advantage of the membrane is to prevent electrical contact between the two electrodes from occurring. Then, all system is soaked in an electrolyte that might be of organic, aqueous or solid state type in accordance with

power required in applications [9]. During charging, positive charges are collected on the surface of one plate and negative charges form on the surface of the other plate. At the same time, an opposite charge emerging from ions in the electrolyte forms both side of the separator. Thus, this creates an electric double-layer inside the supercapacitor. That's why supercapacitors are also named as electrical double-layer capacitor (EDLC) or double-layer capacitors. With the porous surface, the surface area of the plates (i.e. the effective surface area between the electrode and the electrolyte) is increased and with the double layer structure, the effective distance gets lower between the plates (i.e. charge layers) in supercapacitors. Therefore, much more electrical charge can be stored in supercapacitors than ordinary capacitors.

1.4. Impedance

Impedance (Z) can be simply described as an opposition to the flow of alternating current of an electric circuit or circuit component. Impedance exists in all circuits and in all components. In ideal cases, it follows Ohm's Law, as well, thus, it is simply the ratio of voltage to current. However, it is a two-dimensional complex quantity composing resistance as its real part and reactance as its imaginary part. The real part represents its resistive part whereas the imaginary part represents the capacitive and inductive parts. Comprehending resistance and reactance makes better understanding of impedance concept convenient.

The idea of simple direct current electrical resistance (R) is straightforward to follow for researchers of all fields. Essentially it is the ability of a circuit component to oppose the flow of electrical current, more specifically Direct Current (DC). DC means that

current flows steadily in one direction, on the other hand, Alternating Current (AC) is a current which reverses its direction periodically, namely AC oscillates back and forth. Fig. 1.3 indicates the direction of current flow in a circuit when the circuit is powered by a DC supply or an AC supply.

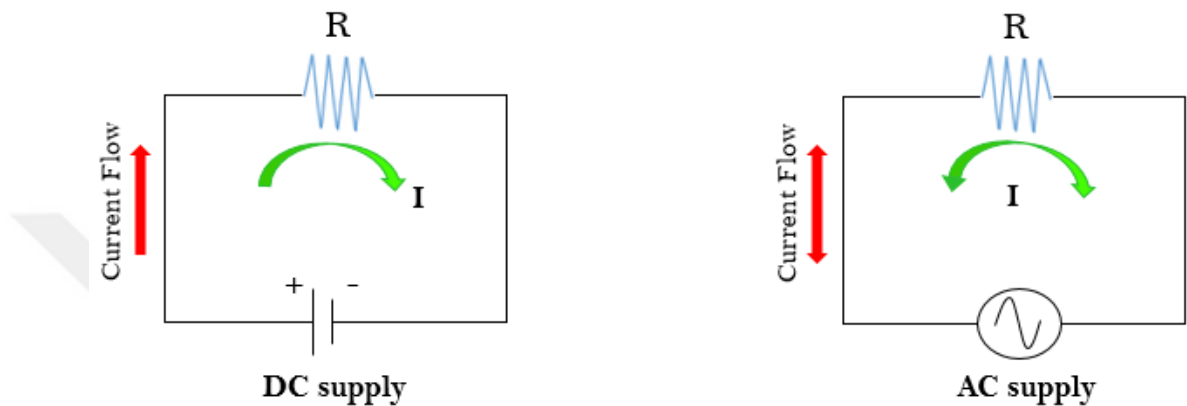


Fig. 1. 3: Representation of direction of current flow in a circuit with DC supply and AC supply. R corresponds to a resistor.

It is assumed that DC supply provides a constant voltage over time. In the voltage versus time graph, constant voltage is observed as in Fig. 1.4. However, in actuality, charge of the supply, generally a battery, will be gradually lost and of course, voltage drop will be observed as long as the battery is used.

In AC supply since current alternates periodically, which is generally fifty or sixty times every second (50 – 60 Hz) in power outlets of houses, voltage also reverses its direction along with the current. Figure 4 also indicates voltage response of resistance against AC in the form of sine wave which is the most common type of AC.

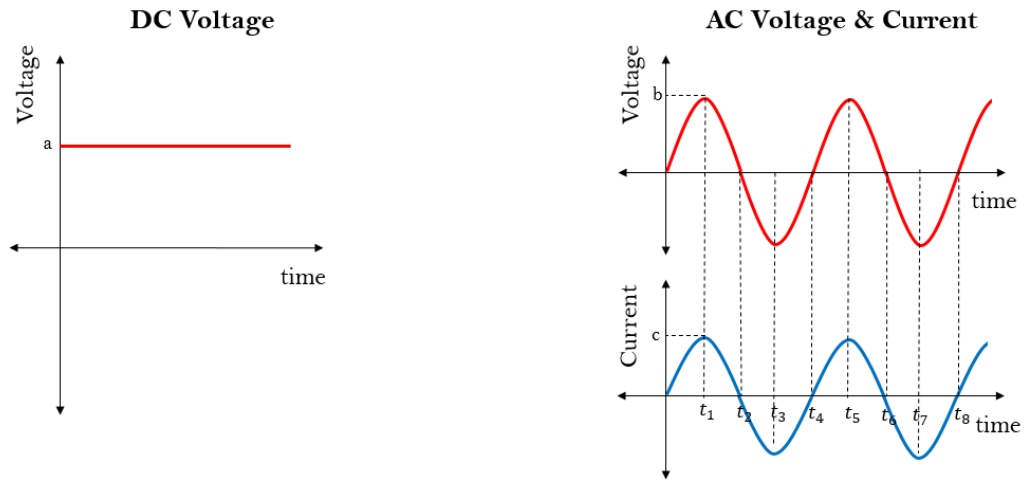


Fig. 1. 4: Voltage response of resistance against DC and voltage response of resistance against most common type of AC which is sine wave

When AC goes through a resistance, waveforms of both voltage and current are in-phase, namely, both reach their maximum value at the same moment and get through zero at the same moment (see Fig. 1.4). Mathematically, phase difference equals zero ($\phi = 0$). Resistance exists prominently in resistors and it is independent of frequency.

Reactance (X) is a form of opposition to flow of current, as well. The main feature of reactance that differs from resistance is to have a particular phase angle between voltage and current responses. Reactance is present most notably in capacitors and inductors. When AC passes through a pure reactance (i.e. an ideal capacitor or inductor), the current waveform is 90 degree out of phase with the voltage waveform as it is seen in Fig. 1.5. More specifically, voltage of a capacitor (V_C) lags the current by 90° and voltage of an inductor (V_L) leads the current by 90° . To cite an example, when a capacitor is fully charged meaning the voltage waveform reaches its maximum value, the current waveform go through zero because no more current is required to

flow at this point. Similarly, during discharge, voltage value goes to zero whereas current reaches its maximum.

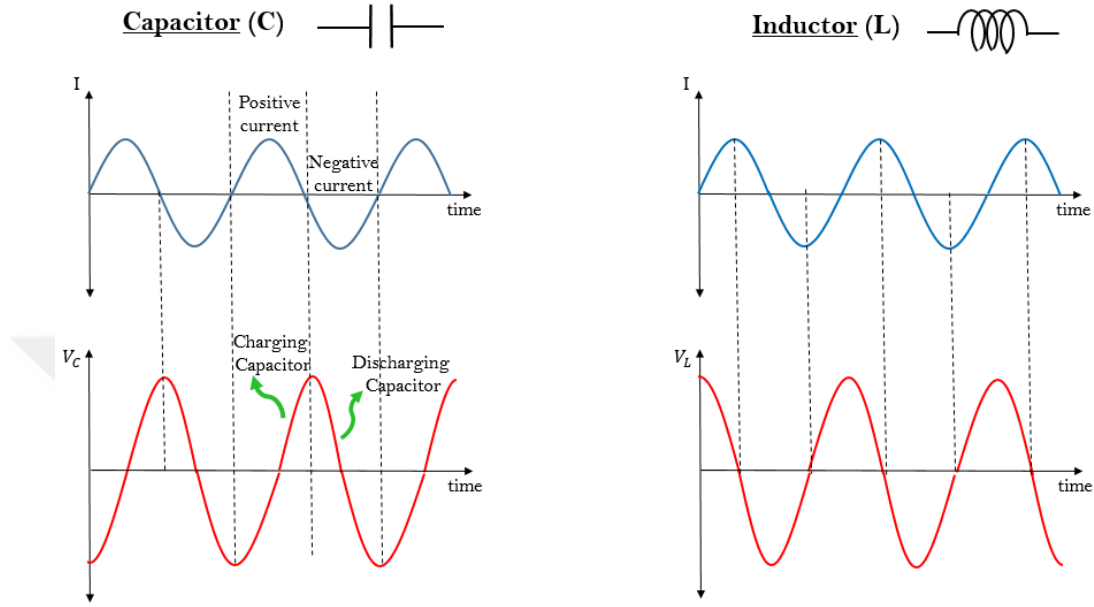


Fig. 1. 5: Current vs Time and Voltage vs Time graphs of both capacitor and inductor

Reactance existing in capacitors is called capacitive reactance (X_C) and similarly, reactance that resides in inductors is designated as inductive reactance (X_L). Both vary with frequency (f). As f increases, X_C decreases and X_L increases since X_C and f have an inversely proportional mathematical relationship whereas X_L is directly proportional with f as these can be seen in Eq. (1.1) and (1.2).

$$X_C = \frac{1}{2\pi f C} \quad (1.1)$$

$$X_L = 2\pi f L \quad (1.2)$$

where C is capacitance in Farads (F) and L is inductance in Henrys (H).

In general, combination of these two, namely ohmic resistance and capacitive/inductive reactance, forms impedance (Z). Of course, impedance of a

resistor has only real part, thus, mathematically impedance equals resistance ($Z = R$). Moreover, impedance of a capacitor or an inductor has only imaginary part and, hence, it equals capacitive or inductive reactance, respectively ($Z = X_C$ or $Z = X_L$).

Impedance is represented in both Cartesian form and polar form. Cartesian form as in Eq. (1.3) makes addition and subtraction of impedance convenient whereas the polar form in Eq. (1.4) clearly indicates its magnitude and phase shift and also, it is more convenient when it is needed to multiply or divide impedance.

$$Z = R + j * X \quad (1.3)$$

$$Z = Z_0 * \exp(j * \phi) = Z_0 * (\cos\phi + j * \sin\phi) \quad (1.4)$$

where R is resistance, j represents imaginary unit ($\sqrt{-1}$), X is reactance, Z_0 is magnitude of Z and ϕ represents phase shift between voltage and current. Impedance measurement can be represented with two types of plots as it can be seen in Fig. 1.6.

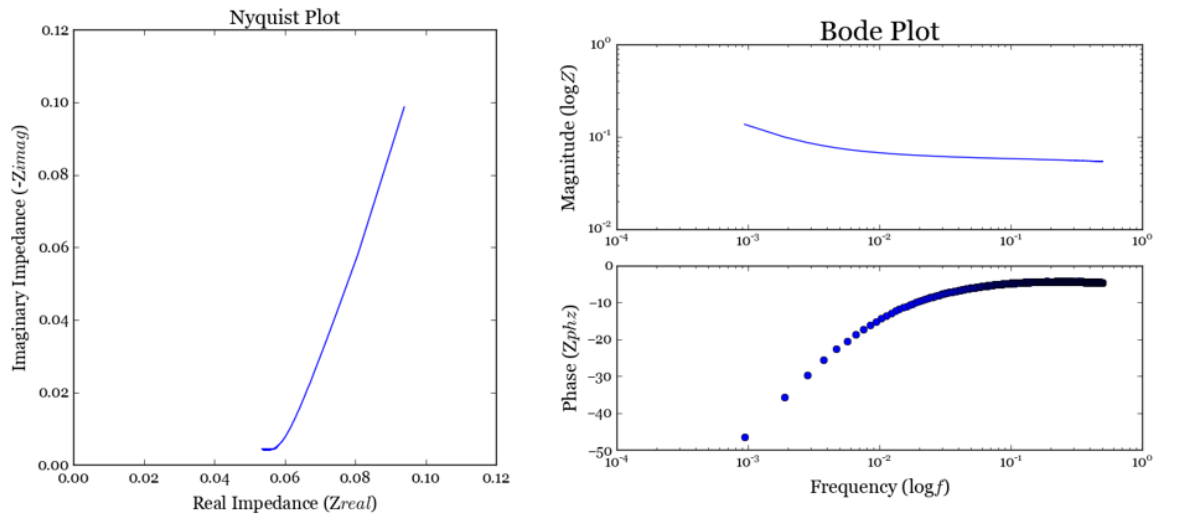


Fig. 1. 6: Representations of Impedance as Nyquist and Bode Plots (These data belongs to a NiMH battery)

One of them is a complex plane plot which indicates the real part on the x -axis and the imaginary part on the y -axis [10]. It is called “*Nyquist Plot*”. It possesses a special feature that 1 cm corresponds to particular Ohm value on both x and y -axis. A disadvantage of this plot is that frequency values cannot be seen unless it is assigned on the curve. It can only be predicted that the high frequency side is the left of the plot and the low frequency side is the right of the plot. The other type is “*Bode Plot*” which includes two plots [10]. They are magnitude of impedance versus corresponding frequency values in logarithmic scale ($\log Z_0$ vs $\log f$) and phase shift versus logarithmic frequency (ϕ vs $\log f$). A disadvantage of the Bode Plot is that it is logarithmic.

1.4.1. Electrochemical Impedance Spectroscopy and Its Applications

Impedance is frequency dependent and measured as a function of the frequency of the AC source. Electrochemical Impedance Spectroscopy (EIS) is a technique where impedance of an electrochemical system is measured vs. frequency. This technique studies the response of the electrochemical system to an applied electrical perturbation, namely potential or current, which is periodical small amplitude AC signal [11].

EIS provides a large amount of information although it cannot answer all questions. In batteries and supercapacitors, EIS is routinely utilized to examine the electrode kinetics and reactions taking place there [12] and to determine capacitance and resistance [10]. It has many applications including interfacial processes such as redox reactions at electrodes, adsorption and electrosorption; geometric effects such as linear, spherical, cylindrical mass transfer and determination of solution resistance;

and applications in power sources such as corrosion, coatings and paints, electrocatalytic reactions and sensors [10].

Examining EIS data enables resolution of the nature of the electrode kinetics and its distinctive parameters. To perform the analysis correctly, an appropriate model is required. This is done using equivalent circuit analysis which consists of simple electrical circuit elements such as resistor, capacitor and inductor in series or parallel. Fig. 1.7 indicates an electrified interface and its corresponding electrical circuit model which is well-known Randles Circuit [13]. Each component on the interface is represented by a particular electrical circuit element. More specifically, lining up of the counterions along the surface and the negatively charged electrode display capacitor like behavior, namely electrochemical double layer, thus, this behavior is expressed as C_{dl} in the equivalent circuit model [14].

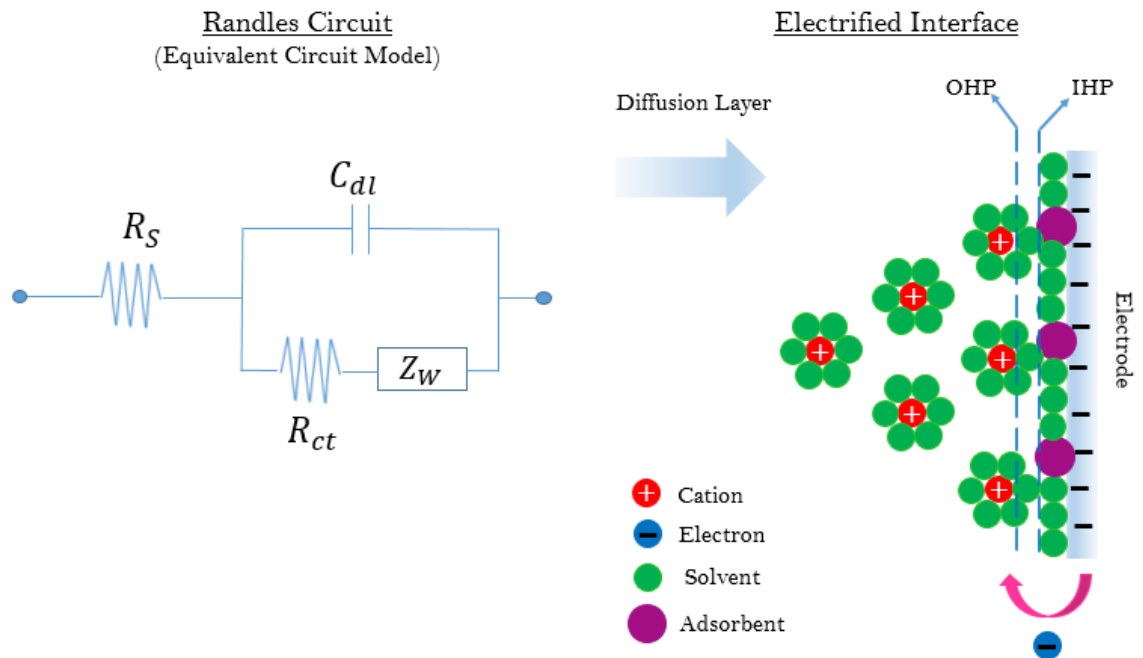


Fig. 1. 7: Electrified Interface and its equivalent circuit model, namely, Randles Circuit. R_s : Uncompensated Solution Resistance, R_{ct} : Charge-transfer resistance, C_{dl} : Double layer capacitor, Z_w : Warburg impedance, OHP: outer Helmholtz plane, and IHP: inner Helmholtz plane).

Any charge transfer between electrode and electrolyte due to an electrochemical reaction such as electrochemical dissolution of the electrode into the electrolyte forms resistance and is represented by a resistor as R_{ct} . Diffusion of reactant in the electrode or mass transport effect can create impedance and it is expressed as Warburg impedance, Z_w . Lastly, the uncompensated solution resistance or electrolyte resistance is represented by a resistor called R_s . The charge transfer resistance (R_{ct}) and Warburg impedance (Z_w) are connected in series and the capacitor (C_{dl}) is connected to them in parallel. The circuit is completed by connecting the electrolyte resistance (R_s) in series to all of them. The simplified version of Randles circuit does not cover Z_w and its Nyquist plot is always a semicircle. The Z_w appears as like a straight, 45° line at the low frequency side of the Nyquist plot. The intercept of the semicircle on the real axis at the high frequency side, which is near the origin of the plot, gives the R_s value whereas the other intercept at the low frequency side shows the sum of R_s and R_{ct} . Thus, the diameter of the semicircle gives the exact R_{ct} value. Randles circuit is a simple yet fundamental example of equivalent circuit models, but different battery systems can be adapted different types of electrical circuit.

In general, the frequencies used are limited by the stability of the system in low frequency end and the response time of the electrode double layer capacitance in the high frequency end. The EIS frequency range has a broad spectrum, namely, from as low as 10 μ Hz for sufficient resolution of interfacial processes, up to 10 MHz or higher, sometimes needed to portray bulk response of the material of interest [15]. This gives the technique its unique ability to resolve effects that are widely varying in time-scales. As a simple example, impedance of a Li-ion battery had been measured by Osaka et.al. in the frequency range of 100 kHz to 0.1 mHz (corresponds to 10 μ s to 10000 s $\sim$ 3 h)

in order to separate and analyze each elemental processes taking place in the battery [16]. Moreover, to date, many research concerning correlation between EIS and material investigation has been published. More precisely, EIS permits the dynamics of the each basic process of the battery reactions to be delicately and separately examined and it does not distract the cell during the measurement [16]. For instance, as regards lithium-ion battery studies, the charge transfer resistance, solid electrolyte interface and the activation energies of the system such as carbonaceous materials [17] [18], silicon nanowire [19], Si-OC composite [20] for the negative electrode have been characterized by using EIS [16]. Moreover, the impedance response of an entire Li-ion battery consists of the response of the positive and negative electrodes, and the electrolyte with separator [16]. The fundamental processes that are presumed to have an impact on the impedance response are electron migrations in a conductive additive [21] and at interface of active material/current collector [22], charge transfer processes, a solid state diffusion consists of finite length Warburg [23] [24]. It is possible to distinguish the response of the two electrodes and the electrolyte with separator, at which these fundamental processes take place, from the impedance response of an entire Li-ion battery by introducing a reference electrode to the cell or using a symmetric or temperature-controlled cell [16].

On top of that, enlargement of the small impedances and shifting of the overlapping frequency domains so as to accurately examine lithium batteries with low impedance are of the view as other possible methods [16]. The resistance and interfacial capacitance values are the principle electrochemical parameters examined in EIS-based investigations [16]. In the literature, increase in the resistance of Li-ion batteries at low temperatures have been revealed since there is a strong inverse relationship

between the mass transfer of charged carriers and temperature [25] [26]. Hence, expanding of the impedance of Li-ion battery by decreasing temperature has been studied by Osaka et al. to differentiate between the responses of the fundamental steps in a Li-ion battery, and thus, impedance data had been acquired in the -20 and 20°C temperature range [16]. Based on the findings belonging to Osaka et al. the frequency domain of solid-electrolyte interface (SEI) impedance response had been discovered to overlap with that of the inductive segment of the external electric lead at 20°C, that's why, it has been concluded that impedance measurements at low temperature are thought to be advantageous for determination of the SEI contribution to Li-ion battery reactions [16].

Aside from the usage of EIS to research and analyze corrosion of metals, adsorption and desorption to electrode surface, the electrochemical synthesis of materials, the catalytic reaction kinetics, the ions mobility in energy storage devices such as batteries and supercapacitors, and battery modeling [27] etc., it has gained more popularity in recent years in a wide variety of application areas such as dental application based on an observation of demineralization of human dentine by acid [28], biosensor application based on detection of tumor necrosis factor [29], and immunosensor application based on detection of HbA1c, the main diabetes marker protein [30], etc.

1.4.2. Time domain, Frequency domain and Fourier Transform

Time (t) domain and frequency (f) domain analyses are terms related frequently to the investigation of signals and systems. Basically, both are alternative ways for representing signals. Time domain is an analysis of signal versus time. In a t-domain graph such as how a signal changes with respect to time, namely amplitude of the

signal is seen. Frequency domain is an analysis of signal over frequency. An f-domain graph indicates how much of the signal exists within each given frequency band over a range of frequencies. Also, it can give information about the phase shift of the signal. The graphs on the left in Fig. 1.8 indicates two different sine waves with particular frequencies in time domain. It gives information about their amplitude and shape of the signals. The graphs on the right in Fig. 1.8 tell how these two sine waves look like in frequency domain. It gives their position in the frequency axis which are 4 and 12 Hz, respectively, and their amplitude, as well.

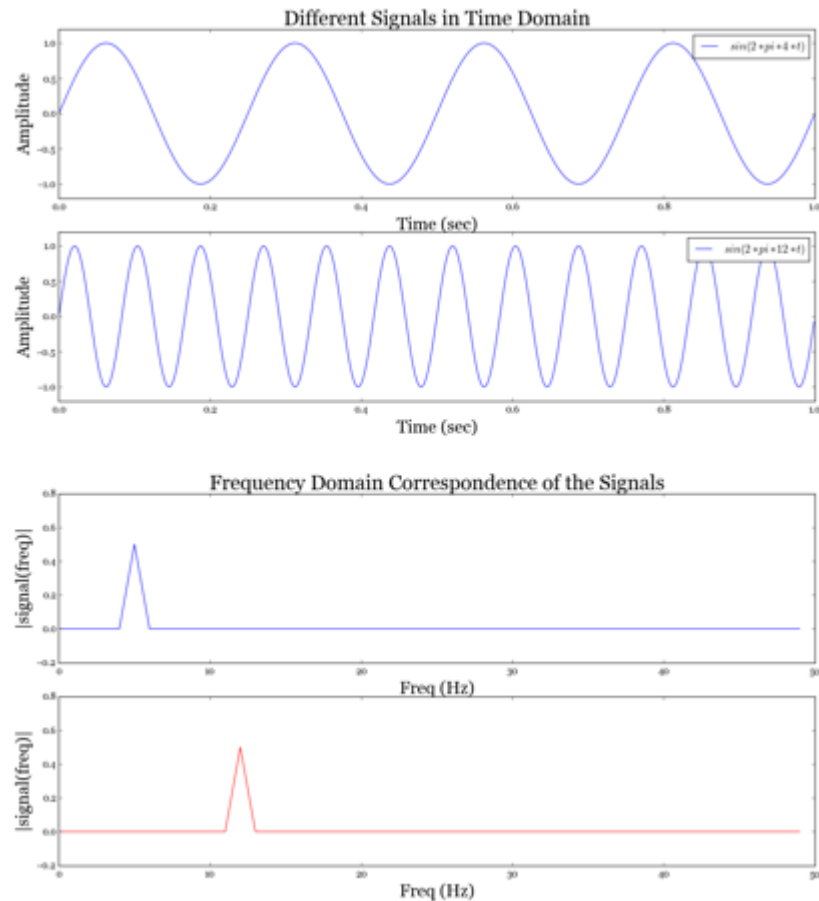


Fig. 1. 8: Two different sine waves [$\sin(2\pi 4t)$ and $\sin(2\pi 12t)$, respectively] in time domain and their correspondence in frequency domain

Fig. 1.9 points out the sum of these signals in both time and frequency domain. When there are more than one wave mixing with each other, it is hard to distinguish each wave from each other in time domain graph. In fact, it is not very simple to understand what's going on there. However, in the frequency domain graph it is easier to see that there are two waves with different frequencies. In real life signals can be much more complicated than these examples. Thus, frequency domain can provide to analyze signals conveniently.

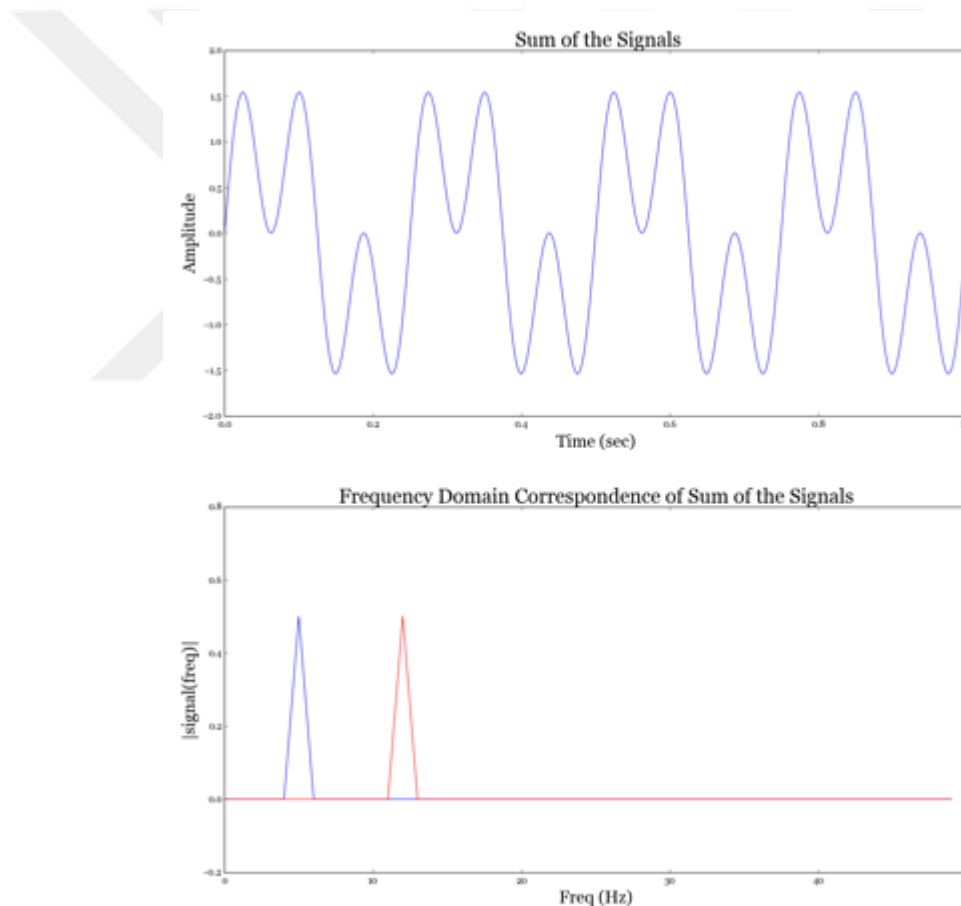


Fig. 1. 9: Sum of the previous signals in both time and frequency domain

Time domain and frequency domain can be transformed into each other with the help of a mathematical relationship called Fourier Transform. What Fourier transform does

is that basically it takes t-domain signal and expresses it in terms of frequencies that form that signal by a mathematical function. It gives both amplitude and phase information about the signal. The Fourier Transform of a function $g(t)$ is in Eq. (1.5):

$$\mathcal{F}\{g(t)\} = G(f) = \int_{-\infty}^{+\infty} g(t)e^{-2\pi jft} dt \quad (1.5)$$

It is a reversible function so that conversion from t-domain to f-domain is done by Fourier transform and the opposite conversion is made by inverse Fourier transform as in Eq. (1.6):

$$\mathcal{F}^{-1}\{G(f)\} = \int_{-\infty}^{+\infty} G(f)e^{2\pi jft} df = g(t) \quad (1.6)$$

1.5. Battery Modeling

Battery modeling or mathematical description of batteries has gained importance recently as battery powered applications increase. Battery modeling provides more information about the battery and estimates of its performance, runtime, capacity etc. beforehand at specific conditions of interest. Instead of trying to measure the response of the battery with respect to every discharge profile of interest, applying all desired profiles to a built model will be much easier when testing becomes too impractical. A 10-20 years life test for automotive applications is a good example of real life measurements.

In the literature, the battery models developed can be divided into two: first principle based models and equivalent circuit based models. First principle models require the

knowledge of numerous parameters regarding the kinetics and transport of various materials inside the system. Equivalent circuit based models, as understood from the name, use equivalent circuit modeling and then use the equivalent circuit models in time domain through a SPICE type approach [31] [32]. In this approach, the components used in the impedance fitting are converted into a time domain analog in order to model the time domain response of the system [33] [34]. Although these two groups of modeling approaches have been applied successfully in many cases, they have some drawbacks. In first principle models, since most of parameters are not exactly known, this issue turns the problem into one of fitting with numerous parameters, which ends up over-defining the problem. With the high degree of free parameters, the number of degenerate solutions increase greatly, in turn, decreasing the accuracy of the fit parameters obtained, precluding any reliable quantitative analysis. In the equivalent circuit based model, it is possible to define the circuits in a way to make sure that the number of degenerate solutions are minimized. However, these simplified circuit models (Simplified Randles and derivatives) fail to capture the full detail of the impedance spectrum [35]. There are models developed in the literature that do capture the fine detail in the impedance spectrum, however, these models have to take into account the porous structure of the electrodes and are generally based on transmission lines. These models are defined in the frequency domain and they are very complicated to get converted into the time domain.

Battery voltage is the principal response of the battery as a function of applied current profiles. The elemental parameter dictating the battery voltage response is the state-of-charge (SOC). In any battery chemistry, an electrochemical potential is present as a function of the activities of the several electroactive species. In theory, this potential

can be described utilizing the appropriate combination of the relevant group of Nernst Equations [36]. Electrochemical potential serves the basis for any modeling approach [37]. Nevertheless, it only reflects the thermodynamic equilibrium condition and does not capture the response of the batteries to current spikes or oscillating currents. Therefore, any fast moving current or voltage response of the battery needs to be modeled in addition to equilibrium voltage of the battery. Here, any fast moving current or voltage response of the battery is designated as AC response while equilibrium voltage of the battery is called DC response. Thus, the sum of the AC response and the DC response yields the actual real-time battery voltage.

1.5.1. DC

As previously mentioned, DC potential represents equilibrium voltage of batteries and its basis leans on electrochemical potential that emerges as a result of chemical reactions in the battery. In order to model the DC response of the battery, literature methods, along with the method developed within this thesis, uses an experimental approach. In theory, this should be approximated by a combined Nernst equation (Eq. 1.4) of all the reactions that are taking place inside the battery [36].

$$E = E^o - \frac{RT}{nF} * \ln Q \quad (1.4)$$

where R is gas constant, T is temperature, n is number of electron, F is Faraday constant and Q is reaction quotient. Experimentally, it is obtained by forming a simple lookup table of voltage as a function of state-of-charge (SOC) and the details of the method is explained in the experimental part. This is a common method in the literature

[38] and the literature holds similar methods for modeling open circuit potential, as well [39].

1.5.2. AC

As stated above, AC voltage is considered to be the non-equilibrium response of batteries against any applied load. In the literature, there exists various modeling methods to simulate AC response of batteries such as electrochemical models, empirical models, equivalent electrical-circuit based models [38]. Electrochemical models intend to catch dynamic behavior of batteries on a macroscopic scale and generally they manage to give results with high accuracies [38]. These kind of models are described by using a high number of partial differential equations (PDE) that must be solved at the same time [38]. Increase in the number and order of the PDEs makes the electrochemical models more complex and can cause enormous requirements for memory and computational power [38]. Furthermore, the PDEs all require the knowledge of fundamental parameters regarding the materials and the interfaces, which are not always available.

Empirical models [40] usually adopt empirically derived equations from experimental data fittings to extrapolate correlation between several battery parameters such as the terminal voltage and SOC [38]. As an example of empirical models, some models endeavor to catch non-ideal discharge behavior utilizing moderately basic equations (i.e. Peukert's law [41]) in which the parameters coincide with empirical data, however, in spite of the fact that simple to arrange and utilize, Peukert's law does not represent time-varying loads. [42].

Equivalent electrical-circuit based models provide an equivalent representation of a battery via electrical circuit models as addressed previously. These type of models have gained a ton of interest for real-time battery state estimation and power management purposes since their simplified mathematical and numerical approaches reduce the need for computationally intensive methodologies [38]. They involve a resistor-capacitor network by aiming to mimic behavioral response of batteries. Thus, they give a chance to characterize the battery response including diffusion and charge transfer processes. In the literature, the number of parallel RC networks varies depending on applied load or obtaining modeling accuracy (one-RC [43] [44], two-RC [45] [46] or more [47]). As another example, Sean Gold has offered PSPICE circuits comprising linear passive elements, voltage sources, and lookup tables to model lithium-ion batteries [48].

On the other hand, EIS based modeling approaches have been preferred, as well [49]. Although to deal with the complexity of modern automotive power nets, simulation-based design techniques are vital and appropriate models of all system components involving the battery as a fundamental part are thus mandatory, nevertheless, simulation models of energy storage devices are hard to obtain since batteries vary with time and they are strongly non-linear [49]. Therefore, the impedance-based modeling has been applied to handle these kind of difficulties. Mentioned references demonstrate that this kind of approach can regenerate the voltage profiles, as accurately as the equivalent circuit model parameters regenerate the impedance spectrum.

Simple models with one-RC network (i.e. Randles cell) clearly fail to capture all the details of EIS data. However, taking the more complex models into time domain makes

the algebra complicated and extend greatly the relevant computation time for the modeling.

1.6. Scope of Current Work

In this thesis, a new approach that combines the best of the two modeling approaches mentioned above is presented. Instead of modeling the impedance spectra utilizing an equivalent circuit model that is either incomplete or very complex, an approach to utilize the raw impedance data without any parametrization will be presented. Our approach makes zero assumptions and possesses no fit parameters, instead, it utilizes directly, the measured impedance spectrum to predict the response. Instead of trying to acquire battery parameters from impedance spectra in order to build a response function in the time domain, modeling is done in the frequency domain for the AC part of the response. At first, the frequency domain current profile is obtained via a Fourier transform of the desired current profile. Then, this frequency domain current profile is simply multiplied by the impedance at every frequency of interest contained by the transform. This step produces the AC voltage response of the battery. Ultimately, the voltage response of the batteries in the time domain is obtained by a simple inverse Fourier transform of the voltage profile. The whole methodology is completed by adding the DC response of the battery in through a simple map of SOC vs DC potential acquired experimentally.

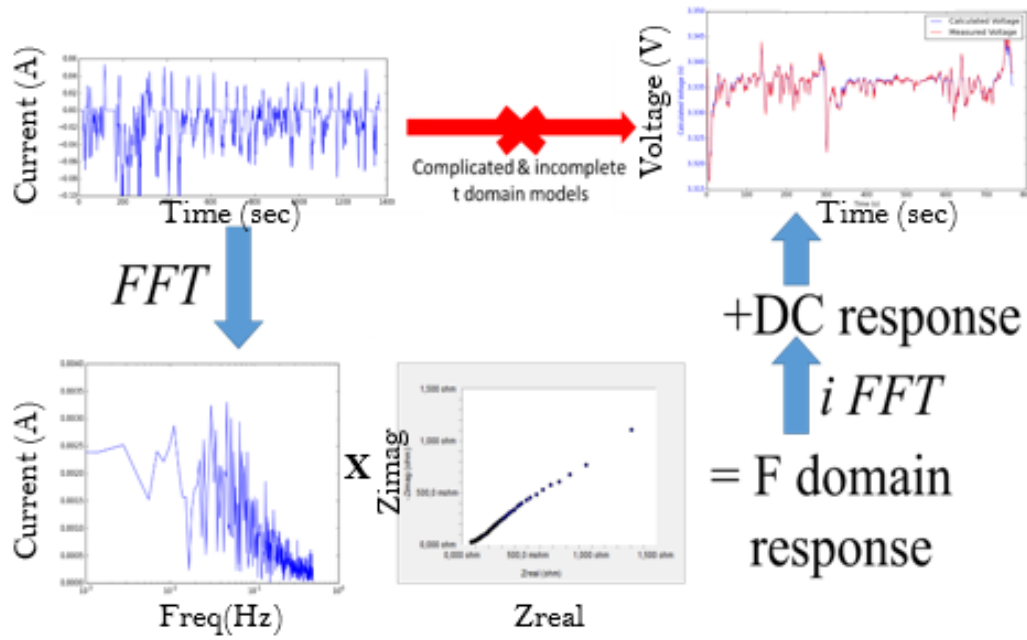


Fig. 1. 10: Steps of the methodology

As indicated in the Fig. 1.10, this offered approach is computationally pretty simple and very straightforward to implement. All steps of the approach are doable analytically and do not include any approximations or assumptions.

Chapter 2

2. Experimental

The current chapter of the thesis is divided into two separate subunits as experimental and numerical parts. In the experimental part there is empirical information such as which type of energy storage systems (i.e. batteries, supercapacitors) and instruments have been used during the measurement, and what the preferred profiles are and also why they have been chosen. Moreover, how all the measurements have been performed is explained in detail. On the other hand, the scripts that have been utilized in order to execute the proposed modeling approach are explained in the numerical part. Besides, number crunching codes associated with the graphs which had been plotted after performing some functions to data during the initial development of the approach is explained in the numerical part, as well.

2.1. Experimental Part

2.1.1. Energy storage systems and instruments employed:

In the whole experimental process, batteries with different chemistries and a supercapacitor as representatives of various electrochemical energy storage systems have been employed. In the initial development of the approach, 4/5SC 1500 mAh Nickel-Cadmium (NiCd) batteries from TNL Technologies had been used. After facing some problems with the NiCd batteries that are explained in detail in chapter 3, two kinds of batteries and a supercapacitor were used, those batteries are Lithium-Iron Phosphate (LiFePO_4) and Nickel-Metal Hydride (NiMH) batteries. IFR 22650 LiFePO_4 battery was from EWT Battery (Shenzhen, China). The NiMH battery was 1200 mAh NiMH battery from GPI International Limited (Hong Kong). In addition, the supercapacitor was BCAP0350, a 350 F ultracapacitor from Maxwell Technologies (USA). All these samples were procured from local wholesalers. Throughout the thesis, LiFePO_4 battery was denoted by LFP and the 350 F supercapacitor was designated as 350F.

During testing of the approach, measurements of impedance, DC potential vs SOC, the response to the discharge profile chosen, open circuit potential and discharge were conducted by Gamry Interface 5000E Potentiostat/Galvanostat/ZRA. Customs scripts had been written in-house using EXPLAIN language employed by the Gamry Framework software for the current profiles utilized in the thesis, along with impedance spectra at relevant frequency values.

2.1.2. Preferred profiles:

The chosen profiles in this thesis are Federal Urban Driving Schedule (FUDS), Heavy Duty Urban Dynamometer Driving Schedule (HDUDDS), Highway Fuel Economy Driving Schedule (Highway-FET) and a made-up profile named Squarewave. All driving schedules except for Squarewave are published by Environmental Protection Agency (EPA) [50]. As required by law in USA, the automobile companies need to have standards of their vehicle fleet conformed to CAFE standards [51] profile before they commence production based on these profiles. Otherwise, they are punished by extra taxes for higher CO₂ emission of their vehicle fleet as leading to air pollution.

FUDS is an auto industry standard vehicle time-speed profile for urban driving that has been utilized for various years for electric vehicle performance testing and it is indistinguishable to the EPA Urban Dynamometer Driving Schedule [3]. Heavy Duty Urban Dynamometer Drive Schedule (HDUDDS) is for urban heavy duty vehicle testing and Highway Fuel Economy Test (Highway-FET) represents highway driving circumstances [52]. Moreover, Squarewave profile stands for slow conditions. In actuality, they had been arbitrarily chosen. Since the idea of this project was formulated many years ago, the well-known, common driving schedule at that time, FUDS, has been worked with in the beginning of the research. After that, the freshly published drive schedules mentioned above have been utilized. To illustrate, Fig. 2.1 indicates Highway-FET and HDUDDS profiles.

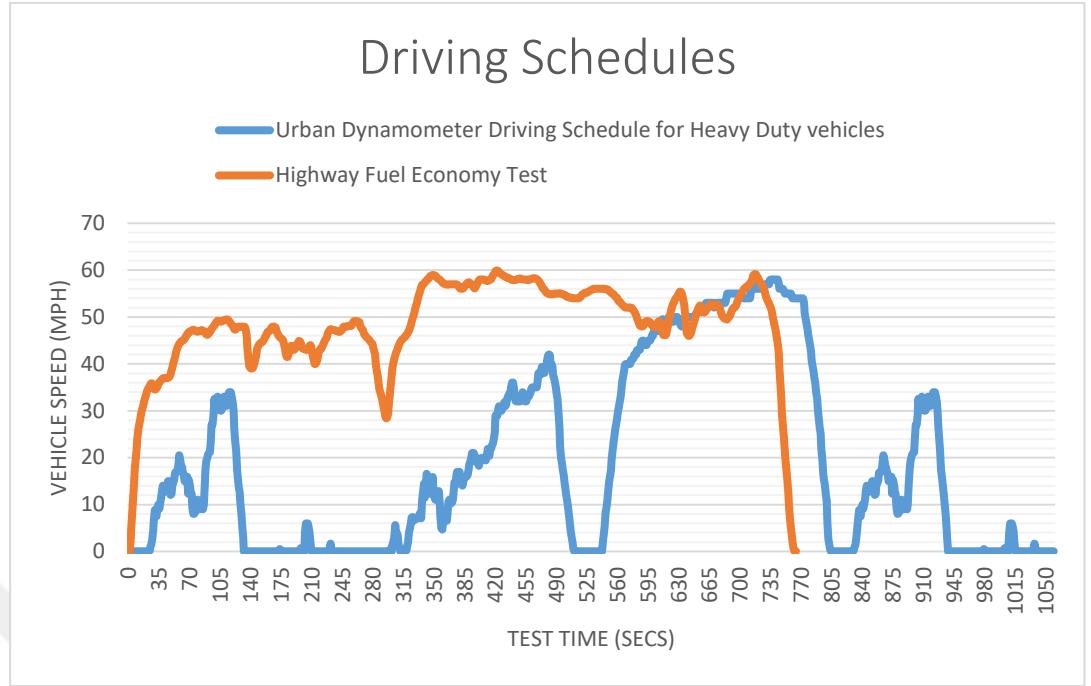


Fig. 2. 1: Speed vs Test Time of HDUDDs and Highway-FET driving schedules [50]

2.1.3. Procedures of the measurements:

(This part is also described in *Elif Özdemir; Can Berk Uzundal; and Burak Ulgut, “Zero-Free-Parameter Modeling Approach to Predict the Voltage of Batteries of Different Chemistries and Supercapacitors under Arbitrary Load” Journal of the Electrochemical Society 2017 164: A1274-A1280.*

“Reproduced with permission from J. Electrochem. Soc., 164: A1274-A1280. Copyright 2017, the Electrochemical Society.”)

The profiles chosen have both high acceleration and deceleration levels, in addition to long flat regions to demonstrate the versatility of our approach. These profiles are published as arrays of speeds at various time points. In order to convert these speeds to current demand from the battery, the following procedure is applied. First, accelerations are calculated as simple two point finite differences. Then, accelerations are normalized to have the highest acceleration level to be unity. In a final step, decelerations that lead to charging of the batteries

are multiplied by 40% in order to account for inefficiencies in regenerative braking¹. In the final step, power is assumed to be directly proportional to the current that is drawn from the energy storage system. This implies that the voltage of the battery does not change appreciably throughout the test. Though this assumption is somewhat valid for a battery based system, it is certainly not valid for a supercapacitor. However, since the particulars of the actual discharge profiles is immaterial for the present work, this point is not considered further. The data, along with a summary of the steps is shown in Fig. 2.2.

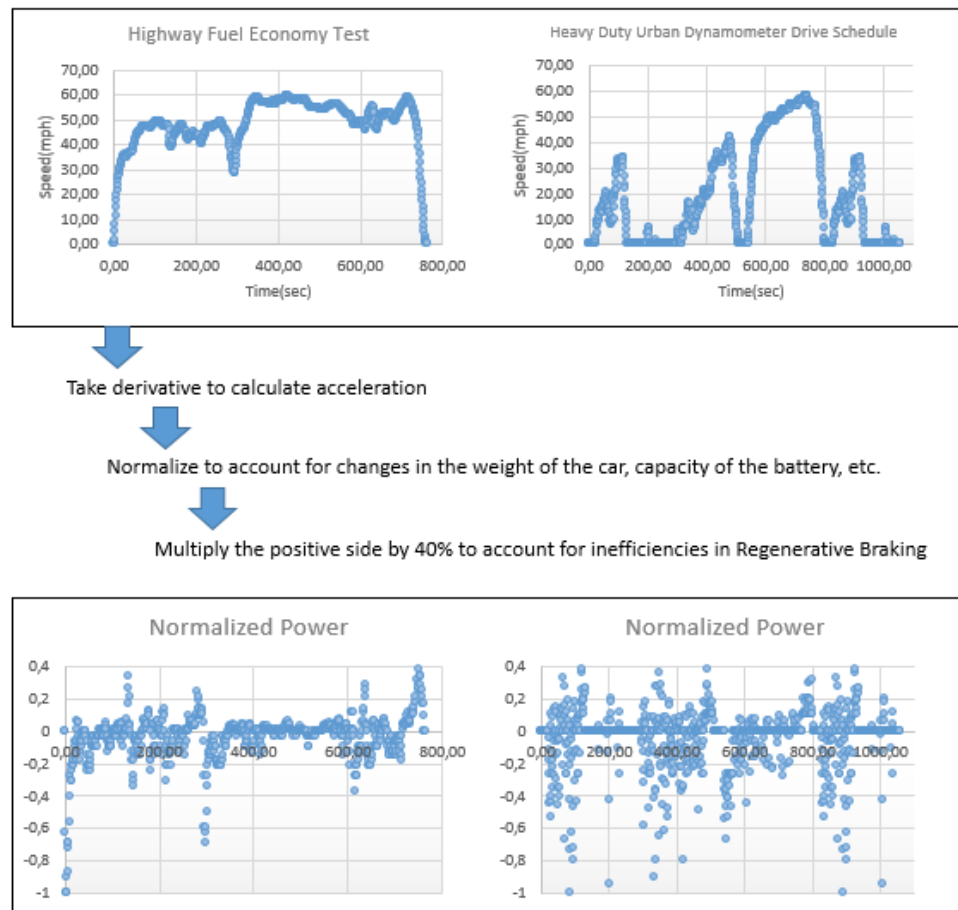


Fig. 2. 2: The procedure used to estimate currents based on drive schedules of the EPA

¹ This number fluctuates a lot in the literature and there is probably no hard single number on the efficiency. However, 40% was chosen as an average for the current study.

In addition, one profile involving a relatively long charge and a relatively long discharge step followed by a rest was used. Since the method is based on impedance spectroscopy, this profile was chosen in order to test the validity of the approach in profiles that involve slowly changing currents. The length and the sampling rate of this profile is adjusted to coincide with those of HDUDDS in order to have the set of frequencies correspond to those of the said profile. This profile will be referred to as a Squarewave as an abbreviation.

The amplitude of the profile is then adjusted according to the battery capacity. For batteries, this current amplitude was chosen to be 10% of the numerical capacity in Ah of the battery for both batteries and all three profiles, except Squarewave for LFP. This amplitude was chosen to be 1% of the numerical capacity to check linearity. For the supercapacitor, experiments were performed at currents that are chosen to be the numerical value of the capacitance in Farads in mA. Finally, in order to check for a deep discharge scenario, the profiles were scaled by 2.2A for the LFP case in one of the tests. As examples, the above mentioned profiles, scaled to 350 mA are shown in Fig. 2.3.

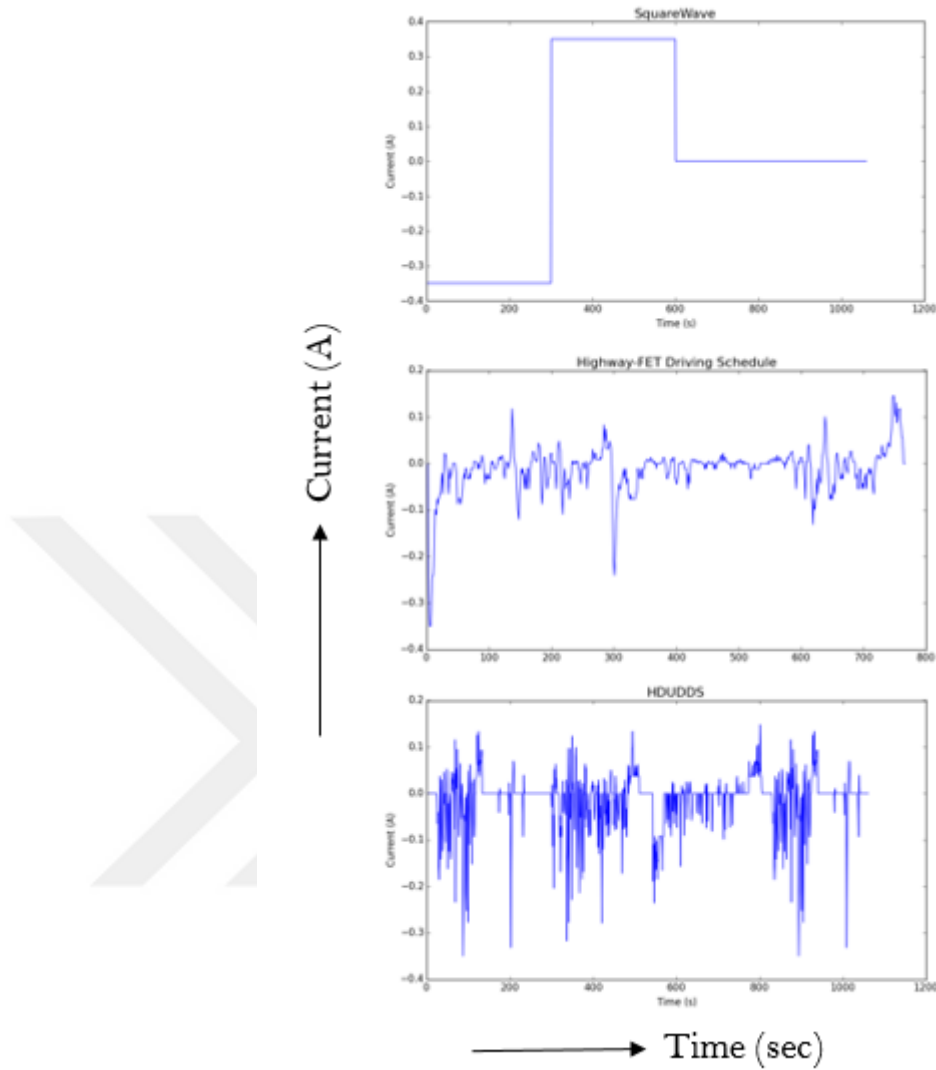


Fig. 2. 3: The current profiles used in this work as an example, 350 mA amplitude profiles are shown that were used for the 350F

The DC voltage vs. SOC map were obtained using a DC current discharge, at a DC current that is adjusted such that the current is 0.1% of the numerical capacity of the battery (e.g. 1.2 mA for the 1200 mAh NiMH battery). For the 350F, this was measured by 3.5 mA. This current is intentionally chosen to be small since a slow discharge is preferred for the potential to accurately reflect the equilibrium potential at the various SOC. A small current ensures that the contributions from non-equilibrium effects are small enough to be ignored. EIS data were gathered in potentiostatic mode with 1 mV AC amplitude.

Potentiostatic measurement ensures that the battery voltage does not drift throughout the measurement and 1 mV AC amplitude ensures linearity of the measured data. The linearity and the stability are verified through a Kramers-Kronig (KK) test using the built-in KK transform test in EchemAnalyst. The impedance data, along with the KK tests are shown in the following figure.

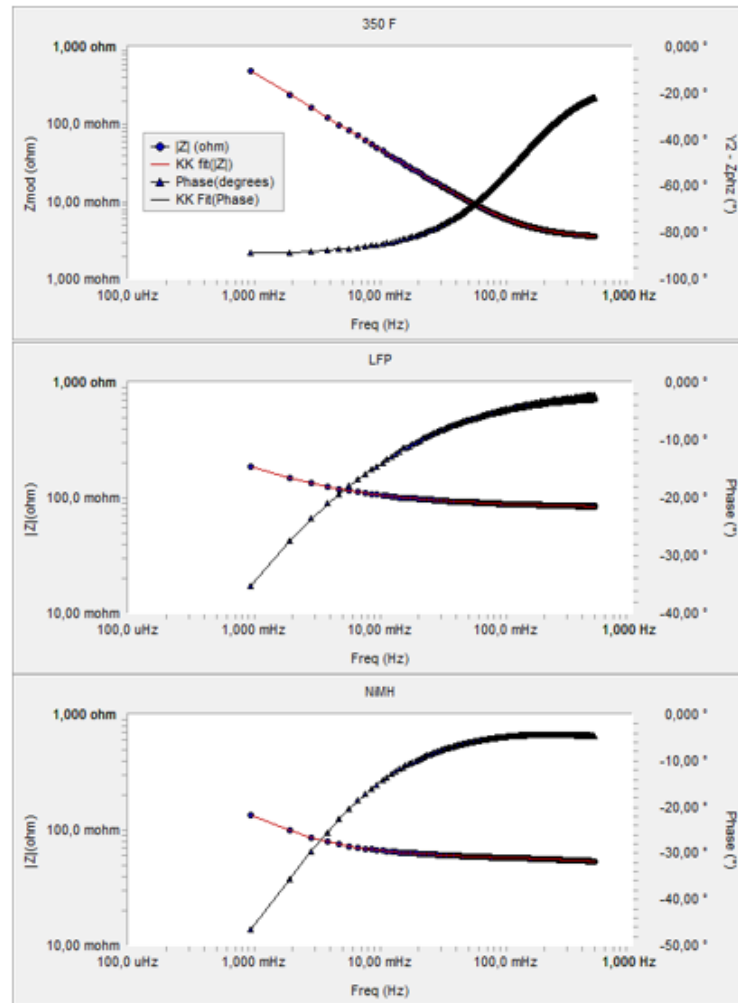


Fig. 2. 4: The Impedance Spectra and the Kramers-Kronig transforms for the three systems measured in the relevant frequency region 350F (top), LFP (middle), NiMH (bottom)

Since the data is gathered potentiostatically to ensure stability, and 1 mV is chosen to ensure linearity, the KK transforms fit perfectly to the data without any noticeable deviation. The χ^2 value for all fits are less than 2×10^{-6} .

Frequencies that are used are linearly and not logarithmically spaced which is generally the case in EIS. The log spacing ensures proper coverage of all processes within a system, however, in the present case, frequencies required are dictated by the length and the sampling time of the given discharge profile. Therefore, for every profile measured, a distinct set of frequencies were measured using a modified version of the custom script.

In between every measurement, the battery was charged to the voltage chosen for the specific system (3.340 V and 3.120 V for LFP, 1.240 V for NiMH and 1.500 V for 350F). This voltage was chosen such that the system under test was not operating at charge/discharge extremes and had minimal side reactions during charge or discharge. The charging was performed using a constant potential hold for 10 hours in order to ensure equilibration of the system at the potential of interest. This ensured that any leftover relaxation from the constant current charging process decayed to below the noise level before the start of the test.

2.1.4. Error analysis:

*(This part is also described in Can Berk Uzundal; **Elif Özdemir**; and Burak Ulgut, “Analysis of Errors in Zero-Free-Parameter Modeling Approach to Predict the Voltage of Electrochemical Energy Storage systems under Arbitrary Load” Electrochemical Society Transactions, in press)*

In the interest of clarity and focus, the experiments presented here will be confined to a Squarewave and 350F supercapacitor. The Squarewave is defined using 1060 secs long sequence which has two periods of current signal in it. The amplitude and the sampling rate of the Squarewave are going to be varied in

order to investigate the effects of the signal parameters to the error structure. Furthermore, the effects of the details of the DC Voltage vs. SOC map were investigated by measuring the DC map using different current values. The supercapacitor used is the Maxwell BCAP0350 E270 T11.

In order to investigate the errors without any bias from the measured voltage level, the errors were defined in a fractional manner, using the below equation.

$$\text{Fractional Error } (t) = \frac{\text{Measured Voltage } (t) - \text{Calculated Voltage } (t)}{\text{Measured Voltage } (t)}$$

The fractional errors as functions of time were investigated visually for signs of structure and amplitude changes as functions of various effects on the experimental parameters.

For the numerical check of the accuracy of a discrete Fourier Transform, the procedure was as follows. A signal was defined using the Pulse sequence that was used in [9]. The sampling rate for the signal was varied without changing the overall structure of the signal. Then, a Fourier Transform and an inverse Fourier Transform were performed. The experimental side of this check was performed using the below signal.

Further, we investigated the structure in the error experimentally through varying parameters regarding the signal amplitude, the current used for the DC map data and others in order to interrogate the main reason for the observed error structure. This error structure was evaluated visually without any further mathematical treatment.

For the experimental check, a square wave sampling frequency was varied from 0.1 sec to 10 sec in factors of 10 and the signal length was kept constant. The investigation was done for two different current amplitudes (350mA and 3.5 mA). The amplitude of the signal was varied from 3.5mA to 35 mA to 350mA for different sampling rates. The DC map was collected with 3 different DC current amplitudes (from 3.5 mA to 350 mA changing in factors of 10). These amplitudes was chosen to vary over three orders of magnitude and their effects to the success of the prediction algorithm were investigated.

2.2. Numerical Part

Computations along with the complex multiplications were done using arrays defined through NumPy v1.9.2 and Fourier transforms were done within SciPy v0.15.1. Spyder v2.3.5.2 was used as the development environment. Basically, Spyder is the abbreviation of Scientific Python Development Environment, and is a basic and lightweight, yet effective interactive development environment for scientific programming in the Python language [53]. It involves advanced editing, interactive testing, debugging and introspection features [54]. Moreover, it provides a numerical computing environment with the help of IPython, which is enhanced interactive python interpreter, and common Python libraries like NumPy enabling linear algebra, and SciPy facilitating signal and image processing, or matplotlib allowing interactive 2D/3D plotting [54].

In the following, number crunching codes associated with the graphs which had been plotted after applying some functions to data during the initial development of the approach is enlightened in detail.

2.2.1. Curve fitting using various functions and background subtraction:

Curve fitting to data by using various function and subtraction of the fit results from data were performed via the following script. In the beginning of the script, it is necessary to import the numerical computing packages that will be used.

```
#####  
import numpy as np  
import scipy  
from scipy.optimize import curve_fit  
import pylab  
import matplotlib.pyplot as plt  
#####
```

After importing the necessary numerical computing packages like above, the voltage response data belonging to NiCd to FUDS profile is imported.

```
#####  
dataarray = np.genfromtxt(r'.\FUDS_measurement_#1_27Oct2015_1E-1.DTA',  
                          skiprows = 3, dtype = [('Pt','i8'), ('T','i8'), ('Vf','f8'),  
                                                  ('Im','f8'), ('Vu','f8'), ('Sig','f8'), ('Ach','f8'),  
                                                  ('IERange','i8'), ('Over','S12')])  
#####
```

Here, `dataarray` is the name of the data array. The `np.genfromtxt` command imports data possessing multiple columns, `skiprows` keyword skips undesired rows of the data or explanatory text, and `dtype` describes the type of the each column as integer, float or string [55]. Specifically, `i8` means 64-bit integer number, `f8` represents 64-bit floating-point number, and `S12` indicates 12-character string [56]. `Pt`, `T`, `Vf`, `Im` and others are the name of the each column and corresponds to point, time, voltage and current, respectively. They are separately redefined as different arrays to pick a desired portion of the data because the data may repeat itself. It is performed by using `[:1372]` operator that means limitation the data from the very beginning (`:`) until 1372nd point since the original data has 1372 points.

```

#####
time = np.array(dataarray['T'][:1372], dtype = int)
voltage = np.array(dataarray['Vf'][:1372], dtype = float)
current = np.array(dataarray['Im'][:1372], dtype = float)
#####

```

Then, the used functions to fit the voltage data are described by using `def` command, enabling description of any desired function [57]. Seven different functions were used but only one of them is shown here to illustrate.

```

#####
def func0(time, a, b, c):
    f0 = a * np.exp(-b * time) + c
    return f0
#####

```

`func0` is the name of the function, and the terms in the parenthesis are parameters of the function, where the first parameter describes the independent variable [57]. The `func0` function corresponds to $(a * e^{-b*time} + c)$ function. The rest of the functions are named as `func1`, `func2`, `func3` etc., too. After that, all fitted functions are made plotted on the voltage data in the same graph.

```

#####
popt, pcov = curve_fit(func0, time, voltage)
plt.plot(time, func0(time, *popt), label = '$y = a.e^{\{-b.x\}} + c$')

popt1, pcov1 = curve_fit(func1, time, voltage)
plt.plot(time, func1(time, *popt1), label = '$y = a.e^{\{-b.x\}} + $
                                     $d.e^{\{-f.x\}} + c$')
#####

```

etc.

Here, `popt` provides a 1-D array containing the optimal values for the parameters so that the sum of the squared residuals of `func0(time, *popt) - voltage` is minimized and `pcov` corresponds to the estimated covariance matrix of parameters contained in `popt` [58]. To perform subtraction of the fitted functions from the voltage data, seven arrays that consist of zeros and named as `backgsubt`, `backgsubt1` etc. are defined to start.

```

#####
backgsubt = np.zeros(1372)
#####

```

Finally, the fitted functions are subtracted from the voltage data by forming seven for-loops as the below one and all are plotted in the same graph.

```

#####
for i in range(0,1371):
    backgsubt[i] = voltage[i]-func0(time[i], *popt)
ax.plot(time, backgsubt, label = '$y = a.e^{\{-b.x\}} + c$')
#####

```

2.2.2. Background subtraction by using piecewise linear approximation:

To perform background subtraction by using piecewise linear approximation, first of all, a function which is called `signaldetrend` is defined by using `def` command. Its parameters are the FUDS data and they are defined as response.

The function is called in another file. The mentioned piecewise linear approximation is done with the help of `signal.detrend` function belonging to SciPy. Basically, it takes the data and separates into desired segments. After separation into segments, it fits lines to these segments and finally it subtracts the lines from signal.

Time, voltage and current data are defined as explained in the previous section. Since there are six different voltage responses to FUDS profile (due to measurements with two different states-of-charge involving three different sampling times), all previously defined time values, voltage and current responses are inserted in 2D-arrays in order to make all calculations consecutively. Also, another 2D-array is defined named `detrendeddataarray` to insert all voltage data after applying the function in.

```

#####
alltime = np.ndarray([6, time.size], dtype = float)
alltime = (time, time1, time2, time3, time4, time5)

allcurrent = np.ndarray([6, time.size], dtype = float)
allcurrent = (current, current1, current2, current3, current4,
              current5)

allvoltage = np.ndarray([6, time.size], dtype = float)
allvoltage = (voltage, voltage1, voltage2, voltage3, voltage4,
              voltage5)
detrendeddataarray = np.ndarray([6, time.size], dtype = float)
#####

```

Then, it is necessary to define segment lengths. They were randomly determined as one fourth and half of the data size.

```

#####
segmentlength = np.array([343, 686])
#####

```

The first for-loop enables calculations based on two segment lengths, separately.

The second one provides the `signal.detrend` function to make approximations for each voltage response in the `allvoltage` 2D-array.

```

#####
for i in range(len(segmentlength)):
    for m in range(0,6):
        detrendeddataarray[m][:] = signal.detrend(allvoltage[m][:],
                                                  bp=np.arange(0, len(allvoltage[m][:]),
                                                  segmentlength[i]))

        fftcurrent = np.ndarray([6, time.size], dtype = complex)
        fftvoltage = np.ndarray([6, time.size], dtype = complex)
        impedance = np.ndarray([6, time.size], dtype = complex)
        st = alltime[0][99]/100

        fftcurrent [0][:] = (scipy.fftpack.fft(allcurrent[0][:]))
        fftvoltage [0][:] =
            (scipy.fftpack.fft(detrendeddataarray[0][:]))
        freqs = scipy.fftpack.fftfreq((time.size), st)
        impedance [0][:] = fftvoltage[0][:]/fftcurrent[0][:]
#####

```

Inside the second for-loop, all voltage and current responses are Fourier transformed via `scipy.fftpack.fft` function and inserted in previously defined 2D-arrays as named `fftvoltage` and `fftcurrent`. Since Fourier transformed data

consist of both real and complex number, the data type of the defined 2D-arrays are indicated as `complex`. In addition to voltage and current responses, time values are also transformed into frequency values by `scipy.fftpack.fftfreq` function. `st` represents sampling time and it calculates the sampling time of responses by taking 99th element of the each row and dividing it by 100. The sampling time is used in the frequency transformation. Finally, impedance is calculated via complex division of Fourier transformed voltage to Fourier transformed current values. The graphs are plotted with the help of `fig, ax = plt.subplots ()` command belonging matplotlib. In order to make piecewise linear approximation based on the segment lengths with different size, the function line below the second for-loop is changed as the below one:

```
#####
detrendeddataarray[m][:] = signal.detrend(allvoltage[m][:],
                                          bp=(100,300,600,1200))
#####
```

The preferred segments were (100, 300, 600 and 1200) based on the extreme points of the data.

2.2.3. Applying Singular Value Decomposition:

Singular value decomposition has been performed by `linalg.svd` function which is a member of SciPy. After importing the necessary Python libraries, NumPy and SciPy, data that singular value decomposition will be applied on are defined via previously mentioned `np.genfromtxt` array operator of NumPy. Since there are six data involving three FUDS response at three different sampling times and three Open Circuit Potential at that sampling times, a 2D-

array named Fullarray is defined and only voltage values of each data are inserted into this 2D-array.

```
#####
Fullarray = np.ndarray([6,1372])
Fullarray=(dataarray1['Vf'], dataarray2['Vf'], dataarray3['Vf'],
            dataarray4['Vf'], dataarray5['Vf'], dataarray6['Vf'])

U,s,Vh = linalg.svd(Fullarray[:6])

for i in range(6):
    Vh[i][i] = 0.0
    pylab.plot(Vh[i],label=i)
#####
```

After applying singular value decomposition function to the data via `linalg.svd`, the factorized unitary matrix, `Vh`, has been plotted via the for-loop above in order to observe different components of the data.

2.2.4. Full Cycle:

In this section, basically what we have done is to transfer time data (i.e. voltage, current, time) into frequency domain and to make necessary computations in frequency domain (i.e. impedance multiplication), then to retransfer the obtained data into time domain. Finally, the data is re-touched up by some calculations in time domain (i.e. DC voltage addition).

At first, a function called `TimeDomain` is defined to follow that cyclic way of the method. Its parameters are title of the graph, response to FUDS profile, measured impedance data, sampling time of the data, and DC Voltage vs. state-of-charge data, respectively.

```
#####
def TimeDomain(graphtitle, FUDS, impedance, st, DCEvsDisCharge)
#####
```

Before beginning computations, the imported sampling time, `st`, is checked whether it coincides with the data.

```
#####
if st != FUDS['T'][99]/100:
    print "Given sampling time and the actual one belonging to data do
          not match. Check your data!"
#####
```

Current values in the FUDS data are transferred into frequency domain by `scipy.fft`. The size of the voltage array that will be calculated is made equal to of Fourier transformed current values, `currentfftarray`. Also, frequency values are computed by `scipy.fftpack.fftfreq`.

```
#####
currentfftarray = scipy.fft(FUDS['Im'])
voltagefftarray = np.ndarray(shape = len(currentfftarray) , dtype =
                             'complex128')
freqs = scipy.fftpack.fftfreq(len(FUDS), st)
#####
```

As a next and crucial step, a for-loop of same as length as `currentfftarray`. This for-loop computes voltage via complex multiplication of impedance corresponding to frequency values in `freqs` data by `currentfftarray`.

```
#####
for i in np.arange(1,len(currentfftarray)):
    j = MatchAbsNearest(impedance['Freq'],freqs[i])
    voltagefftarray[i] = np.complex(currentfftarray[i].real *
    impedance['Zreal'][j] - currentfftarray[i].imag *
    impedance['Zimag'][j], currentfftarray[i].real *
    impedance['Zimag'][j] + currentfftarray[i].imag *
    impedance['Zreal'][j])
#####
```

The impedance data is measured by using sine waves in the traditional manner. The frequency values of that impedance slightly vary with `freqs` obtained by `scipy.fftpack.fftfreq`. The selection of the impedance based on the frequencies in `freqs` is performed by another defined function, `MatchAbsNearest`.

```

#####
def MatchAbsNearest(array, element):
    mindif = 1e38
    imin = 0
    for i in range(len(array)):
        idif = abs(abs(element)-abs(array[i]))
        if idif < mindif:
            imin = i
            mindif = idif
    return imin
#####

```

Frequencies of the impedance data are placed in `array` and `element` takes each value in frequencies of the FUDS data, obtained via Fourier transform. Then, the subtraction process of them begins and thus, the impedance values corresponding the nearest frequency values of the FUDS data can be picked. Since `1e38` is the highest one of 8-bit float number, the subtraction process is began with that in `MatchAbsNearest` function. It is aimed that the loop always find a result during the subtraction and is completed successfully.

After computing voltage values in frequency domain via complex multiplication of impedance by current, the voltage values are transferred into time domain via Inverse Fourier transform.

```

#####
calculatedvoltagearray = scipy.ifft(voltagefftarray)
#####

```

At this step, the only thing that remains to be done is the addition of DC voltage values that had been obtained by slow discharge to `calculatedvoltagearray`, calculated time domain voltage values. This addition is done with the help of a for-loop.

```

#####
charge = 0.0
for i in np.arange(0,len(calculatedvoltagearray)):
    charge = charge + FUDS['Im'][i]*st
    nearest = MatchNearest(DCEvsDisCharge['Q'], charge)

    calculatedvoltagearray[i]=calculatedvoltagearray[i] +
                                DCEvsDisCharge['V'][nearest]
if (debug):
    print ('charge=%f' %charge, 'DCV=%f'
          %DCEvsDisCharge['V'][nearest])

#####

```

In order to choose the appropriate voltage values from the slow discharge data, the nearest charge values to the calculated charge are determined with the help of `MatchNearest` function. It has the similar working principle with `MatchAbsNearest` function. Thus, the voltage values corresponding to the nearest calculated charge values are determined successfully.

```

#####
def MatchNearest(array,element):
    mindif = 1e38
    imin = 0
    for i in range(len(array)):
        idif = abs(element-array[i])
        if idif < mindif:
            imin = i
            mindif = idif
    return imin
#####

```

Finally, an adjustment is done for small offset on the voltage.

```

#####
diff = np.mean(calculatedvoltagearray.real) - np.mean(FUDS['Vf'])
calculatedvoltagearray = calculatedvoltagearray - diff
if(showoffset):
    print ('Voltage Correction =%f' %diff)

if (abs(diff)>0.005):
    print ('LARGE DC OFFSET(%f V) -- CHECK THE CALCULATIONS' %diff)
#####

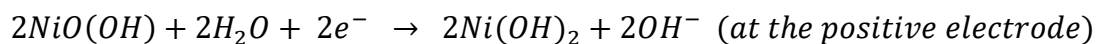
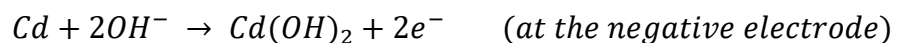
```

All graphs are plotted thanks to `fig, ax = plt.subplots ()` command belonging matplotlib.

Chapter 3

3. Initial Development of the Approach Using NiCd Batteries as a Testbed

Nickel/Cadmium (Ni-Cd) batteries are a type of rechargeable batteries comprising cadmium hydroxide (Cd) as a negative active material, nickel hydroxide (Ni(OH)₂) as a positive active material [59]. Potassium hydroxide (KOH) serves as an alkaline electrolyte [59]. The reactions that occur during discharge in the NiCd chemistry are [59]:



Passing electrical current in the system enables these reactions to be reversed during charging process of the battery. The main advantage of NiCd for daily use is its safety

since it does not vent toxic material [60]. Also, it is easily stored and there is no need to have extra, special conditions for transport [60]. Its lower selling prices and good performance at low temperature are the other advantages of NiCd for being chosen and used [60]. Nonetheless, relatively low energy density of NiCd batteries than Li based chemistries and high self-discharge² rate, and problem with its disposal due to Cd limit its usage area [59]. As a testbed for the formalism that is developed throughout this thesis, NiCd batteries were chosen due to low cost, high availability, simplicity to use and relative safety.

In the measurements done with NiCd batteries FUDS has been used as the current profile. The details of the FUDS profile, along with others have been all explained in the experimental chapter. The rest of this chapter will follow a chronological timeline of the measurements and analyses done and the results obtained.

3.1. FUDS profile measurement with different capacity

($I_{\max}$) values:

In order to observe effects of different amplitude values for voltage response of a battery on FUDS profile measurement, five different AC amplitude values have been determined, those are 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} Amperes (A). A proper AC amplitude would enable to prominently observe the voltage response of the battery. The following figure indicates the voltage vs time curves at different capacity values.

² Self-discharge means the part of the energy that was initially accumulated and that has dispersed over a given amount of idle time [79].

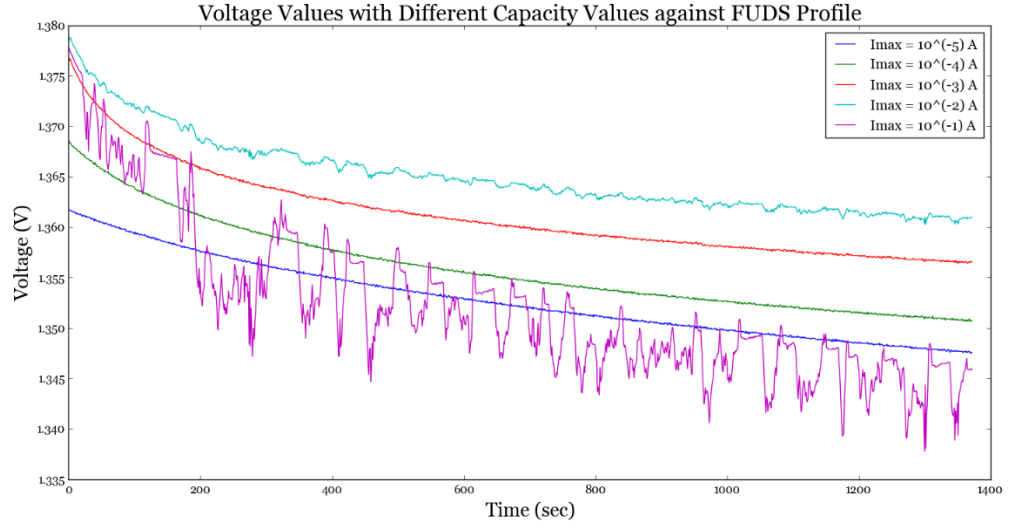


Fig. 3. 1: Voltage response of the NiCd battery to applied FUDS profile at different capacity values

As the AC amplitude has changed, the voltage modulation of the battery has gotten more distinct. As clearly seen in the Voltage vs Time curves, the most prominent voltage response namely, the distinct charging and discharging processes, to FUDS profile has been observed at 10^{-1} A. Therefore, the experiments have been continued with 10^{-1} A as a maximum current value for the rest of the experiments. The descending trend observed in the graphs results from relaxation of the battery itself (i.e. self-discharge) in addition to the net discharge that the profile causes.

3.2. Measurement with FUDS profiles in greater lengths:

To get more information about impedance in low frequency value FUDS profile data has been added at the end of the profile itself, and longer FUDS profile has been obtained. Thus, the experiments have been made with the profiles in 4 different lengths, which are FUDS profile itself, doubled, tripled, and quadrupled FUDS. Impedance data are obtained via complex division of voltage by current in frequency

domain based on Ohm's Law. Figure 3.2 indicates the voltage response and magnitude

($|Z| = \sqrt{(Z_{real}^2 + Z_{imag}^2)}$) of impedance data of the battery for both FUDS profile itself and quadrupled FUDS. These two graphs are placed here for the illustration since the other graphs belonging to doubled and tripled ones have similar trend, as well.

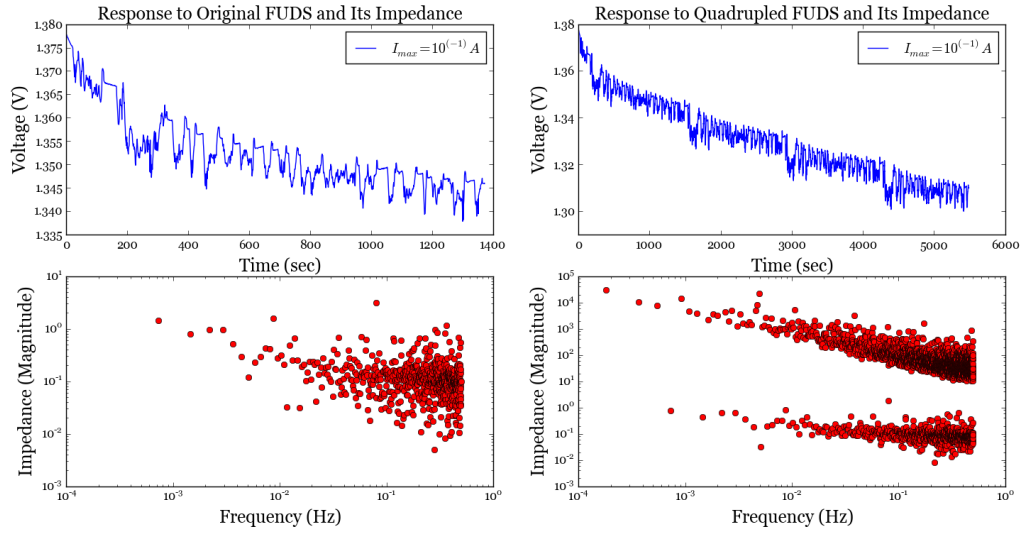


Fig. 3. 2: Voltage responses of the NiCd battery to applied FUDS profile (top left) and quadrupled FUDS profile (top right), and Magnitude of their impedance (bottom row - red).

At the end of the experiment, information at the lower frequency values could not be obtained. Instead, many points around zero were observed in impedance data. The reason behind those points around zero is that Fast Fourier Transform assumes that the given signal is already periodic in time domain [61]. Thus, making the same signal repeating basically means “making the signal periodic” and does not give us any additional information about the signal in frequency domain except points around zero.

3.3. FUDS profile measurement with different sampling time:

Since concatenation didn't work, in order to change our frequency ranges, the sampling rates were modified. The chosen sampling rates were 0.01, 1, and 10 s. Fig 3.3, 3.4 and 3.5 indicates voltage responses of the battery to FUDS at particular sampling time and magnitude of their calculated impedance data by complex division of voltage to current. Here, voltage versus time plots have been obtained after fitting a curve to the voltage graphs and subtraction of the curve from them. The reason behind this procedure is given in detail in “Curve fitting using various functions and background subtraction” part below.

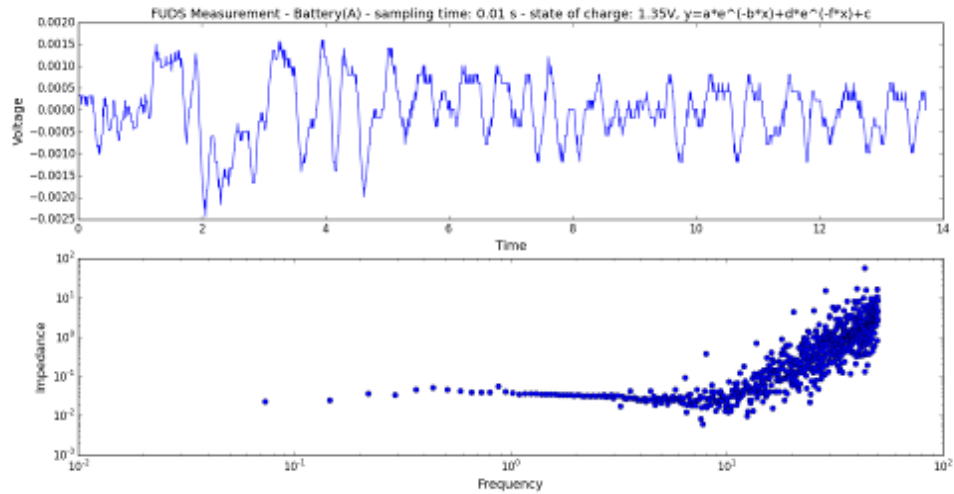


Fig. 3. 3: Voltage response of the battery (top) to FUDS profile with 0.01 s sampling time and 10^{-1} A maximum capacity (I_{max}), and Magnitude of its impedance (bottom).

The impedance plot that is seemed increasing at high frequencies in the graph above may be kind of misleading but have nothing with the results of the measurement. The filter settings of the instrument have caused that kind of graph to be obtained. This

instrumental error was ironed-out by arranging the filter settings of the instrument going further.

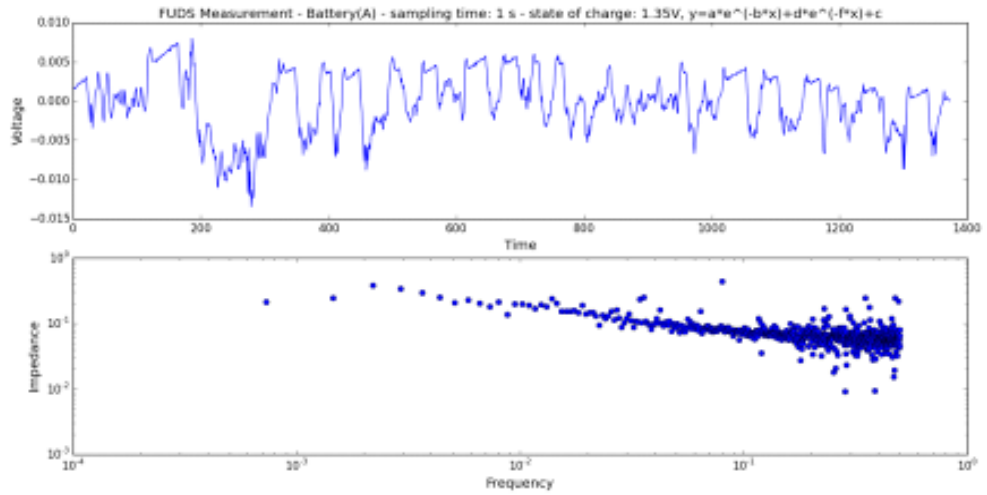


Fig. 3. 4: Voltage response of the battery to FUDS profile with 1 s sampling time and 10^{-1} A maximum capacity (I_{max}), and Magnitude of its impedance.

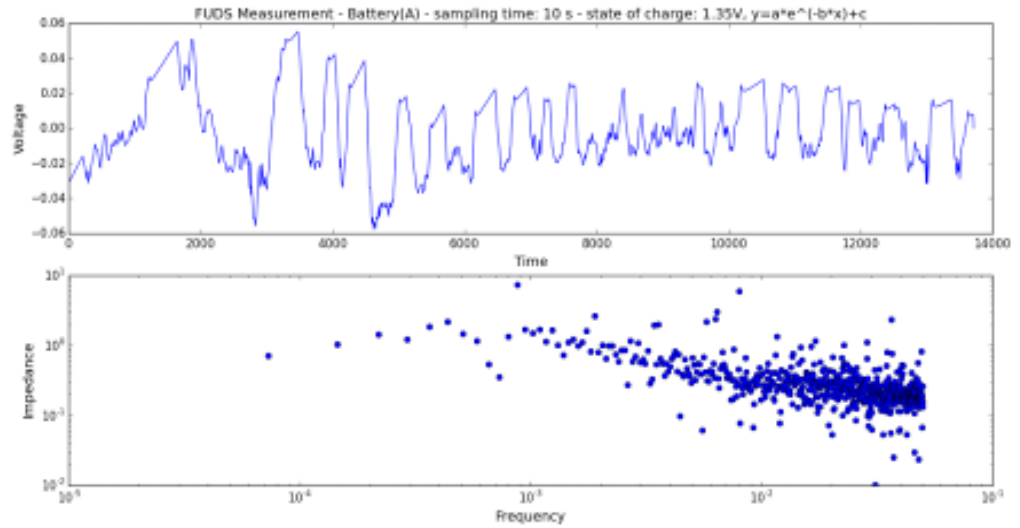


Fig. 3. 5: Voltage response of the battery (top) to FUDS profile with 10 s sampling time and 10^{-1} A maximum capacity (I_{max}), and Magnitude of its impedance (bottom).

This approach worked in order to access different frequency regions properly.

3.4. Curve fitting using various functions and background subtraction:

To observe only battery response to FUDS profile and get rid of any effects of self-discharge of the battery that is not due to any current drawn from the battery, a curve was fitted to voltage vs time graph at first and then, it was subtracted from the signal. The functions used for background subtraction were selected simply by observing the behavior of the voltage. As also confirmed by our experiments, actual waveforms for the relaxation are complicated and cannot, in general, be explained with a single analytical function. The battery response and fitted curves of several functions are plotted together in Fig. 3.6.

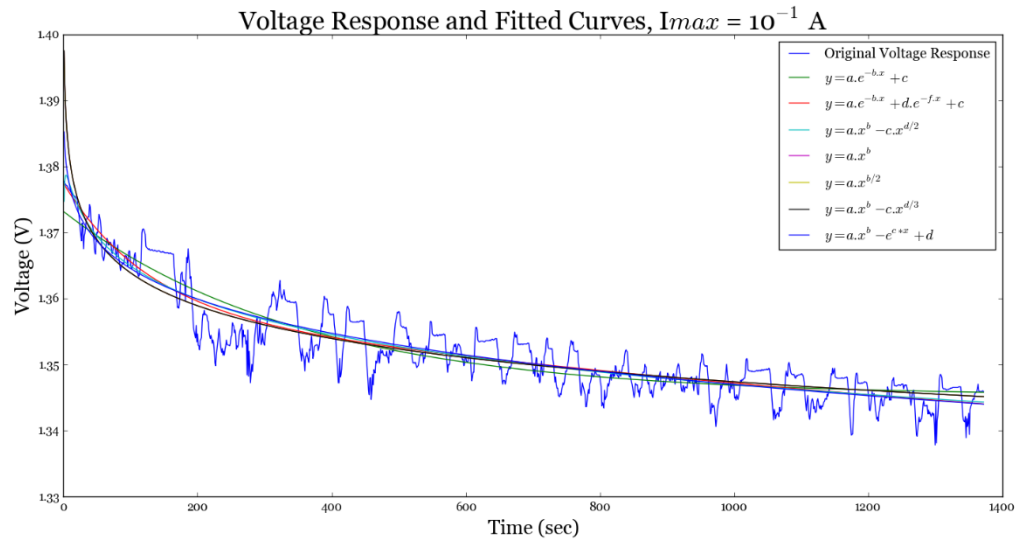


Fig. 3. 6: Various analytical functions that are fitted to the voltage response of the NiCd battery

The fitted functions above are:

$$y = a * e^{-b*x} + c$$

$$y = a * e^{-b*x} + d * e^{-f*x} + c$$

$$y = a * x^b - c * x^{d/2}$$

$$y = a * x^b$$

$$y = a * x^{b/2}$$

$$y = a * x^b - c * x^{d/3}$$

$$y = a * x^b - e^{-c*x} + d$$

Fig. 3.7 displays residual signals after subtraction of each fitted curve from the actual battery response.

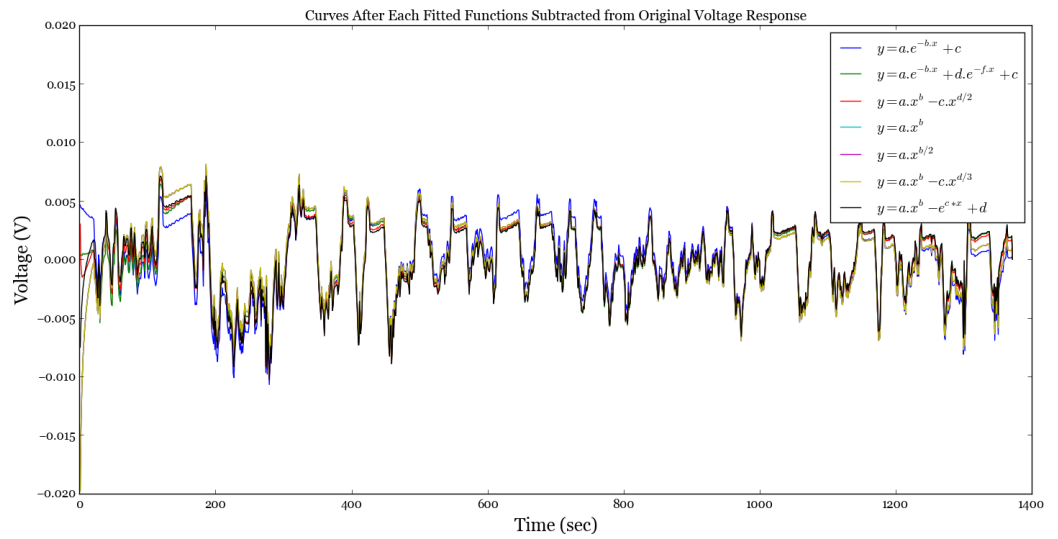


Fig. 3. 7: The residuals after each of those analytical functions is subtracted from the voltage response of the NiCd battery

Attempts to create an appropriate curve for the signal by various functions had remained inconclusive, unfortunately. Thus, the other methods had been searched for better background subtraction to get rid of the self-discharge of the battery.

3.5. Open Circuit Potential measurement for background subtractions of the curves:

After using various functions for background subtraction and obtaining not good enough results, open circuit potentials of the battery have been measured for each sampling time and used them for background subtraction. Fig. 3.8 indicates open circuit potentials of the NiCd battery at three different sampling times, namely, 0.01, 1 and 10 s.

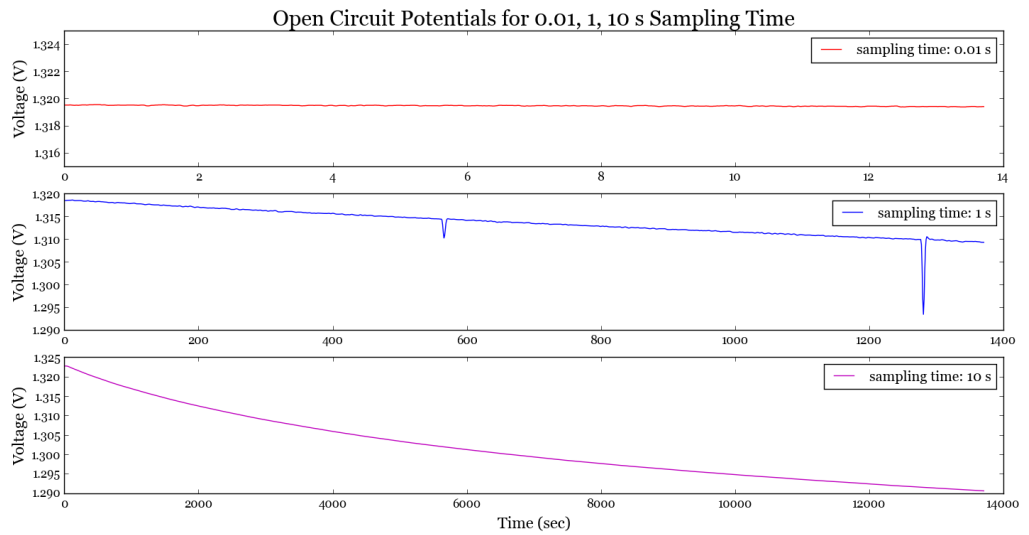


Fig. 3. 8: Open Circuit Potential (OCP) curves of the NiCd battery at 0.01 s (top), 1 s (middle) and 10 s (bottom) sampling time.

After measuring open circuit potentials at 3 different sampling times, they have been subtracted from the actual voltage response at each sampling time. The residual voltage values are shown in Fig. 3.9.

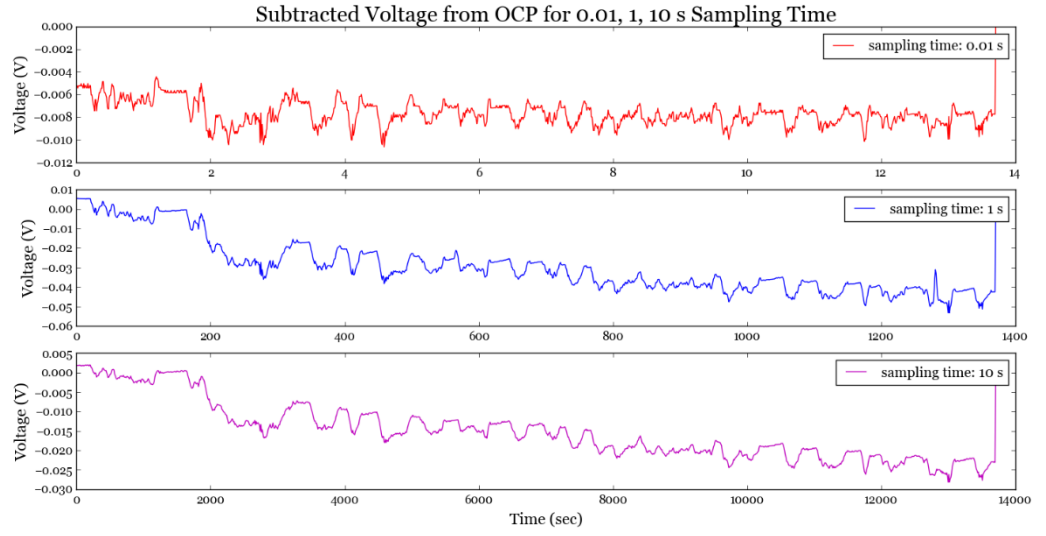


Fig. 3. 9: The residuals after each OCP curves are subtracted from the voltage response of NiCd battery to FUDS profile. Top: 0.01 s Middle: 1 s Bottom: 10 s sampling time

Then, impedance values of these residual voltage data have been calculated and plotted as displayed in Fig 3.10.

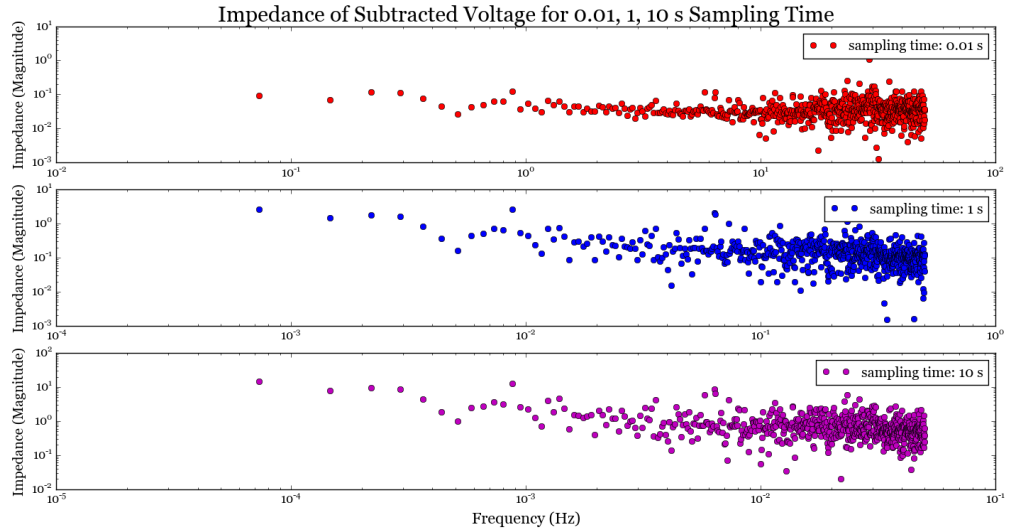


Fig. 3. 10: Magnitudes of the impedance of those residuals obtaining from subtraction of OCP from the voltage response of the NiCd battery. Top: 0.01 s, Middle: 1 s, and Bottom: 10 s sampling time

In actuality, after open circuit potentials are subtracted from the total voltage response, it was believed that the actual voltage response that is purged of self-discharge of the

battery will be obtained since it is a more experimental approach. Unfortunately what it is seen in the graphs was not what it was expected. Even the beginning point of voltage belonging to both FUDS and OCP was different from each other, so negative numbers are obtained instead of data around zero in voltage vs time graphs.

3.6. Background subtraction by using piecewise linear approximation (scipy.signal.detrend function):

Studies of getting rid of the self-relaxation of the battery and obtaining purely its voltage response against the profile have continued with different methods. As another method for background subtraction, a python function that is `scipy.signal.detrend` has been utilized. Working principle of this function is quite straightforward. Basically, it takes the data and separates into desired segments. After separation into segments, it fits lines to these segments and finally it subtracts the lines from signal. The segment length has randomly determined as one fourth of the FUDS profile length, namely 343. The function has been applied to the voltage results of the battery with both 1.35 V and 1.25 V state of charge at the sampling times mentioned in the previous section. Fig. 3.11 points out the voltage values of the battery with 1.35 V state of charge after the `scipy.signal.detrend` function has been performed.

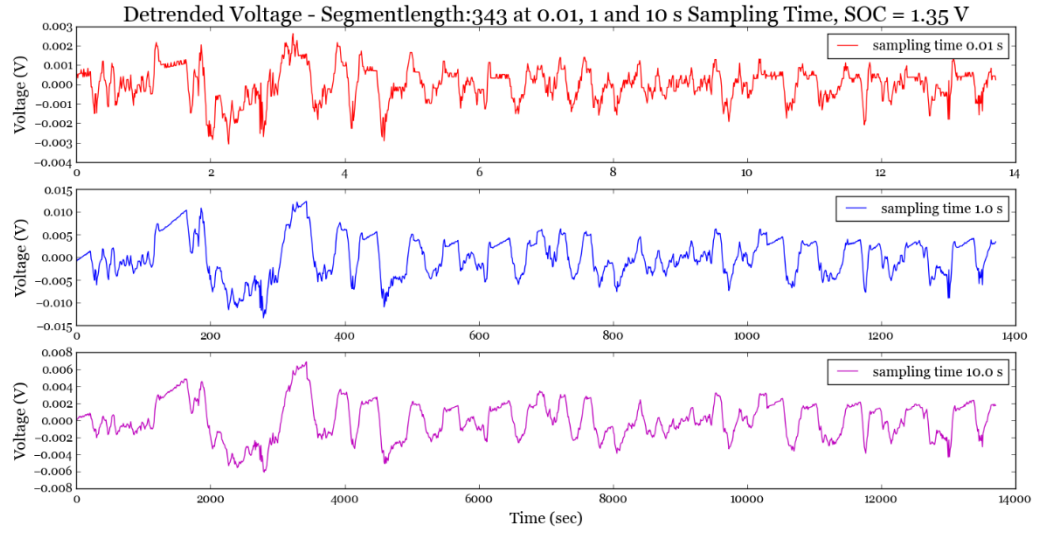


Fig. 3. 11: The residual voltage values after applying `scipy.signal.detrend` function to the voltage response of the NiCd battery to FUDS profile at 0.01 s (top), 1 s (middle) and 10 s (bottom) sampling time. The preferred segment length for the function is 343. The state-of-charge of the battery is 1.35V.

The residual voltage values of the battery with 1.25V state of charge that the function is applied to are shown in Fig. 3.12.

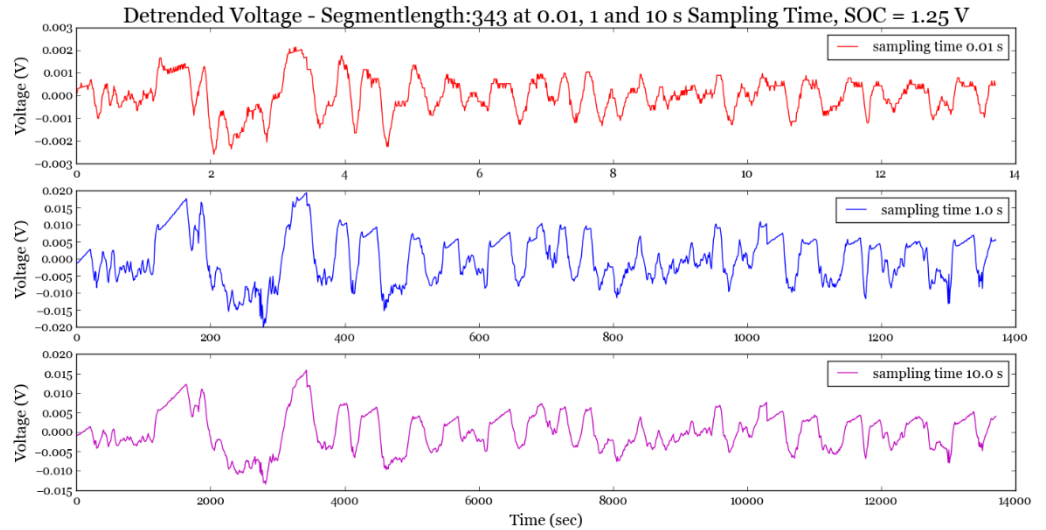


Fig. 3. 12: The residual voltage values after applying `scipy.signal.detrend` function to the voltage response of the NiCd battery to FUDS profile at 0.01 s (top), 1 s (middle) and 10 s (bottom) sampling time. The preferred segment length for the function is 343. The state-of-charge of the battery is 1.25V.

Impedance graphs of those residual voltage values are pointed out in the following figures. Fig. 3. 13 belongs to the battery with 1.35 V state of charge.

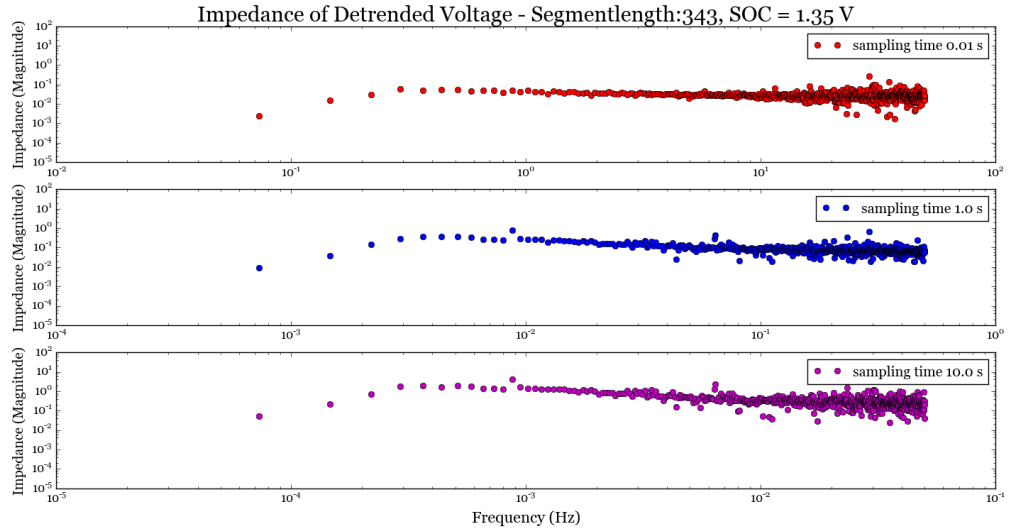


Fig. 3. 13: Magnitudes of the impedance belonging to those residual voltage values that `scipy.signal.detrend` function has been previously applied. Top: 0.01 s, Middle: 1 s, and Bottom: 10 s sampling time. The state-of-charge of the NiCd battery is 1.35 V.

Fig. 3.14 belongs to the battery with 1.25 V state of charge.

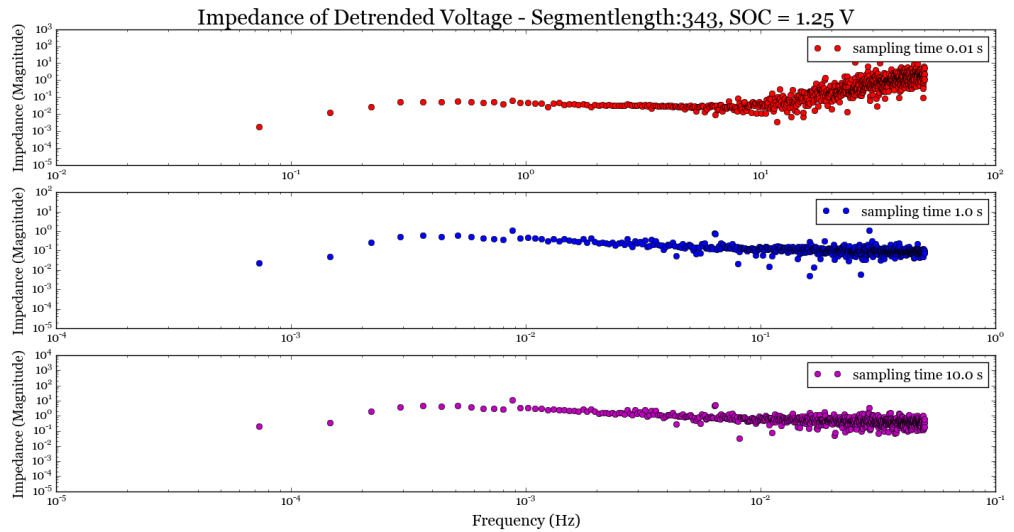


Fig. 3. 14: Magnitudes of the impedance belonging to those residual voltage values that `scipy.signal.detrend` function has been previously applied. Top: 0.01 s, Middle: 1 s, and Bottom: 10 s sampling time. The state-of-charge of the NiCd battery is 1.25 V.

Although the results are better in this method than the curve fitting and subtraction method, as it is clearly seen in the graphs there is still a problem in low frequency side. Points are decreasing in low frequency side unlike the actual impedance data. The reason behind this decrease is explained in the next section. As a footnote, the increasing of impedance in high frequency side of the one with 1.25 V state of charge is due to filter setting of the instrument as mentioned in the previous sections.

3.7. Plotting voltage and current in frequency domain for background subtraction with `scipy.signal.detrend` function

To analyze what the problem is in low frequencies of impedance data, voltage and current responses of FUDS profile are plotted in frequency domain for specific sampling times and states of charge. The Fourier transformed current and voltage values for 1.35 V SOC are displayed in Fig. 3.15. The voltages here are the residual voltage values after being performed the `scipy.signal.detrend` function with segment length 343.

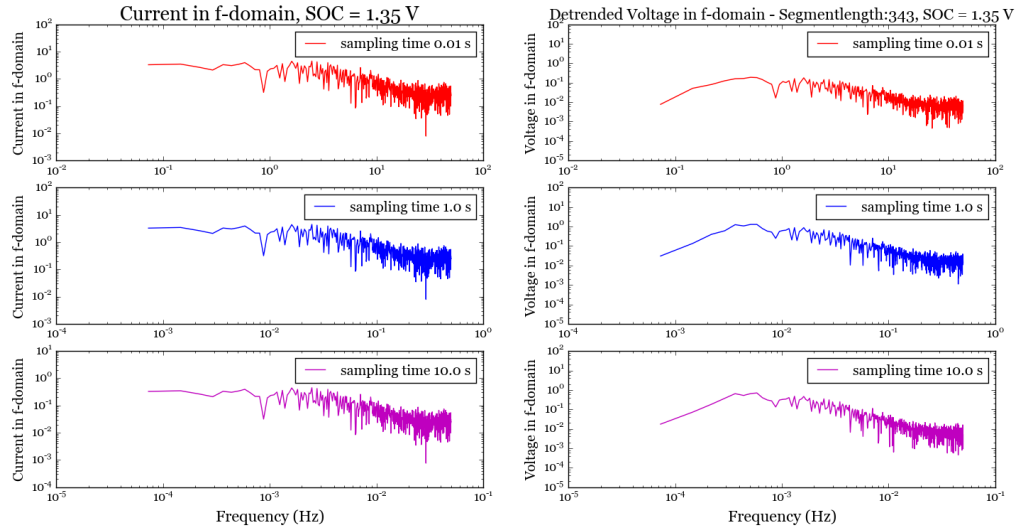


Fig. 3. 15: Left Column: Current data in frequency domain at 0.01 s (top), 1 s (middle), and 10 s (bottom) sampling time. Right Column: The `scipy.signal.detrend` function applied voltage values in frequency domain at 0.01 s (top), 1 s (middle), and 10 s (bottom) sampling time. The state-of-charge of the battery is 1.35 V.

As it can be conveniently noticed from the graphs above, in the low frequency side the voltage and current responses exhibit some divergences from each other. Following the Ohm's Law, impedance decreases at the low frequency side so long as voltage decreases at the same frequency range.

3.8. Effect of segment length in `scipy.signal.detrend` function upon background subtraction:

For observation of effects of segment length on the background subtraction, the segment length has been changed. Previously the segment length used in `scipy.signal.detrend` function was one fourth of FUDS data, namely 343, for the background subtraction. All data below in this section have segment length as half of FUDS profile length, namely 686.

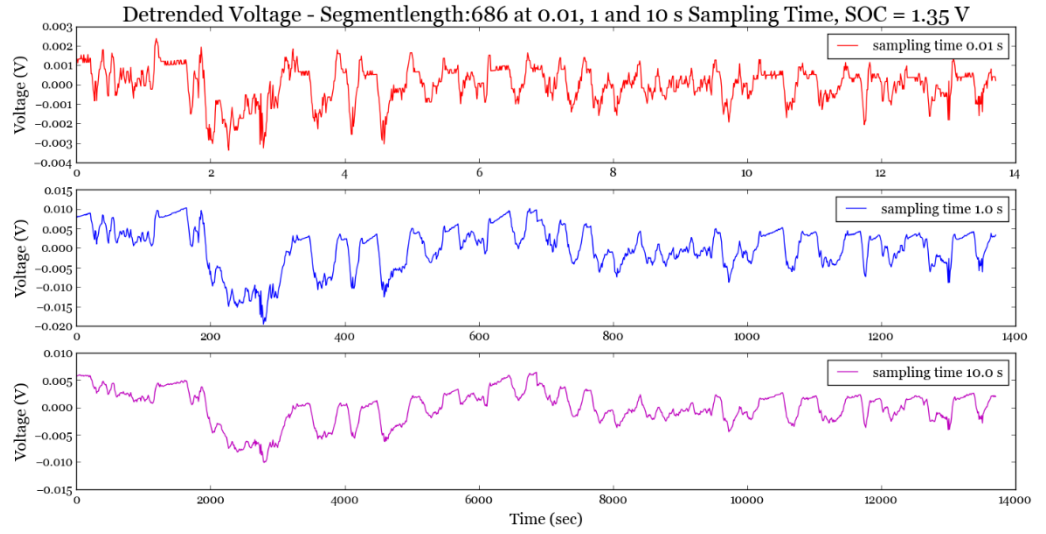


Fig. 3. 16: The residual voltage values after applying `scipy.signal.detrend` function to the voltage response of the NiCd battery to FUDS profile at 0.01 s (top), 1 s (middle) and 10 s (bottom) sampling time. The preferred segment length for the function is 686. The state-of-charge of the battery is 1.35V.

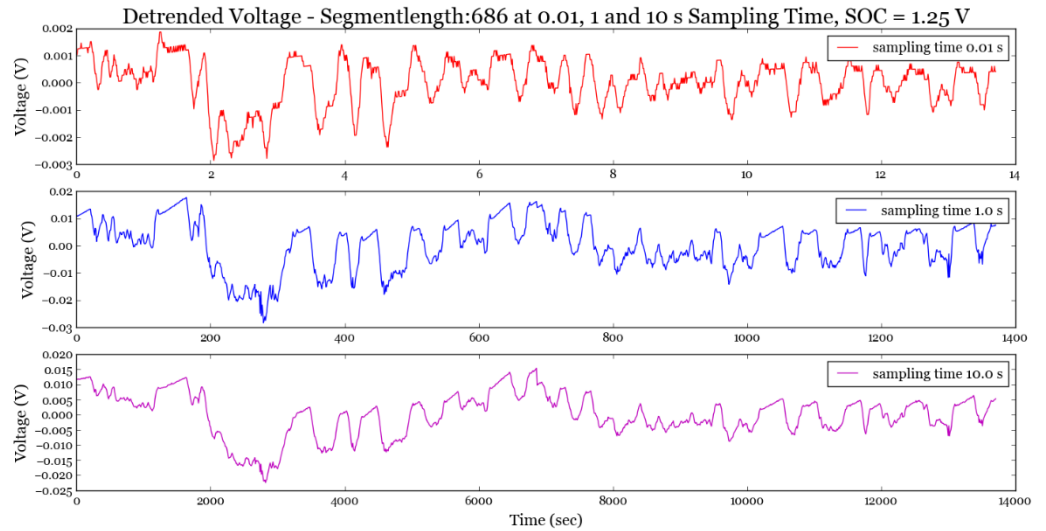


Fig. 3. 17: The residual voltage values after applying `scipy.signal.detrend` function to the voltage response of the NiCd battery to FUDS profile at 0.01 s (top), 1 s (middle) and 10 s (bottom) sampling time. The preferred segment length for the function is 686. The state-of-charge of the battery is 1.25V.

Calculated impedance of those residual voltage values after application of the `scipy.signal.detrend` function of which the segment length is half of the profile are exhibited in the following graphs.

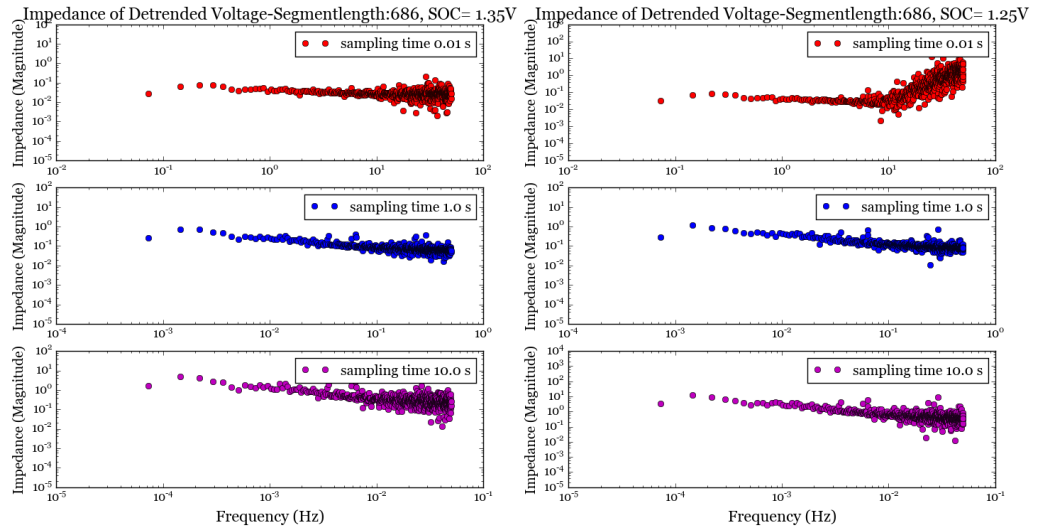


Fig. 3. 18: Magnitudes of the impedance belonging to those residual voltage values that `scipy.signal.detrend` function has been previously applied. Top: 0.01 s, Middle: 1 s, and Bottom: 10 s sampling time. The state-of-charge of the NiCd battery is 1.35 V in the left column and it is 1.25 V in the right column.

With these results it is observed that increasing the segment length does not give better results.

3.9. Arranging segment length in `scipy.signal.detrend` function based on values in data instead of using equal segments for background subtraction:

Instead of dividing the profile equal segments such as by two or four, the extreme points of the profile have been considered for obtaining better subtraction results. Then, the segments have been determined based on those extreme points: (100, 300, 600, and 1200). The `scipy.signal.detrend` function has been applied to the voltage values considering those segments. The obtained results are shown in the figure below for the battery with both 1.35 V and 1.25 V state of charge, separately.

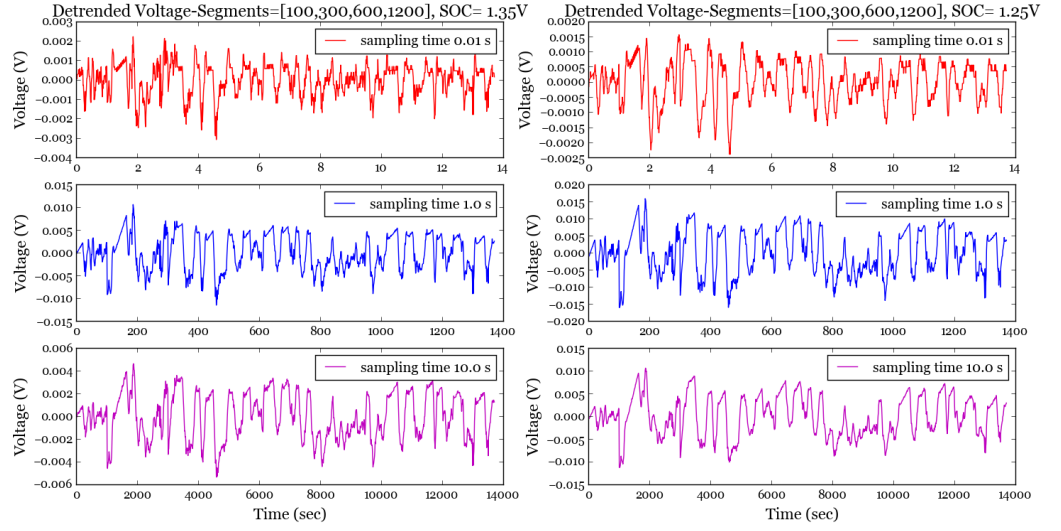


Fig. 3. 19: The residual voltage values after applying `scipy.signal.detrend` function to the voltage response of the NiCd battery to FUDS profile at 0.01 s (top), 1 s (middle) and 10 s (bottom) sampling time. The determined segments for the function are (100, 300, 600, and 1200). The left column data has 1.35V state-of-charge while the right one has 1.25V state-of-charge.

The calculated impedance of those voltage values above are displayed in the Fig 3.20.

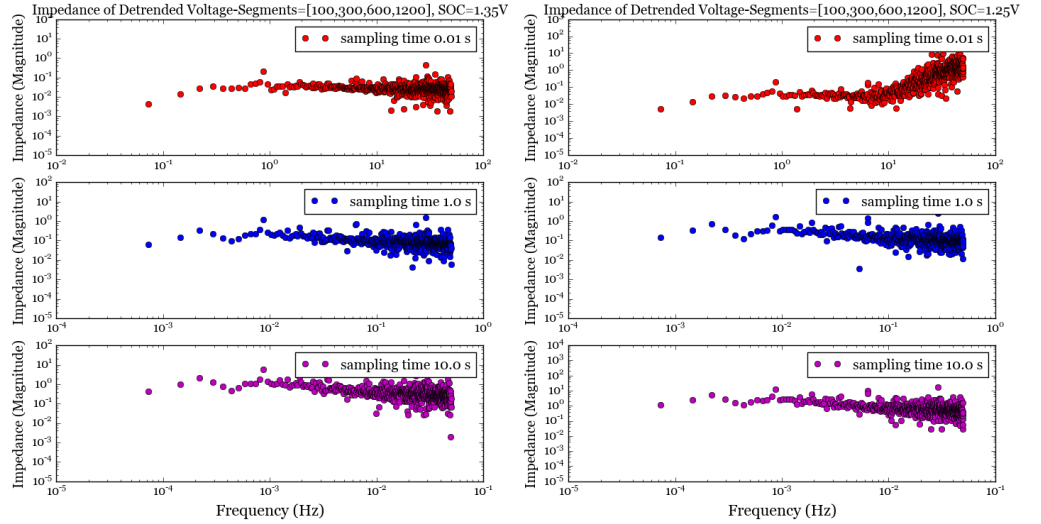


Fig. 3. 20: Magnitudes of the impedance belonging to those residual voltage values that `scipy.signal.detrend` function has been previously applied. Top: 0.01 s, Middle: 1 s, and Bottom: 10 s sampling time. The state-of-charge of the NiCd battery is 1.35 V in the left column and it is 1.25 V in the right column.

Still it could not have been acquired any better results. The search for another method to solve self-relaxation issue of the batteries has been going on.

3.10. Applying Singular Value Decomposition to voltage values of FUDS and OCP:

Singular value decomposition (SVD) is a factorization of a real or complex matrix, with many useful applications in signal processing. Specifically, the `scipy.linalg.svd` function factorizes the matrix into two unitary matrices U and V_h , and a 1-D array s of singular values. Here, the matrix is voltage values of both FUDS profile and OCP of the battery. The basic premise behind this approach is that the non-causal non-correlated processes should be able to be distinguished from the causal and potentially correlated response. It has been aimed with this method to distinguish the voltage response of the battery to the FUDS profile and its self-discharge from each other as separate eigenvectors. However, as the data below shows in Fig. 3.21, the correlation levels in the FUDS response is also so low that the SVD algorithm did not lead to a significant eigenvector that is common in all signals.

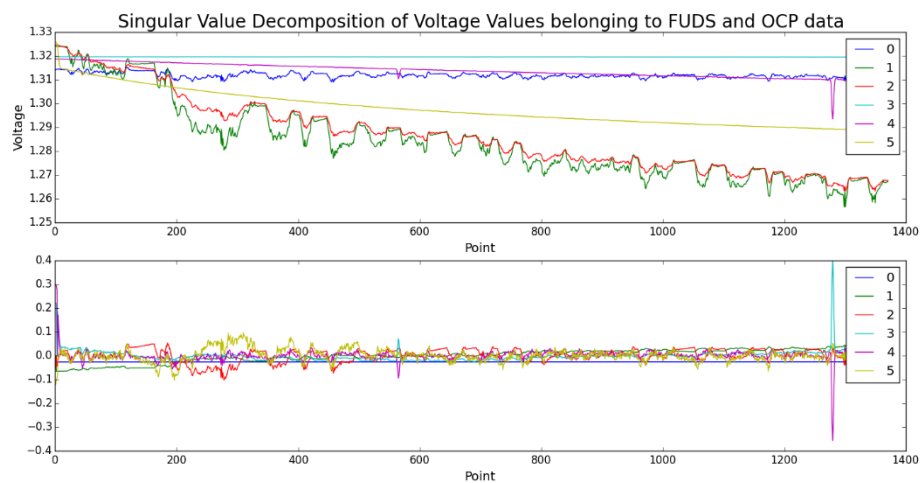


Fig. 3. 21: Top: Singular Value Decomposition analysis of the voltage responses to FUDS and OCPs at 0.01 s, 1 s, and 10 s sampling time. Bottom: Eigenvectors of the matrix composed of voltage values of FUDS and OCPs. The state-of-charge of the NiCd battery is 1.35V.

3.11. Impedance measurement via Gamry instrument:

It is important to validate each result at each step of the methodology in order to correctly predict voltage response of the battery at the end of the methodology. To this end, namely to check accuracy of the impedance data calculated by complex division, the impedance of the same NiCd battery is measured directly from the Gamry Interface 5000 by applying sine waves at the same frequencies that the Fourier Transform of the FUDS profile yields. Then, the impedance spectra calculated using the response to the FUDS scheme is compared to the impedance data measured using sine waves in the traditional manner. The Fig. 3.22 points out the Nyquist and Bode plots of the measured impedance belonging to 1.35 V SOC at the desired frequencies.

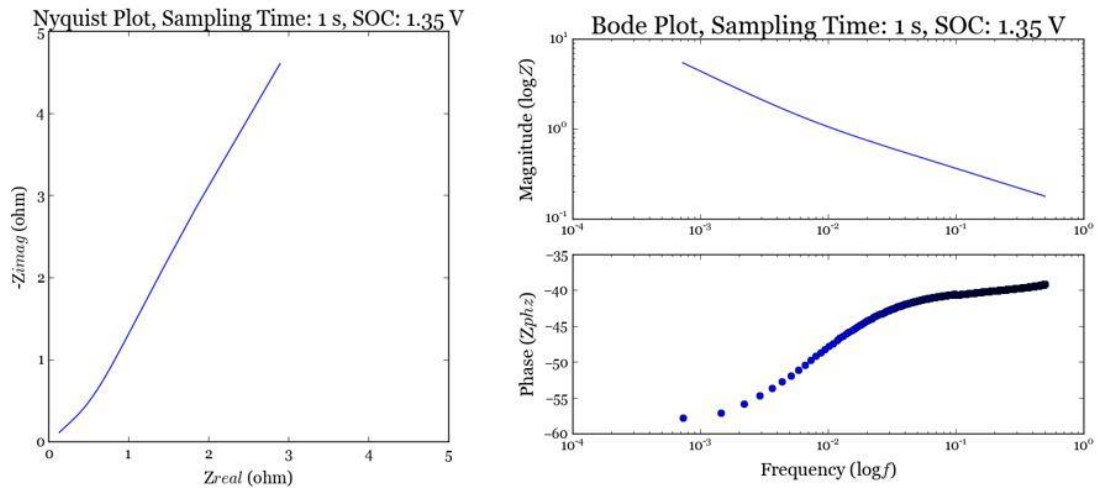


Fig. 3. 22: The Nyquist and Bode plots of the NiCd battery at 1 s sampling time. The state-of-charge of the battery is 1.35V.

Magnitude comparison of measured and calculated impedance at the desired frequencies is shown in Fig. 3.23.

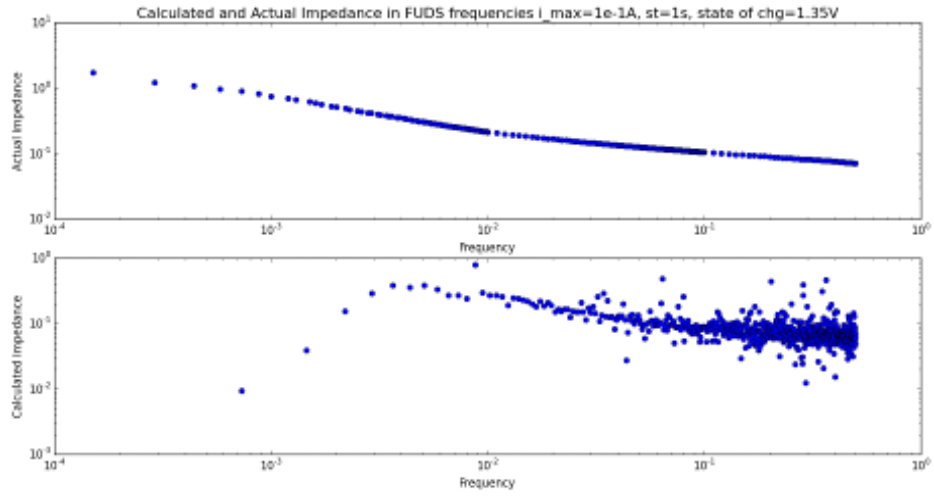


Fig. 3. 23: Magnitudes of both the measured impedance (top) and calculated impedance (bottom) at 1 s sampling time. The state-of-charge of the battery is 1.35V.

To observe whether state of charge has an impact on the measurement or not, the same measurements have been done with the same NiCd battery of which SOC is 1.25 V.

The Nyquist and Bode plots of that measurement are indicated in Fig. 3.24 below.

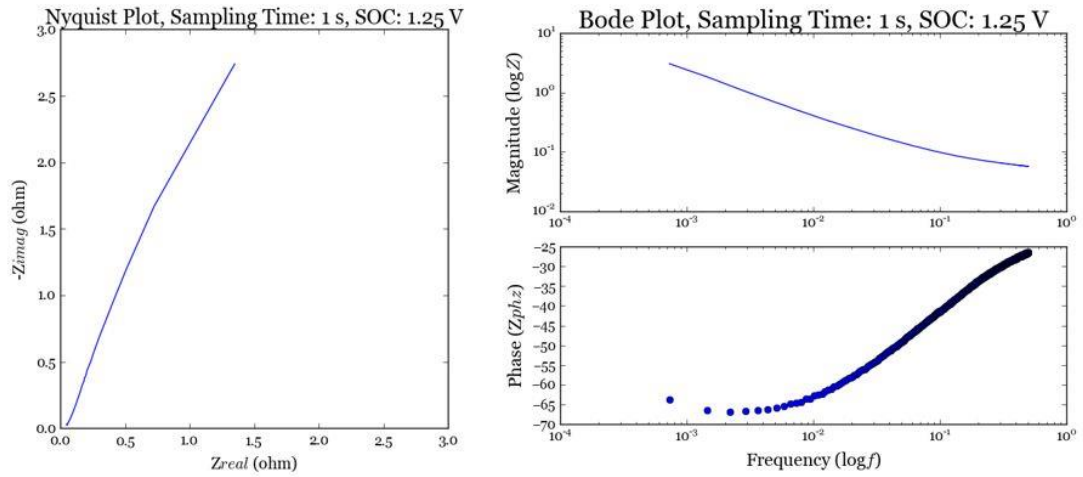


Fig. 3. 24: The Nyquist and Bode plots of the NiCd battery at 1 s sampling time. The state-of-charge of the battery is 1.25V.

Amplitude comparison of measured and calculated impedance for the one with 1.25 V SOC is shown in Fig. 3.25.

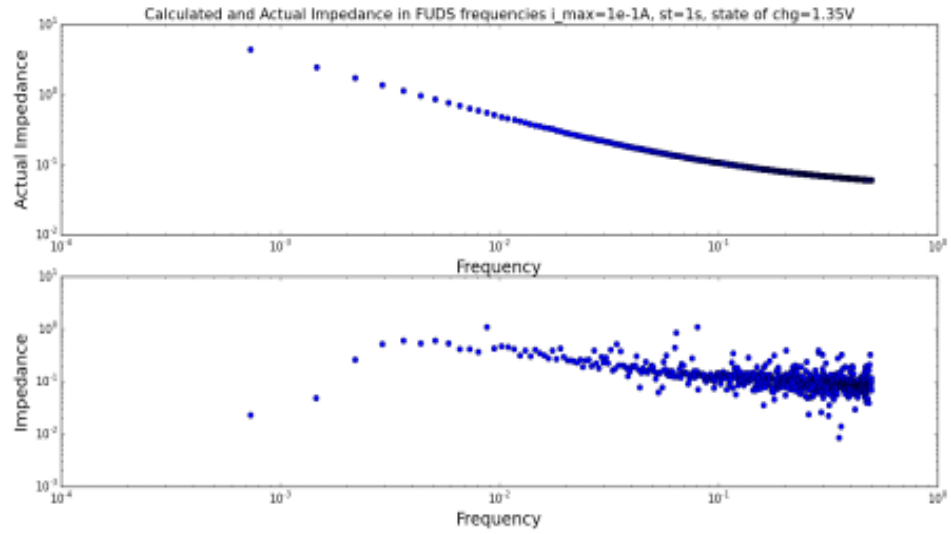


Fig. 3. 25: Magnitudes of both the measured impedance (top) and calculated impedance (bottom) at 1 s sampling time. The state-of-charge of the battery is 1.25V.

As an elucidation, the calculated impedance data have been acquired after the voltage had been edited by performing background subtraction with `scipy.signal.detrend` function. The actual and calculated data have similar trend in graph but still it has to be worked on it to solve problem in low and high frequency sides.

3.12. Full Cycle:

As it is introduced in the aim part of the thesis, the method comprises three steps. These are the following: First is to carry the current profile into frequency domain by the Fourier Transform. Second is to calculate battery response in the frequency domain by a complex multiplication at every frequency of interest with the impedance spectroscopy data measured. Final is to make a simple inverse transfer of previously calculated battery response into the time domain. At the end, it is claimed that the battery response in the beginning will be obtained. Since the method follows cyclic way, it is named as full cycle. The measurements have been done with three sampling

times, these are 0.01, 1 and 10 s and at two different state of charges which are 1.25 and 1.35 V, as well. Here, the measurements with 10 s sampling time are not shown for each full cycle sections to reduce excessive amount of graphs.

3.12.1. Returning to time domain:

The Fig. 3.26 shows measured voltage from FUDS profile experiment versus time, calculated voltage, which has been obtained by complex multiplication of current and impedance versus time, and lastly, current versus time curves at 0.01 s sampling time.

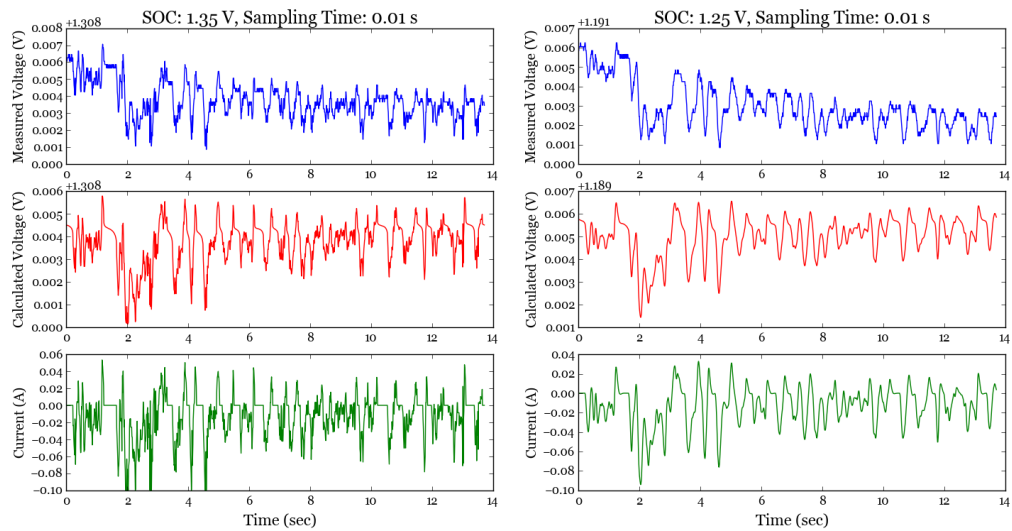


Fig. 3. 26: Top: The measured voltage response to the applied FUDS profile. Middle: The calculated voltage response obtained via the Full Cycle method. Bottom: The current data. All measurements done here have 0.01 s sampling time. Left column: The state-of-charge of the battery is 1.35V. Right column: The state-of-charge of the battery is 1.25V.

Fig. 3.27 involves the same type of graphs with the above one but here the sampling time is 1 s.

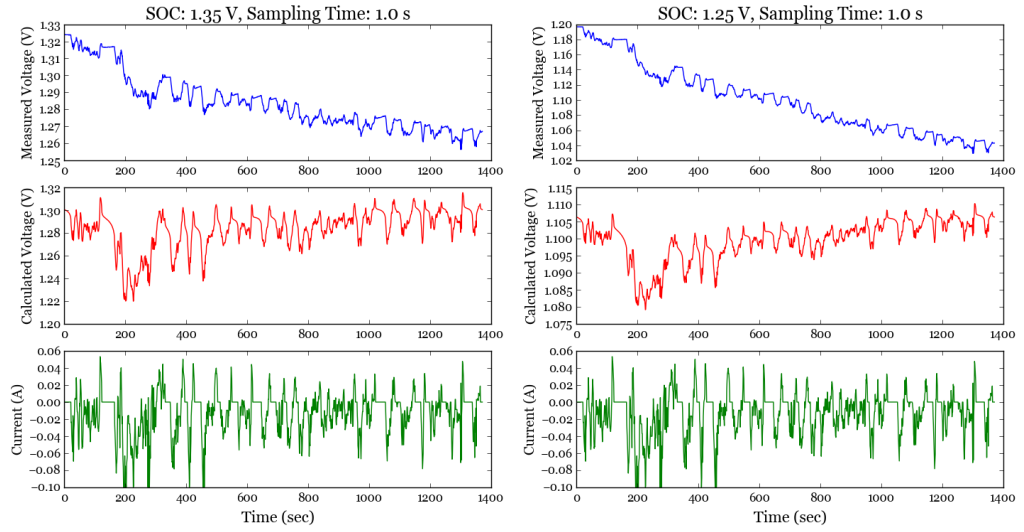


Fig. 3. 27: Top: The measured voltage response to the applied FUDS profile. Middle: The calculated voltage response obtained via the Full Cycle method. Bottom: The current data. All measurements done here have 1 s sampling time. Left column: The state-of-charge of the battery is 1.35V. Right column: The state-of-charge of the battery is 1.25V.

In order to compare calculated and measured voltage in more convenient way the measured and calculated voltage values has been plotted in the same graph. As it is seen in Fig. 3.28 and 3.29 below the right y-axis belongs to the calculated voltage and the left one belongs the measured voltage.

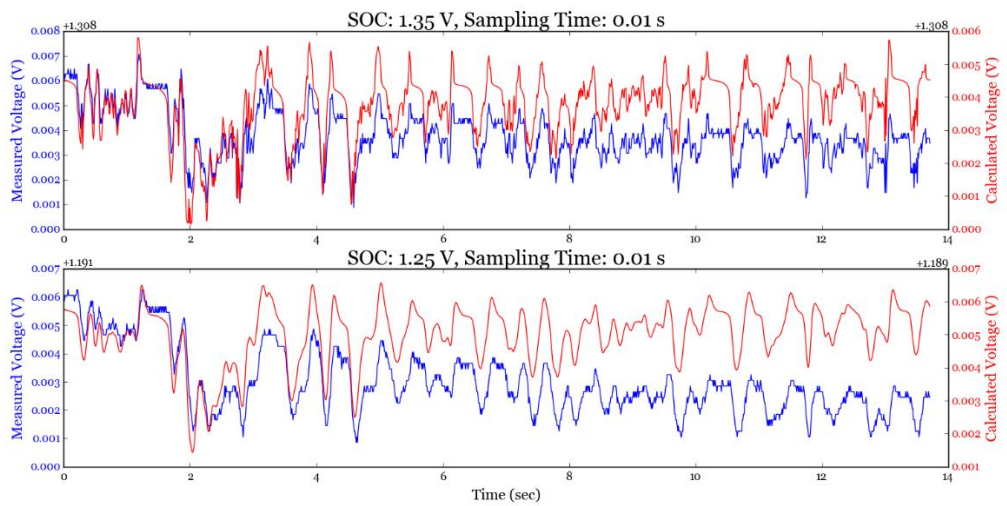


Fig. 3. 28: The measured voltage responses to the applied FUDS profile (left y-axis - blue) and the calculated voltage responses (right y-axis - red) at 0.01 s sampling time are shown here. In the top plot the state-of-charge of the battery is 1.35 while it is 1.25V in the bottom plot.

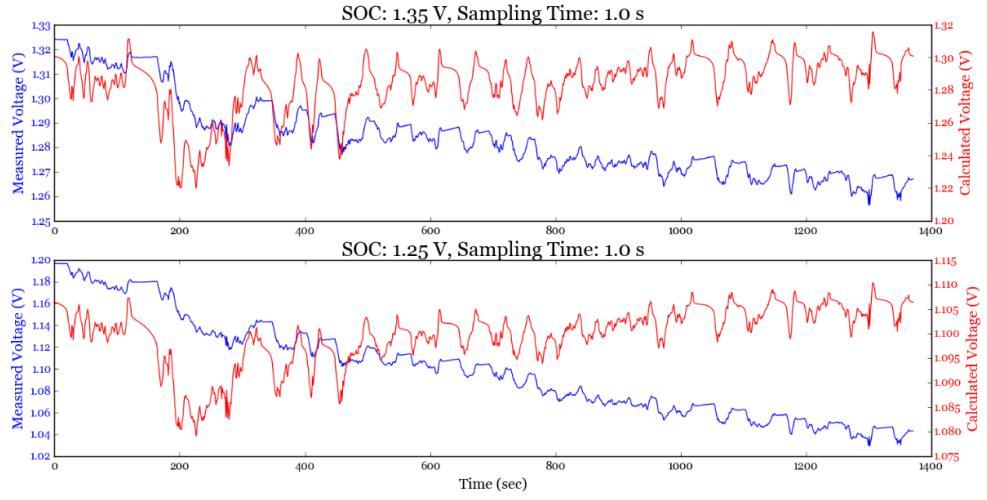


Fig. 3. 29: The measured voltage responses to the applied FUDS profile (left y-axis - blue) and the calculated voltage responses (right y-axis - red) at 1 s sampling time are shown here. In the top plot the state-of-charge of the battery is 1.35 while it is 1.25V in the bottom plot.

Based on the data and the plots shown above, it is clear that the fast moving part of the data can be clearly modeled using our approach. However, the slower part, mostly related to the self-discharge of the battery, is not well explained, nor properly subtracted from the measured voltage profile.

3.12.2. Difference of the measured and calculated voltage in time domain:

After transferring the calculated voltage data into time domain, it has been subtracted from the measured voltage data and their differences have been plotted as in Fig. 3.30.

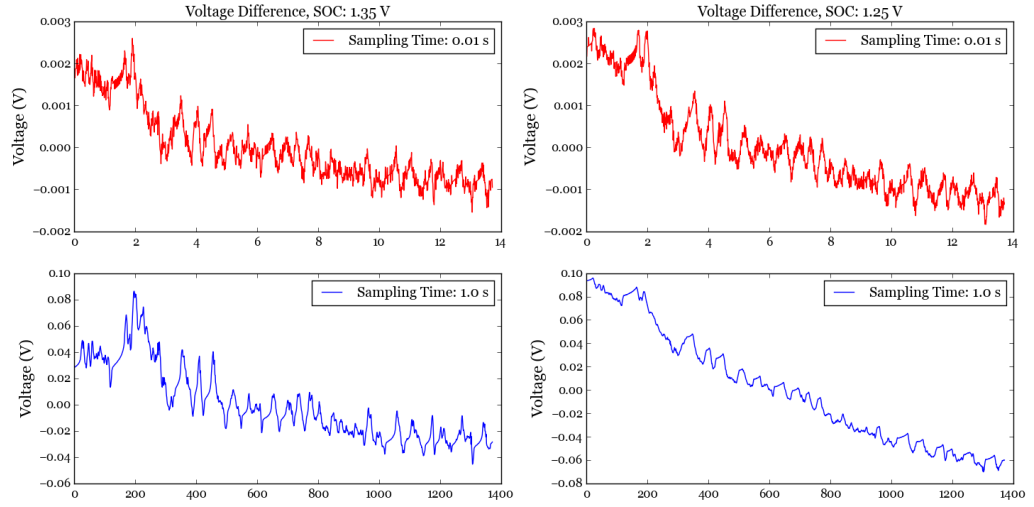


Fig. 3. 30: Residual voltage obtaining from the subtraction of the calculated voltage response from the measured ones. Left column: The state-of-charge of the battery is 1.35V. Right column: The state-of-charge of the battery is 1.25V. Top row: The sampling time is 0.01 s. Bottom row: The sampling time is 1.0 s

3.12.2.1. Shifting the calculated voltage data:

Here, the calculated data are shifted as (5, 10, 20, 30, 40, and 50) data points, separately. The subtraction of the calculated voltage data from the measured one has been made with these delay values for only the data of 0.01 sampling time. The data are shown in Fig. 3.31 and 3.32.

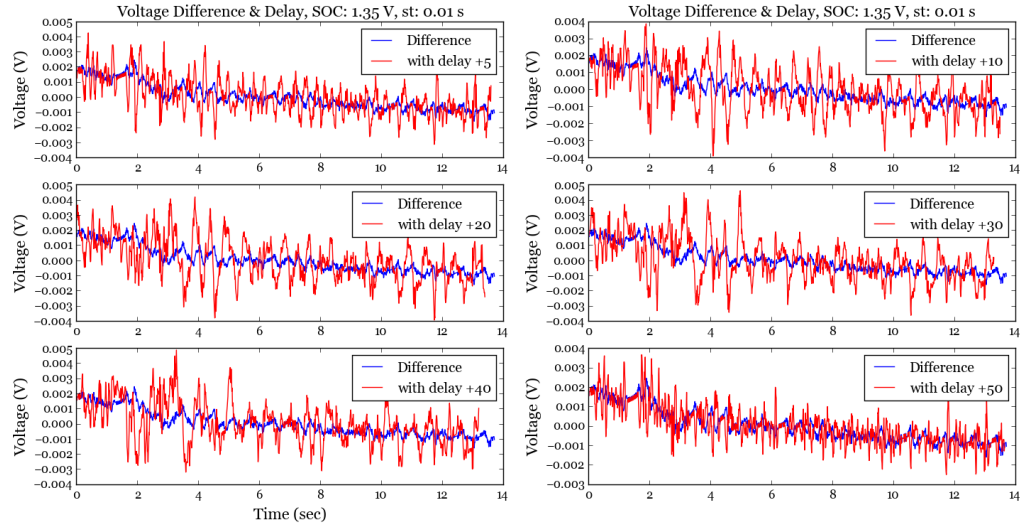


Fig. 3.31: Voltage differences between the calculated voltage response and the measured ones (blue). The voltage difference between the calculated voltage responses, which have been shifted with +5, 10, 20, 30, 40, and 50 points delay, and the measured one (red plot). For all the state-of-charge is 1.35V.

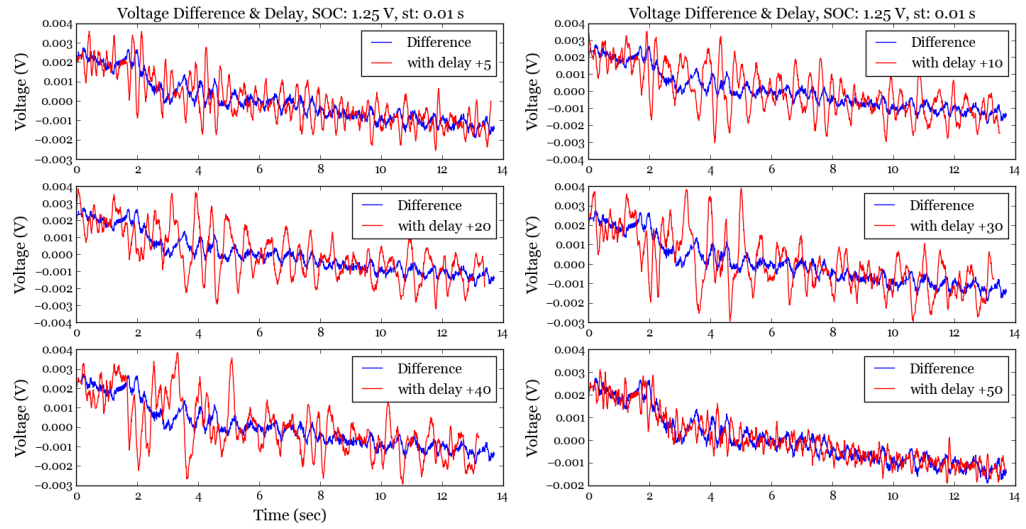


Fig. 3.32: Voltage differences between the calculated voltage response and the measured ones (blue). The voltage difference between the calculated voltage responses, which have been shifted with +5, 10, 20, 30, 40, and 50 points delay, and the measured one (red plot). For all the state-of-charge is 1.25V.

3.12.3. Comparing measured and calculated voltage in frequency domain:

To examine deeply what it has been obtained both the measured and calculated voltage have been plotted at frequency domain as portrayed in Fig. 3.33 and 3.34. As it is known, they have complex numbers in frequency domain. Thus, the real and imaginary parts of both have been plotted, separately.

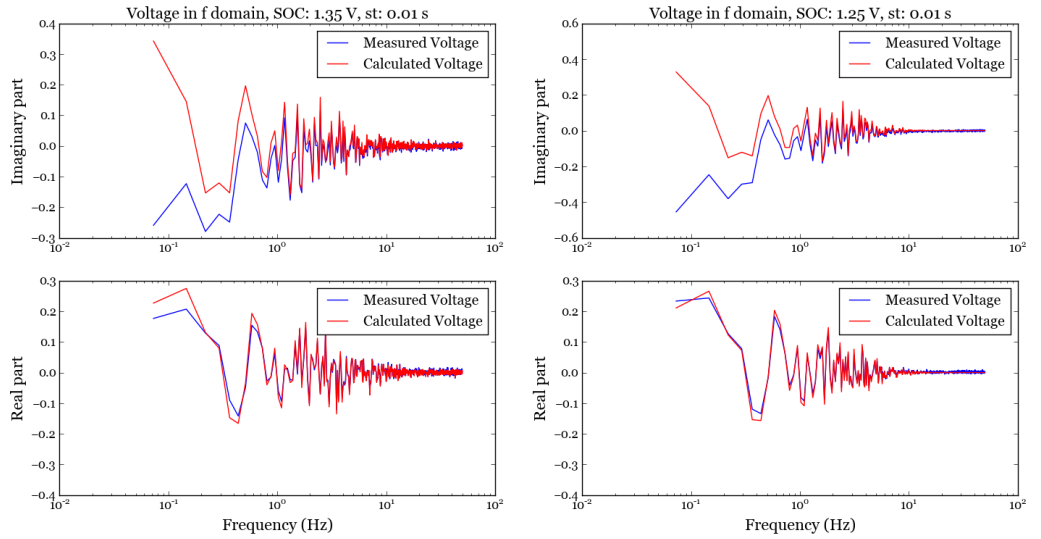


Fig. 3. 33: Imaginary and real part of both the calculated and measured voltage response in frequency domain. All have 0.01 s sampling time. The state-of-charge is 1.35V in the left column whereas it is 1.25V in right column.

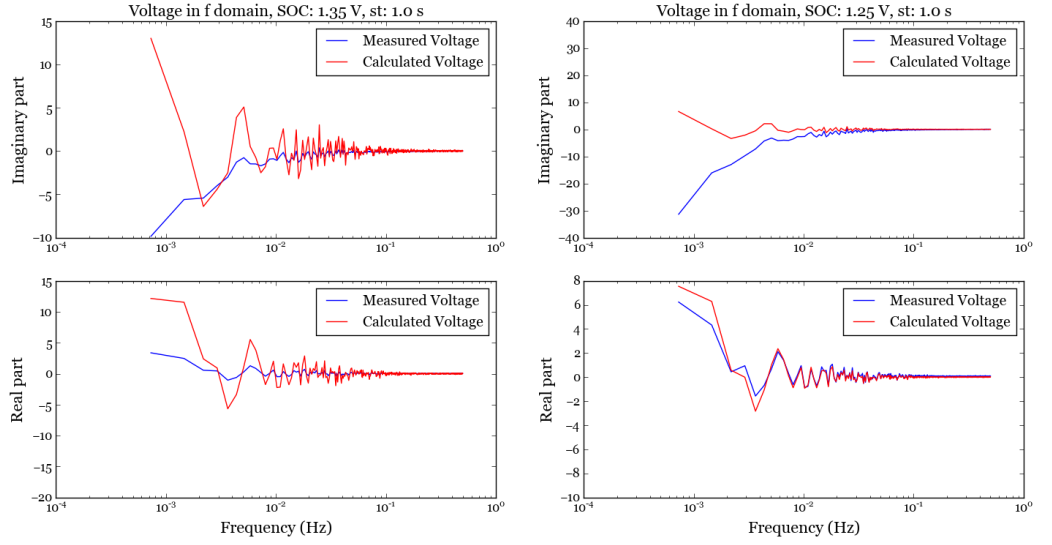


Fig. 3. 34: Imaginary and real part of both the calculated (red) and measured (blue) voltage response in frequency domain. All have 1.0 s sampling time. The state-of-charge is 1.35V in the left column whereas it is 1.25V in right column.

Generally it seems we can get almost same value for real part, however, for imaginary part some dissimilarities are observed at low frequency side.

Moreover, the followings are the voltage comparison in Bode plots and phase angles in radians of these voltage values.

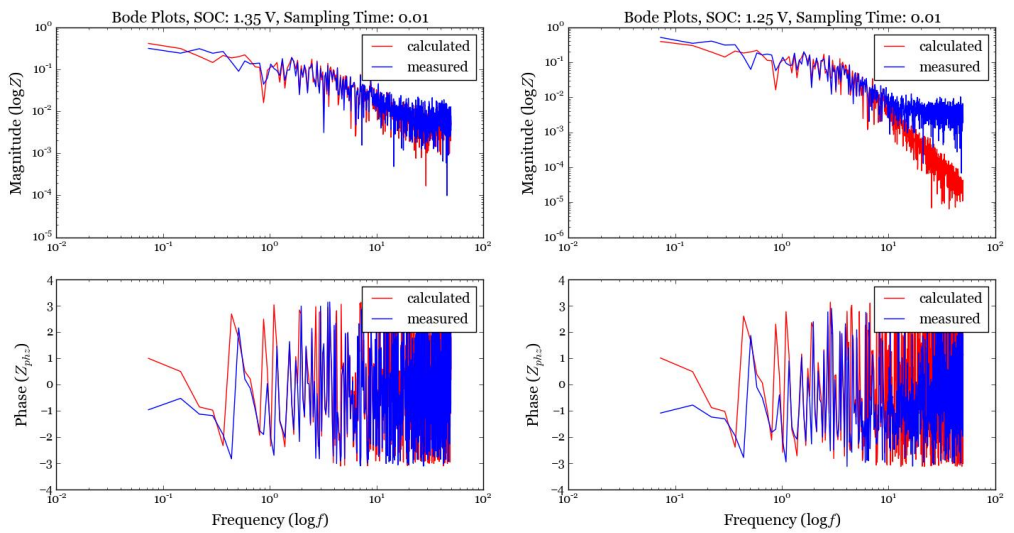


Fig. 3. 35: Bode Plots of both the calculated and measured voltage responses. For all, the sampling time is 0.01 s. The state-of-charge is 1.35V in the left column whereas it is 1.25V in right column.

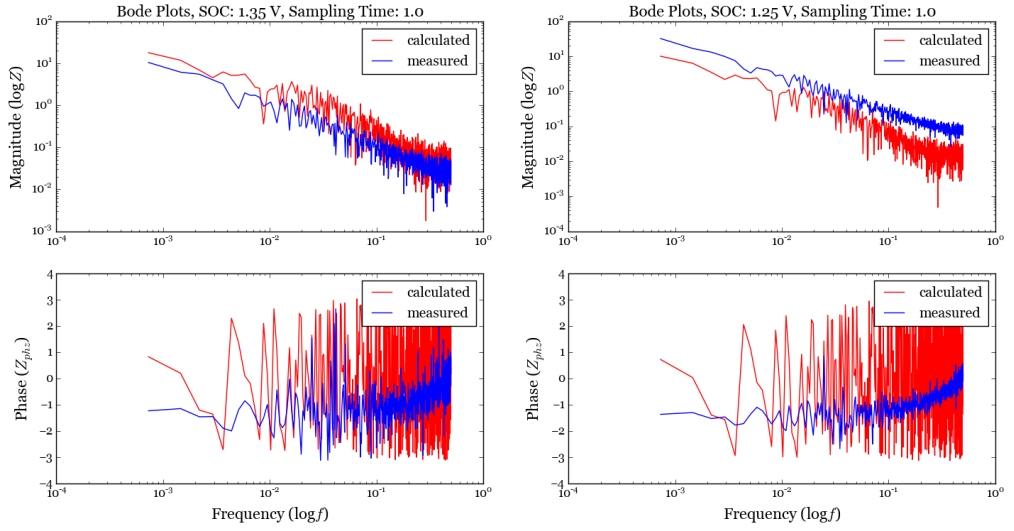


Fig. 3. 36: Bode Plots of both the calculated and measured voltage responses. For all, the sampling time is 1.0 s. The state-of-charge is 1.35V in the left column whereas it is 1.25V in right column.

It was concluded that the observed dissimilarities in both imaginary part and phase of voltage may be due to the failure in elimination of self-discharge of the battery.

3.13. Discharging the battery with constant current mode:

In order to analyze the self-relaxation of the battery and to determine its amount of decrease it has been decided to discharge the battery with a constant current. The current value has been obtained by taking average of the maximum current values in FUDS profile. That is 12.74 mA. It has been expected that the voltage values obtained from discharge process has approximate values with the one in the self-relaxation of the battery during the FUDS measurements. However, the voltage decreased rapidly and reached the voltage limit which is a need for protection of battery itself. Thus, it stopped without completing the determined maximum discharge time. At first the voltage limit was determined as 1 V, then it was changed as 0.9 V. Finally, it was determined as the least value, namely 0.1 V. Although the voltage limit has been

decreased to 0.1 V, the discharge process still has finished earlier than it should be. Thus, in addition to decreasing the voltage limit the current value has been also decreased hundred times, namely it turned to 0,127 mA.

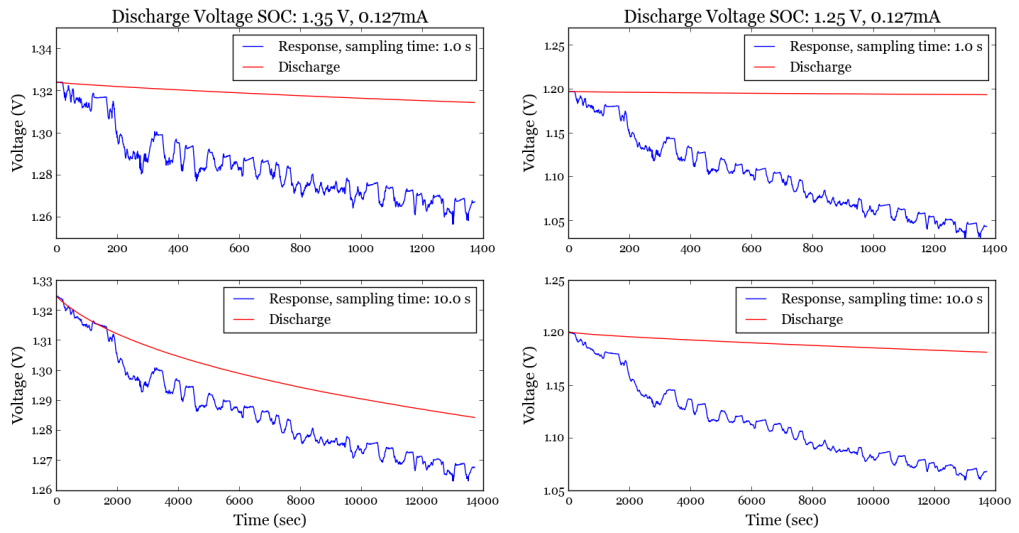


Fig. 3. 37: Discharge curve at 0.127 mA (red) and the measured voltage response (blue) to the FUDS profile. In the left column, the state-of-charge is 1.35V while it is 1.25V in the right column. For the top row, the sampling time is 1.0 s whereas it is 10 s for the bottom row.

However, it has been observed from the graphs that this current value was too small to discharge. Then, the current value has been doubled and the new current value became 0.255 mA.

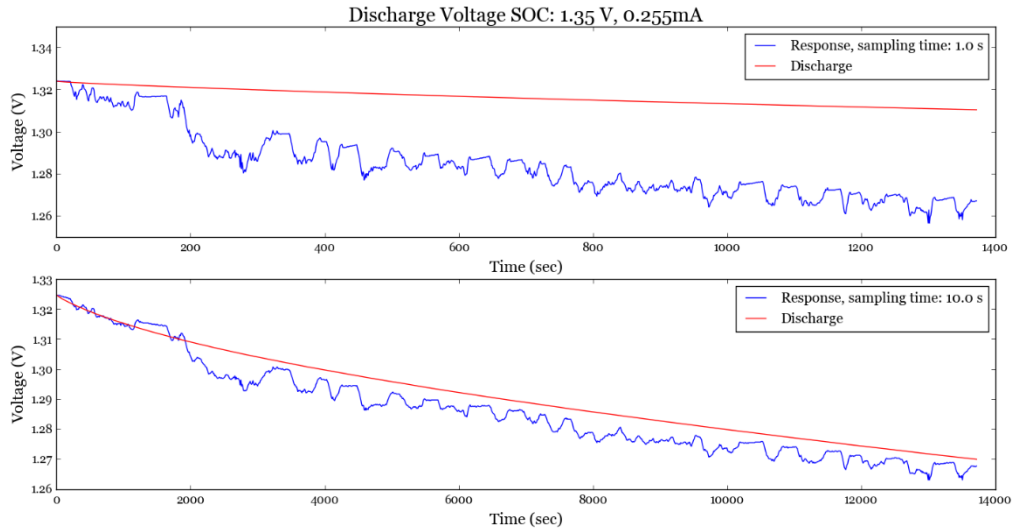


Fig. 3. 38: Discharge curve at 0.255 mA (red) and the measured voltage response (blue) to the FUDS profile. The sampling time is 1.0 s for the top, and 10.0 s for the bottom. The state-of-charge for both is 1.35V.

As it can be seen in the graphs the same current value does not give better result for each sampling time and state of charge. It seems that it is needed to arrange current values for each sampling time by trying several current values to find the best discharge curves that fit the FUDS profile.

3.14. Leaving the batteries resting for reaching their own equilibrium:

In order to analyze the batteries' own equilibrium the voltage of the batteries has been observed until they reach a constant value. It has been started with two batteries of which state of charges 1.35 V and 1.25 V, separately. Reaching a particular constant value took about 35 days. At the end they both remain unchanged at 1.16 V.

3.15. FUDS profile measurement with a battery having state of charge as 1.16 V:

After obtaining equilibrium value of the batteries, the FUDS profile measurements have been begun to make with them. First, the battery has been charged to 1.16 V and then, made FUDS profile measurements with two different sampling time, these were as usual, 0.01 s and 1 s. Moreover, the experiment has been conducted as two runs with two batteries, A and B. The data are presented in Fig. 3.39 and 3.40.

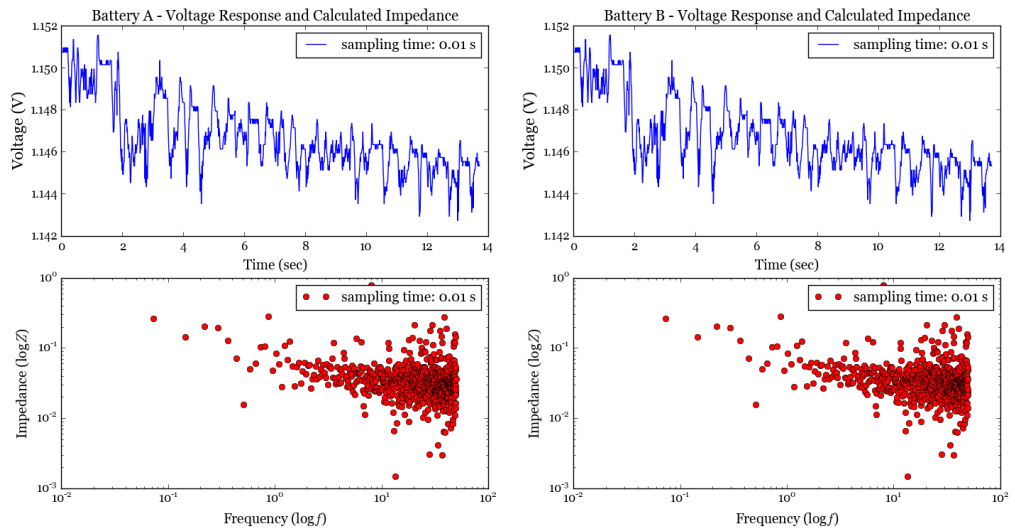


Fig. 3. 39: (Top - blue) the voltage responses of the battery to the applied FUDS profile and (bottom - red) magnitudes of their calculated impedance. The state-of-charge of the batteries is 1.16 V here and the sampling time is 0.01 s. Left column belongs to the battery named A while right column represents the battery named B.

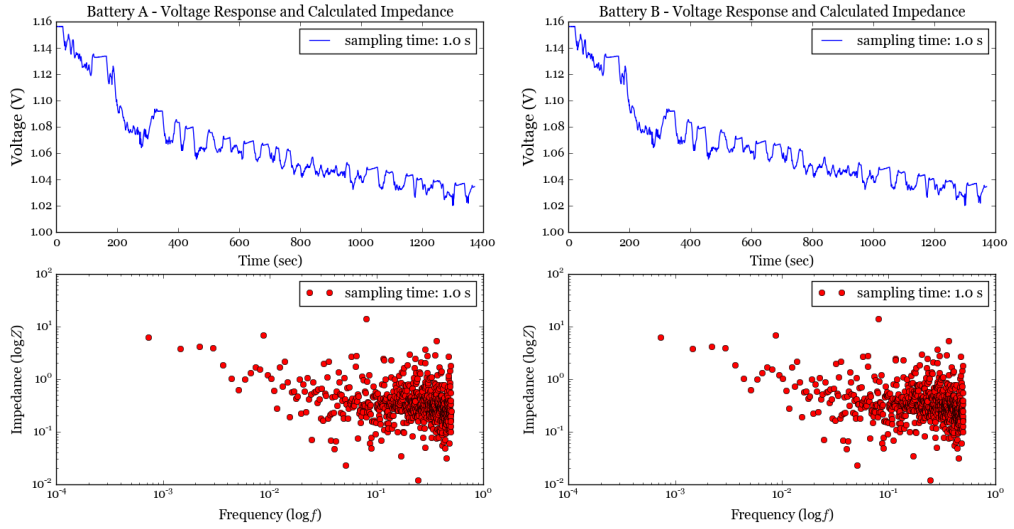


Fig. 3. 40: (Top - blue) the voltage responses of the battery to the applied FUDS profile and (bottom - red) magnitudes of their calculated impedance. The state-of-charge of the battery is 1.16 V here and the sampling time is 1.0 s. Left column belongs to the battery named A while right column represents the battery named B.

As a next step for this section it is needed to measure impedance by Gamry after charging the battery 1.16 V. Then, the full cycle can be completed. However, the results does not seem to be promising.

To conclude, for NiCd batteries various methods that are explained in details in previous sections for getting rid of the self-discharge of the battery have been intensively worked on after determining the appropriate capacity value. However, it has been deduced that it is not easy to eliminate the self-discharge of the NiCd batteries for now. Further studies are needed to be accomplished.

After all studies about the NiCd batteries, the methods developed and the lessons learned from this experience is applied to systems where self-discharge processes are less relevant.

Chapter 4

4. Further Development of the Model Using Batteries of Different Chemistries and Supercapacitors with Minimal Self-Discharge

(This part is also described in *Elif Özdemir; Can Berk Uzundal; and Burak Ulgut, “Zero-Free-Parameter Modeling Approach to Predict the Voltage of Batteries of Different Chemistries and Supercapacitors under Arbitrary Load” Journal of the Electrochemical Society 2017 164: A1274-A1280.*

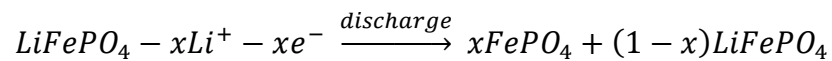
“Reproduced with permission from J. Electrochem. Soc., 164: A1274-A1280. Copyright 2017, the Electrochemical Society.”)

Performance modeling of electrochemical energy storage systems is gathering increasingly higher attention in recent years. With the ever increasing power demand of mobile applications, predicting voltage behavior under different load profiles is of utmost importance for communications, automotive and consumer electronics. The

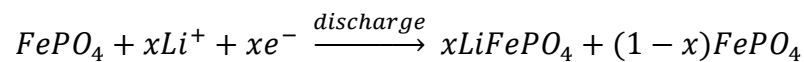
ideal modelling approach needs not only to accurately predict the response of the battery, but also be robust, easy to implement and have low computational complexity. We will present a new algorithm that is algebraically straightforward, that has no adjustable parameters and that can accurately predict the voltage response of batteries and supercapacitors. The approach works well in a variety of discharge profiles ranging from simple long DC discharge/charge profiles to pulse schemes based on drive schedules published by regulatory bodies. Our approach is based on Electrochemical Impedance Spectroscopy measurements done on the system to be predicted. The spectrum is used in the frequency domain without any further processing to predict the fast moving portion of the voltage in the frequency domain. DC response is added in through a straightforward lookup table. This widely applicable approach can predict the voltage of with less than 1% error, without any adjustable parameters to a large variety of discharge profiles.

In order to test the validity of our approach, two kinds of batteries with different chemistries (LiFePO₄ and NiMH) and a supercapacitor was chosen to be representative of different energy storage systems.

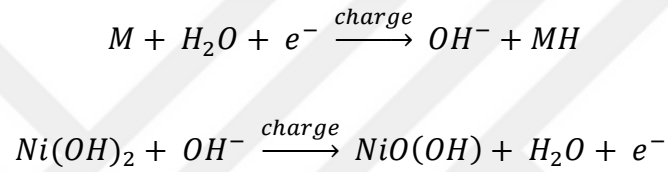
In LiFePO₄ batteries, the discharge process makes Li ions extracted from the negative electrode, which is *LiFePO₄*, for insertion into the positive electrode [62]:



Then, the insertion process of lithium ions into the positive electrode, *FePO₄* is [62]:



In the charge process these reactions take place inverse direction. In NiMH batteries, the negative electrode is $NiMH$, which is a hydrogen-absorbing alloy, while the positive electrode is nickel hydroxide ($Ni(OH)_2$), electrochemically reversible with nickel oxide hydroxide ($NiO(OH)$) [63]. In the charging process, water splits into hydrogen and hydroxyl ion and hydrogen ion reacts with the metal in the negative electrode and forms MH while the hydroxyl ion reacts with the positive electrode $Ni(OH)_2$ for the formation of $NiO(OH)$ [63]:



The route is inversed as the discharge takes place. The working principle of supercapacitors has been mentioned in Introduction. Besides, all details about how to conduct the experiments have been explicated in Measurements chapter.

4.1. Modeling Methodology:

The modeling methodology is broken into two separate but equally important parts given the discharge profiles. The AC part (any fast moving current or voltage) of the response is calculated in the frequency domain based on the impedance spectrum of the system to be modeled. The DC part (the equilibrium voltage of the battery as a function of its SOC) is added in an additional step, using a simple map of voltage as a function of SOC, which is commonly done in the literature [64].

The AC part of the voltage response is calculated based on a frequency domain complex multiplication. The arbitrary current profile is Fourier transformed to yield

the current as a function of frequency along with the corresponding frequencies. In order to calculate the voltage at the frequencies of interest, impedance values at all required frequencies are measured. Complex impedance values are then multiplied by complex frequency domain current values to yield an expected complex voltage response in the frequency domain. At this point, a simple inverse Fourier transform is performed to obtain the fast moving part of the time domain voltage response. The DC part of the voltage is then added using a map of SOC vs. DC voltage. This map is measured using a low current discharge as explained in the Experimental section. In order to employ this map, the overall charge (Q) as a function of any time point (j) in the discharge profile is calculated by a sum of current (I) of the profile multiplied by time intervals (Δt) at all points (i) up to the time point (i).

$$Q(j) = \sum_{i=1}^j I(i) * \Delta t$$

The resulting charge values are then matched to corresponding voltage values in the map of SOC vs. DC voltage. The DC voltages are added to the fast moving part calculated above to yield the final result.

4.2. Results and Discussions:

Three types of samples studied have distinctly different impedance spectra in the relevant frequency region. These spectra are shown in Fig. 2.4. in Experimental part. The 350F shows a distinctly more capacitive spectrum where as two battery systems chosen show a more resistive character. Differences in the EIS data are only relevant

to the present study in showing the wide applicability of the model and they are presented as evidence of the said issue.

Fig. 4.1, 4.2, and 4.3 show comparisons of the calculated voltage and the measured voltage overlaid on each other for LFP, 350F and NiMH respectively with all three discharge profiles studied.

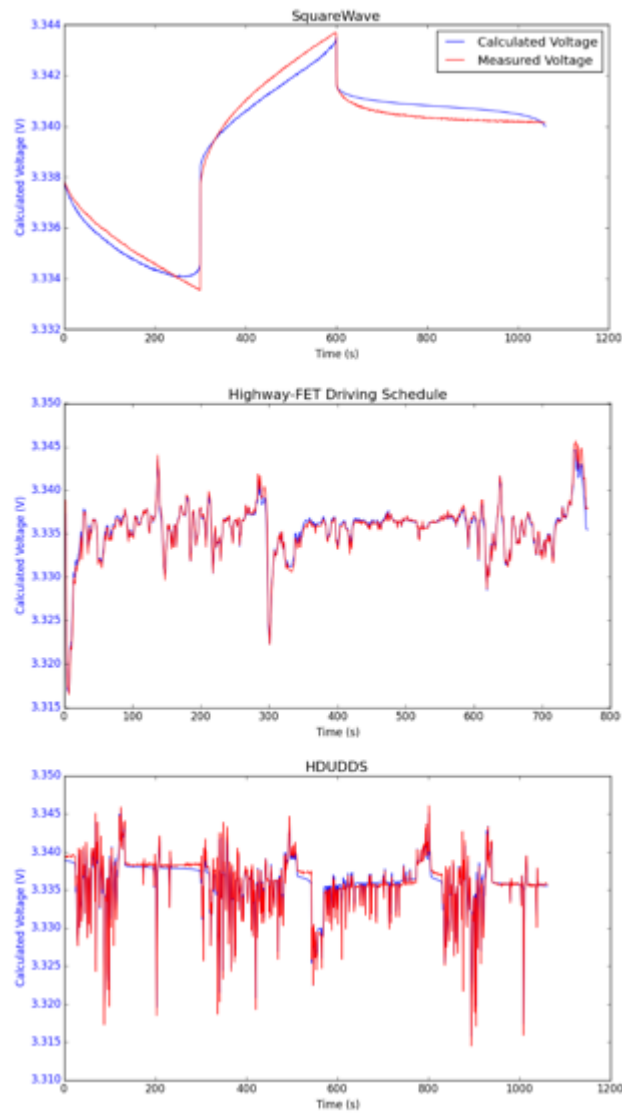


Fig. 4. 1: The response of LFP (in red) and the predicted value (in blue) for three profiles. Squarewave applied at 22 mA and both Highway-FET and HDUDDS applied at 220 mA.

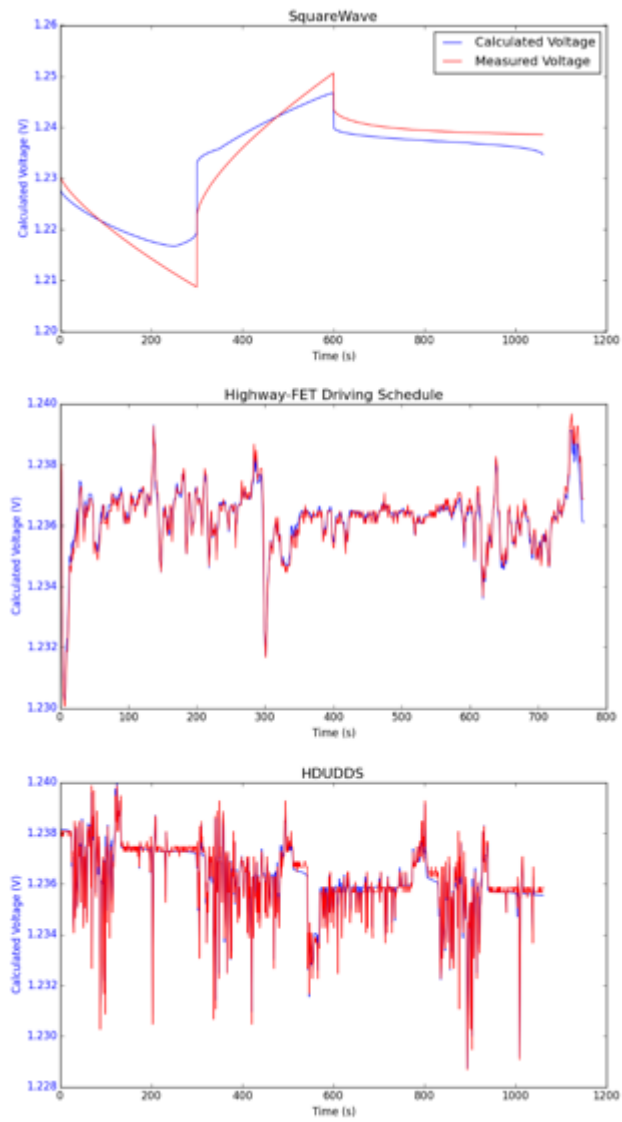


Fig. 4. 2: The response of NiMH (in red) and the predicted value (in blue) for three profiles at 120 mA.

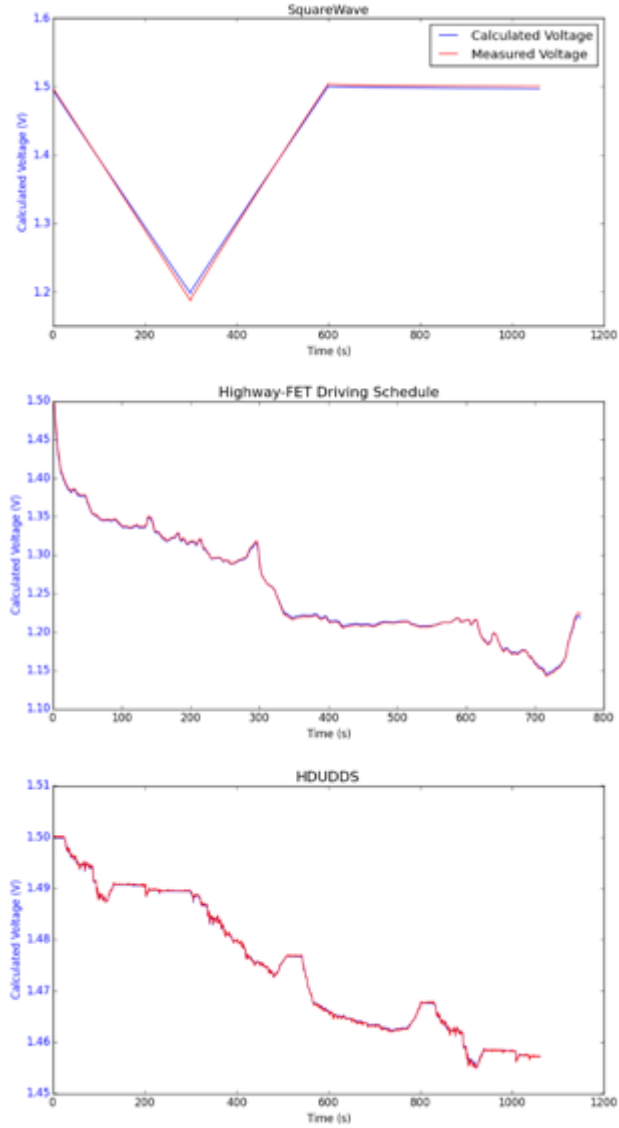


Fig. 4. 3: The response of 350F (in red) and the predicted value (in blue) for three values at 350 mA.

In all cases, the prediction error is less than 1%. In the HDUDDS and Highway FET profiles, errors are much less than 1% as shown in Table I.

Table I. Error table of three different systems with three different profiles:

	LFP	NiMH	350F
HighwayFET	< 0.08 %	< 0.33 %	< 0.04 %
HDUDDS	< 0.08 %	< 0.22 %	< 0.03 %
Squarewave	< 0.03 %	< 0.91 %	< 0.92 %

The success of the predictions is impressive given the algorithm has no adjustable parameters and is only based on measurements of DC Voltage vs. SOC and a proper impedance spectrum. Using these two datasets and nothing else, the response of the battery is predicted with a model that relies on straightforward algebra and with minimal computational complexity. This model can be used to predict the performance of batteries under arbitrary load without any adjustable parameters.

Below, we will discuss our various results and compare the effects of certain issues on the performance of the predictive power of the approach.

4.2.1. Details of the energy storage chemistry/mechanism:

The approach presented in the current work has no implications or assumptions regarding the underlying mechanism of the electrochemistry of energy storage. As the impedance spectrum is measured and is used directly without any fits or modeling, the details of neither the impedance spectrum, nor the electrochemistry within compromise the wide applicability of the model. Since the approach presented only relies on the measured parameters through impedance spectroscopy and a slow discharge without any assumptions about neither, it is expected to work irrespective of the sample. The NiMH, LFP and the 350F are modeled equally as well with minimal error. This clearly shows that the approach is fundamentally sound and can predict the voltage response of the system. As demonstrated by the successful predictions across different systems with different electrochemical energy storage chemistries and mechanisms, the approach described here is applicable to batteries of various chemistries as well as supercapacitors.

4.2.2. Discharge profile:

Three discharge profiles that are studied are chosen such that they have very fast moving parts in addition to relatively long and constant portions. Even though the approach works in a way that errors are less than 1% for all cases, as seen from the table, Squarewave is the one with the largest error. The main reason for this larger than others error is non-linearity of the fast moving part of the profile as explained in the next section.

4.2.3. Non-linearity:

One major assumption in the present report is that the system is linear. This assumption is warranted given the current algorithm relies heavily on the ability to measure a valid impedance spectrum of the system using the standard methods. Linearity of the system measured is an underlying assumption in doing any EIS measurement [65]. The AC part of our approach cannot capture those nonlinearities that are not present in the EIS measurement, even though the DC part of the model does not have any linearity requirements.

The frequency domain response of the profile that is used to test slow moving performance of the approach has a distinct peak in the frequency domain that dominates the response³. The amplitude at this frequency corresponds to a very large modulation that cannot be accurately explained with the linear EIS measurement that was done. This is the reason for the discrepancy that is higher than the other profiles which have a more uniform structure in the frequency domain. As a check for this

³ At 1/600 s frequency. This is simply because of the way the profile is constructed. Data not shown.

phenomenon, Squarewave for LFP is shown in Fig. 4.1. The error for this case is much smaller. For comparison, the Squarewave data for LFP at 220 mA is shown in Fig. 4.4.

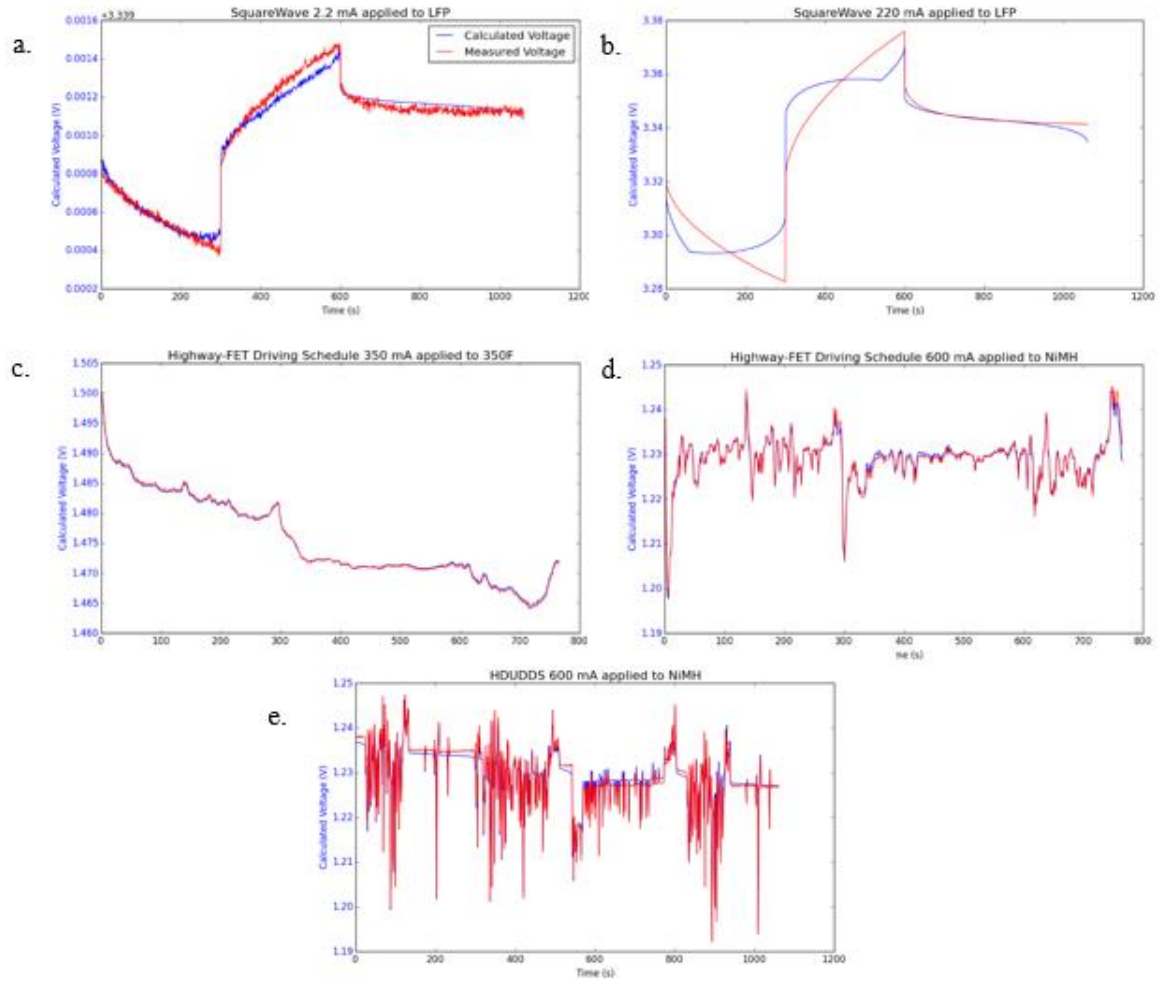


*Fig. 4. 4: Selected experiments with varying amplitudes across different systems: **a.** Squarewave profile applied to LFP at 2.2 mA, **b.** Squarewave profile applied to LFP at 220 mA, **c.** Highway-FET applied to 350F at 350 mA, **d.** Highway-FET driving schedule applied to NiMH at 600 mA, **e.** HDUDDS applied to NiMH at 600 mA.*

4.2.4. Variance of EIS characteristics with respect to SOC:

One major assumption in the modeling approach presented herein is that the impedance spectrum does not change appreciably through the period predicted. There are a number of reports in the literature that show that the impedance spectrum varies measurably, albeit not greatly, with the SOC for certain chemistries [66] [67]. Though this variance was not significant in systems and the SOC tested within this work, it is conceivable that this is part of the reason for the observed error. In cases where this variance can potentially effect the results significantly, it can be taken into account using a SOC weighted average of the impedance spectra. In order to confirm that this was not a problem in the present case, the tests were repeated at 3.12 V for the LFP cell. The data can be found in Fig. 4.5. The total error is less than 0.08%, 0.08% and 0.06% for Squarewave, Highway FET and HDUDDS respectively. Thus, the errors are still all less than 0.1%. This shows that in the present case, the above stated assumption is correct.

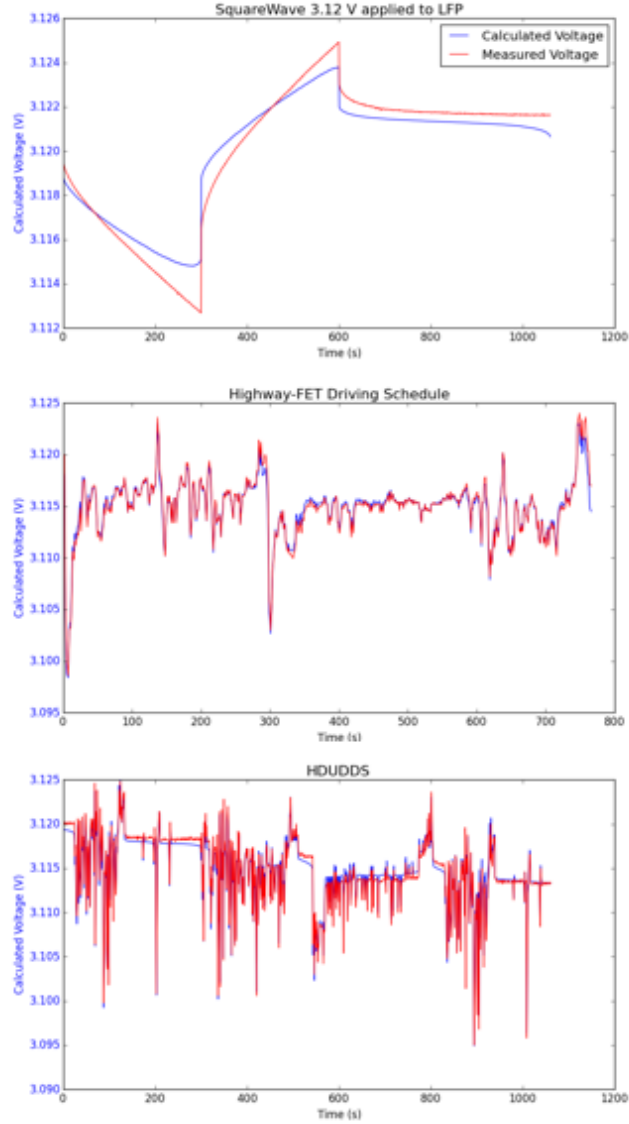


Fig. 4. 5: The profiles repeated for LFP at 3.12V. The current amplitudes are chosen to be the same for the 3.34V experiment

4.2.5. Performance of the approach at different amplitudes:

Tests were repeated at different amplitudes for three systems presented. Selected examples of those tests and the modeling performances are shown in Fig. 4.4. None of the cases have more than 1% error. The data clearly show that, provided linearity is not compromised, the approach is valid across a wide range of amplitudes. In order to test an edge-case scenario to find the limits of the modeling approach, the amplitude

for the test was increased to 2.2A (i.e. 1C discharge rate) for the LFP sample. As shown in Fig. 4.6, the predictions are still within 1% for HighwayFET and HDUDDS, however, the error is 2.1% for the Squarewave signal.

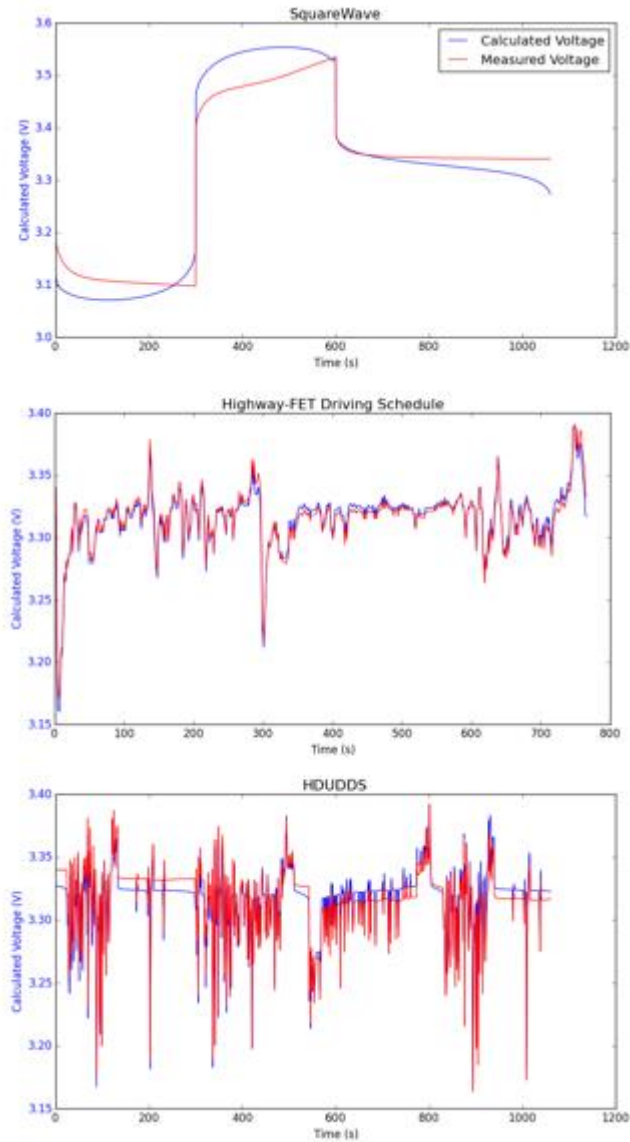


Fig. 4. 6: The response of LFP (in red) and the predicted value (in blue) for 2.2A discharge amplitude for all profiles used in this study. The maximum errors are less than 2.1% for Squarewave, 0.7% for Highway FET, 0.5% for HDUDDS.

As mentioned above for NiMH cell, this is a problem with the nonlinearity of the response. As the signal in the frequency domain gets higher in amplitude, the

contribution from the nonlinear parts of the response start becoming more significant. As mentioned above, this is particularly significant in the Squarewave case since the frequency domain counterpart of the current profile has a very large peak at the frequency $1/600\text{s}$.

4.3. Conclusions:

A new approach to modeling voltage behavior of batteries and supercapacitors is presented. This new approach is independent of battery chemistry or charge storage mechanism and relies on measurements of EIS and slow discharge. The approach is designed to be algebraically straightforward, with low computational complexity and with zero adjustable parameters. The described approach predicts the voltage response in all presented cases with less than 1% error in all and less than 0.3% in cases where linearity is maintained in the frequency domain.

Chapter 5

5. Error Analysis

*(This part is also described in Can Berk Uzundal; **Elif Özdemir**; and Burak Ulgut, “Analysis of Errors in Zero-Free-Parameter Modeling Approach to Predict the Voltage of Electrochemical Energy Storage systems under Arbitrary Load” Electrochemical Society Transactions, in press.)*

The current chapter deals with the sources of error in the prediction approach described in this thesis and looks for the effects of the various sources of error. The current analysis concludes that two big contributors to the overall error are the inaccuracies in the DC part of the prediction and the non-linearities that are not modeled by a linear impedance spectrum.

Discussions are also made regarding ways to improve the performance of the modeling approach the most and where future work is going to be looking to improve.

The developed method has been successful in predicting the response of batteries and supercapacitors across a wide variety of discharge profiles. As was described in the previous chapters, this method is a zero-free-parameter method with straightforward algebra that clearly can predict the voltage response of the electrochemical energy storage system.

However, like in any prediction algorithm, the structure of the errors are worth investigating to not only decrease the errors, but also develop an understanding of the underlying phenomenon deeper. The present contribution is an attempt at investigating the errors and the contributing factors to the said errors.

5.1. Error Analysis

One way to investigate the success of the model is to look at the residuals [68]. The residuals in any fitting or prediction algorithm show if the errors seen are random or systematic. The observation of any systemic structure in the residuals indicate a fundamental part that is missing from the algorithm. Residuals for the model developed across different energy storage systems and the different discharge profiles are shown in Fig. 5.1 bottom. The fact that the residuals are not random and that there is structure in the residuals indicates that a systematic error exists in the model that is developed. Furthermore, the errors visually display more structure in regions where the discharge is stationary.

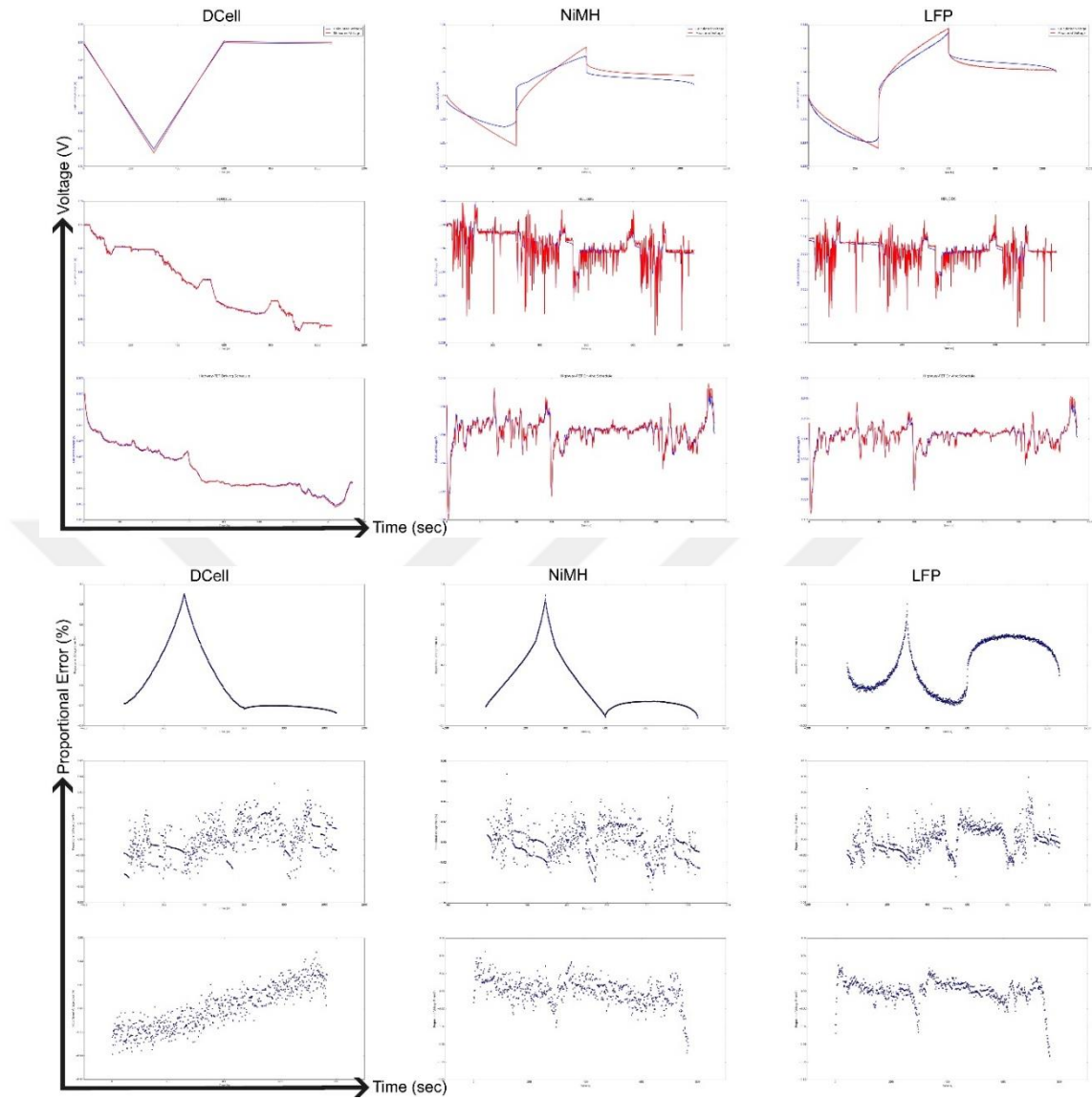


Fig. 5. 1: The calculated results (top) and the fractional error (bottom) of the modeling approach shown. The fractional errors show non-random structure, especially in the Squarewave signal. The columns show the three energy storage systems(350F, the NiMH and the the LiFePO₄, where the rows show three different discharge profiles, squarewave, HDUDDS from EPA and Highway FET from EPA.

The existence of increased structure before the parts with sharp changes in current led us to believe that the reason for the systematic error might be introduced due to the approximation of the Fourier transform through a discrete Fourier Transform [69] [70]. This approximation is necessary for any sampled real system, but the validity is

questionable under certain conditions. In order to validate our methodology, we have performed a numerical test and an experimental check.

5.2. Results & Discussion

The difference between the resulting data and the original data in the numerical test described above is plotted in Fig. 5.2 in a normalized fashion.

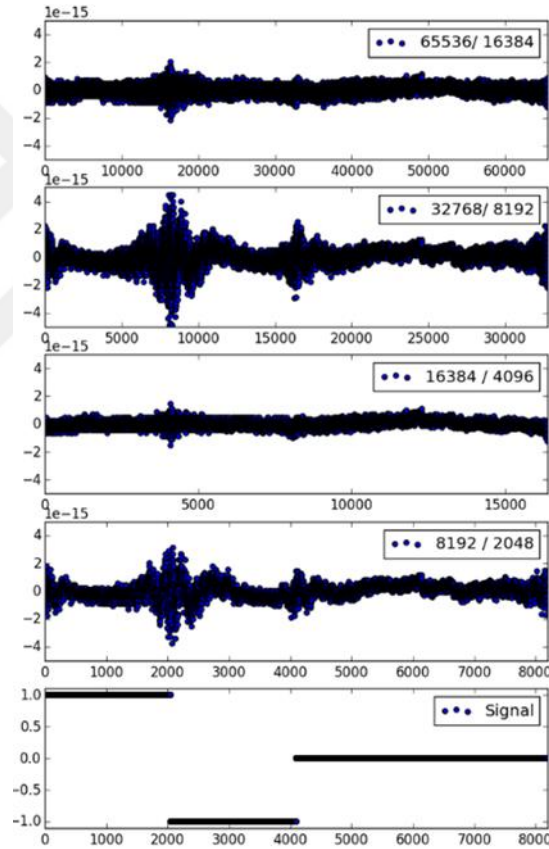


Fig. 5. 2: The results of the numerical test showing that the errors are not improving with improved sampling and that the error magnitude is too small to account for the observed errors.

The results clearly indicate that first, the increased sampling rate doesn't change the errors significantly and second, the overall errors neither have the structure, nor the amplitude to explain the errors that was observed in the results. The exact nature of

the error structure in this numerical experiment is beyond the scope of this study, however, it is curious to observe that the errors seem the worst in regions of the curve where the derivative is undefined.

The sampling issue was also checked experimentally where the same signal was used to measure the response with 0.1 sec, 1.0 sec and 10.0 sec sampling times respectively with different DC maps and different current amplitudes. Across the two orders of magnitude that the sampling rate changed, the changes in the sampling rate do not seem to change the error structure, nor the amplitude by any measure as shown in Fig. 5.3. For clarity, only two DC maps are shown, but this is reproducible across different DC maps and different amplitudes.

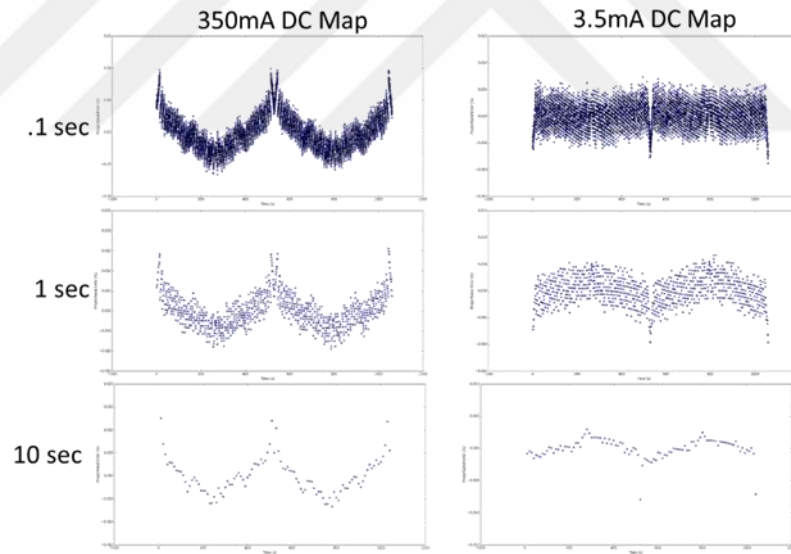


Fig. 5. 3: Experimental verification that changing the sampling rate does not affect the magnitude, nor the structure of the observed errors.

This experiment clearly shows that neither the error structure, nor the amplitude is not a function of the sampling rate.

Both the numerical and the experimental evidence clearly show that within the range of parameters relevant to this system and the approach, the sampling rate is not a major factor in determining the amount nor the structure in the error.

In order to check for effects of linearity, the amplitude of the current pulse used was varied. As the amplitude gets lower, the nonlinearities should start decaying and the verifiably linear impedance measurement should start explaining the behavior of the system more accurately.

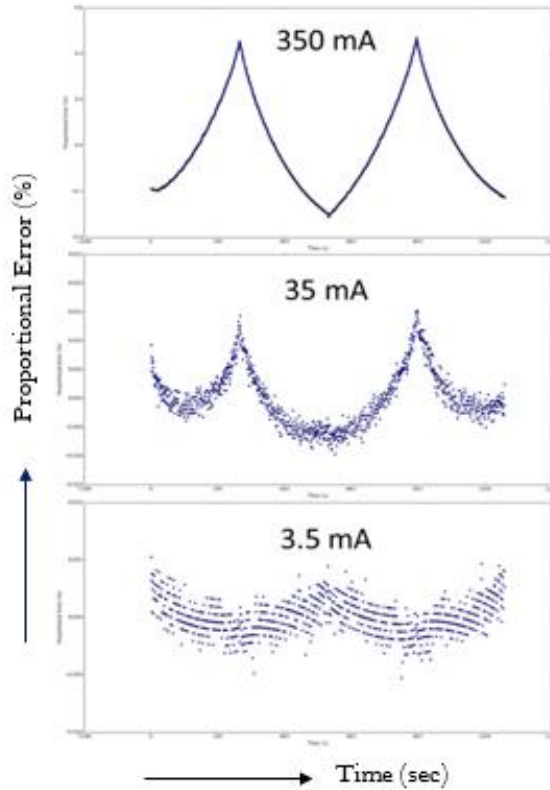


Fig. 5. 4: The observed errors at different current amplitudes. At higher amplitudes, the errors go higher since the nonlinearities get worse with increasing amplitudes

As shown in Fig. 5.4, as the current amplitude decreases, the error starts diminishing in amplitude and the overall structure starts to fade. More work is necessary in the modeling process to incorporate the non-linearities of the system into this approach.

The last effect we have checked is the effect of how the DC map is measured. The DC map is acquired with three different amplitudes, decreasing with factors of 10 from 350mA to 3.5mA. The DC maps obtained are shown in Fig. 5.5.

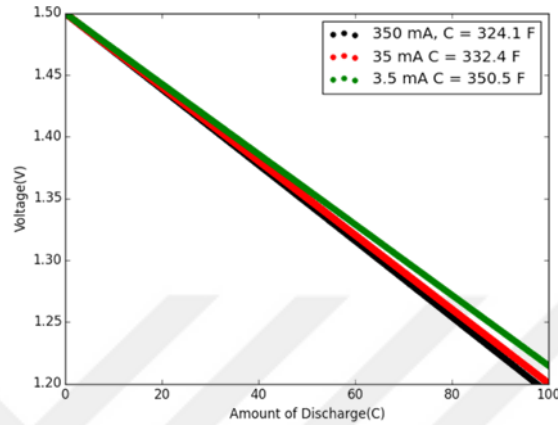


Fig. 5. 5: The cell voltage vs. amount of discharge map for the same 350F supercapacitor measured at different discharge rates. Lower currents result in higher apparent capacitance.

Using simple linear fits, the apparent capacitance of the sample can be calculated. The calculated capacitance for the 350F nameplate supercapacitor is 324.1 F for a DC map measured with 350mA, goes up to 332.4 F for 35 mA and 350.5 F for 3.5mA. The 350F nameplate, as specified by the manufacturer specifies the capacitor using a 72 hour charging and has a precision of +20% / -10%.

Intuitively, the DC map is expected to be more accurate as the DC current used to collect the map goes down, which is shown to be experimentally true as shown in the above discussion. When the error is investigated as a function of the DC map used, the data gathered is shown on Fig. 5.6.

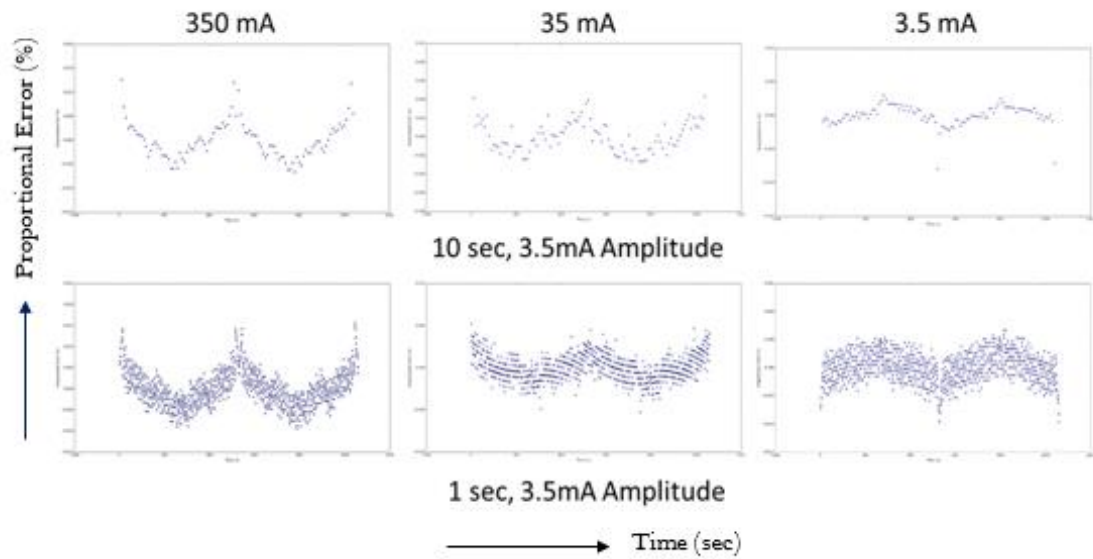


Fig. 5. 6: The effect of the quality of DC map is shown. The current values shown as column headings indicate the current that was used to collect the DC map data.

The magnitude of the error, in addition to the structure seem to decay with the decreasing current that was used to collect the DC map. This is a clear sign that at least part of the structure in the error is due to inaccuracies in defining the cell potential as a function of the state-of-charge.

5.3. Conclusions and outlook

Based on the evaluations presented, the overall error magnitude and the structure seems to be dominated by the accuracy of the DC map in addition to the inaccuracies regarding linearity.

Further research will start looking into incorporating the higher harmonics of the EIS measurement. There is already theoretical work that is published regarding the investigations of higher harmonics [71], that we intend to build upon in the experimental side.

Chapter 6

Future Work

A linear system, in continuous or discrete time, is a system that has the property of superposition: if an input comprises the weighted sum of the various signals, at that point the output is the superposition, namely, the weighted sum, of the responses of the system to each those signals [72]. Mathematically, let $y_1(t)$ be the response of a continuous time system to $x_1(t)$ and let $y_2(t)$ be the output corresponding to the input $x_2(t)$, then, the system is linear if:

- i. The response to $x_1(t) + x_2(t)$ is $y_1(t) + y_2(t)$.
- ii. The response to $a * x_1(t)$ is $a * y_1(t)$, where a is any complex constant [72].

Theoretically, linearity of a given electrochemical system means that there is a constant relationship between the applied voltage and the measured current or vice versa depending on being a potentiostatic or galvanostatic system (recall Ohm's Law). However, in practice, electrochemical cells generally are not linear. In a potentiostatic system, the input is the potential and the output is the current. Doubling the applied voltage does not mean that the measured current will double, as well [73]. The nonlinearity can be result of AC voltage amplitude or applied electrochemical (DC) potential or other factors [73].

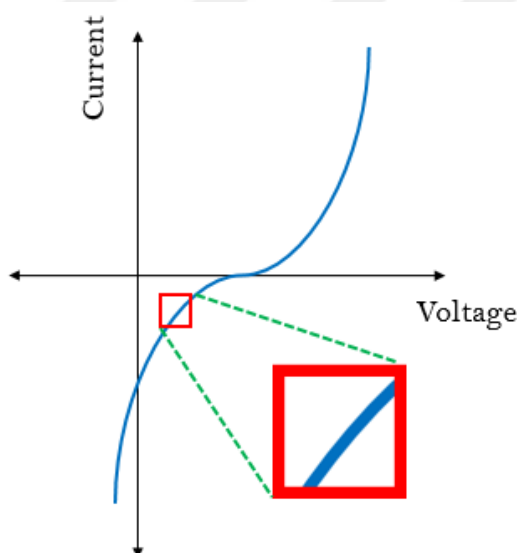


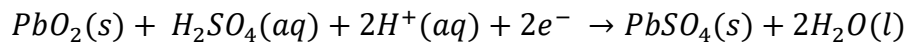
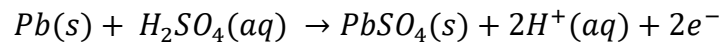
Fig. 6. 1: Characteristic Curve of Current vs Voltage showing its pseudo-linearity.

Although an electrochemical cell is not linear, it can be thought as pseudo-linear at some point as it is shown in the current versus voltage characteristic above [73]. When the AC perturbation is the issue to cause nonlinearity, it can be handled by applying small enough (1 – 10 mV) AC amplitude to catch quasilinear conditions [73]. In fact, the applied signal is sufficiently small to be restricted to a pseudo-linear portion of the cell's current versus voltage curve [73].

Taking into consideration all that, in this thesis, the AC amplitude was chosen from that interval, specifically, 1 mV for LiFePO₄, NiMH and 350F, 10 mV for NiCd (determined by considering signal-to-noise ratio, as well). Nevertheless, the pseudo-linearity of the systems has broken down in the cases of quite slow profile with high amplitudes in a given frequency range, Squarewave, for LiFePO₄, NiMH and 350F. As future work, it is better to overcome the nonlinearity of those systems that can be result of any other factor to widen the applicability of the model.

During the testing of the model, the used batteries and the supercapacitor has been tested as solo. However, it is a well-known fact that several batteries are used together and utilized as pack for many application fields such as electric vehicles [74], backup power sources [75] etc. Thus, another work that is necessary to be done is to apply the model to pack of those tested batteries.

Finally, studying battery systems of which electrolytes participate in battery reactions is necessary to work on to diversify applicability of the model. A well-known example for such battery systems is lead-acid batteries. The reactions that take place in lead-acid batteries are [76]:



As it is realized from the reactions above, the electrolytes lose ions to the electrode during the discharge process. In all battery systems studied in this thesis, namely LiFePO₄, NiMH and NiCd, no electrolyte consumption occurs during charging and discharging [77], and electrolytes enable to transport the ion stream between the electrodes or reduce dendrites formation [78]. It was assumed that the impedance does

not change during the measurements that have been done in this thesis. On the other hand, since the electrolyte participation to the battery reactions might change impedance during measurement, it is quite essential to apply the model to lead-acid battery-like systems, as well, to check applicability of the model to various system.

In order to achieve this modeling, multiple approaches will be checked. The first attempt will be made through dividing the data up into pieces where the impedance is staying pseudo-constant.



Chapter 7

Conclusion

This thesis, as a result of two-year intensive working, exhibits a new approach to modeling voltage behavior of batteries and supercapacitors and also, all steps going through until reaching that final stage of the model in details.

The work has begun with NiCd cells, however, it has been continued with LiFePO₄, NiMH batteries and a supercapacitor due to high self-discharge rate of NiCd cells.

It has been proven that this suggested new approach is independent of battery chemistry or charge storage mechanism. The basis of the approach relies on measurements of EIS and slow discharge. It uses EIS data as-is without fitting any parameters nor any models. All steps are broadly doable since it is conceived to be algebraically straightforward, with low computational complexity and with zero adjustable parameters.

The portrayed approach predicts the voltage response in all demonstrated cases, (i.e. LFP, NiMH and 350F with three different discharge profiles of various properties) with less than 1% error in all, and under 0.3% in cases where linearity is kept up in the frequency domain.

Lastly, error analysis for those cases has been performed and it is concluded that the overall error magnitude and the structure appear to be dominated by the accuracy of the DC map in addition to the inaccuracies regarding linearity. Further work regarding the effects of linearity needs to be performed.

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9. Appendix

9.1. Code

9.1.1. Full Cycle

```
import numpy as np
import scipy
import scipy.fftpack
import pylab
import matplotlib.pyplot as plt

def MatchAbsNearest(array,element):
    mindif = 1e38
    imin = 0
    for i in range(len(array)):
        idif = abs(abs(element)-abs(array[i]))
        if idif < mindif:
            imin = i
            mindif = idif
    return imin

def MatchNearest(array,element):
    mindif = 1e38
    imin = 0
    for i in range(len(array)):
        idif = abs(element-array[i])
        if idif < mindif:
            imin = i
            mindif = idif
    return imin
```

```

def TimeDomain(graphtitle, FUDS, impedance, st, DCEvsDisCharge,
debug=False, showoffset=False, plotdiff=False, ploterrorhist=False,
plotcurrent = False):
#graphtitle: general title of the whole graphs, it should include state of
charge of the battery and sampling time of the measurement
#FUDS: FUDS measurement array, the file should be imported.
#impedance: impedance measurement result, array, the measurement done by
gamry.
#st: it corresponds to sampling time of the measurement.

#sampling time check: the imported sampling time is compared to the actual
one that measurement has.

    if st != FUDS['T'][99]/100:
        print "Given sampling time and the actual one belonging to data do
            not match. Check your data!"
    # else:
    #     print "Sampling time of this data is %s sec" % st

#Current data are transfered into frequency domain.
#The size of the Voltage array that will be calculated is determined.
#Frequency values are calculated.
    currentfftarray = scipy.fft(FUDS['Im'])
    voltagefftarray = np.ndarray(shape = len(currentfftarray) , dtype =
                                'complex128')
    freqs = scipy.fftpack.fftfreq(len(FUDS), st)

#For each value of i this loop checks whether each ith value of freq meet
the given condition with impedance freq.
#Current and impedance values corresponding to the ith values meeting the
condition are taken.
#By complex multiplication voltage values in frequency domain are
obtained.
    for i in np.arange(1,len(currentfftarray)):
        j=MatchAbsNearest(impedance['Freq'],freqs[i])
        voltagefftarray[i]=np.complex(currentfftarray[i].real*
            impedance['Zreal'][j] - currentfftarray[i].imag*
            impedance['Zimag'][j], currentfftarray[i].real*
            impedance['Zimag'][j] + currentfftarray[i].imag*
            impedance['Zreal'][j])

#By inverse fast fourier transform voltage values are transfered into time
domain.
    calculatedvoltagearray = scipy.ifft(voltagefftarray)

#Correct for the DC level ## BU
    charge = 0.0
    for i in np.arange(0,len(calculatedvoltagearray)):
        charge = charge + FUDS['Im'][i]*st
        nearest = MatchNearest(DCEvsDisCharge['Q'],charge)
        calculatedvoltagearray[i] = calculatedvoltagearray[i] +
            DCEvsDisCharge['V'][nearest]

    if(debug):
        print ('charge=%f'%charge,'DCV=%f'
            %DCEvsDisCharge['V'][nearest])

#Adjust for small offset on the voltage

```

```

diff = np.mean(calculatedvoltagearray.real) - np.mean(FUDS['Vf'])
calculatedvoltagearray = calculatedvoltagearray - diff
if(showoffset):
    print ('Voltage Correction =%f'%diff)

if(abs(diff)>0.005):
    print ('LARGE DC OFFSET(%f V) -- CHECK THE CALCULATIONS'%diff)

#Time vs Voltage from FUDS, Time vs calculated Voltage, and Time vs
Current graphs are plotted.
fig, ax1 = plt.subplots(figsize=(11,6))
#pylab.subplot(211)
if graphtitle[0]=='S':
    labels = ['Calculated Voltage', 'Measured Voltage']
else:
    labels = ['__nolegend__', '__nolegend__']
ax1.plot(FUDS['T'],calculatedvoltagearray.real, 'b-', label =
        labels[0])
ax1.set_xlabel('Time (s)', fontsize=20)
ax1.set_ylabel('Calculated Voltage (V)', fontsize=20, color='b')
for tl in ax1.get_yticklabels():
    tl.set_color('b')
ax1.plot(FUDS['T'], FUDS['Vf'], 'r-', label = labels[1])
plt.title(graphtitle, fontsize=24)
'''pylab.subplot(212)
pylab.plot(FUDS['T'],FUDS['Im'])
pylab.xlabel('Time', fontsize=20)
pylab.ylabel('Current', fontsize=20)
pylab.show()'''
plt.legend()
plt.show(True)

if(plotdiff):
    fig,ax = plt.subplots(figsize=(11,6))
    ax.scatter(FUDS['T'],100.0 * (calculatedvoltagearray.real -
        FUDS['Vf']) / FUDS['Vf'])
#    ax.plot(FUDS['T'], calculatedvoltagearray.real - FUDS['Vf'])
    ax.set_ylabel('Proportional Voltage Error(%)', fontsize=20)
    ax.set_xlabel('Time (s)', fontsize=20)
    plt.show(True)
if(ploterrorhist):
    hist,binends = np.histogram(100.0 * (calculatedvoltagearray.real -
        FUDS['Vf']) / FUDS['Vf'],bins=50,range=(-1.0,1.0))
    plt.plot(binends[:len(hist)],hist)
    plt.show(True)
if(plotcurrent):
    fig2, ax2 = plt.subplots(figsize = (11,6))
    ax2.plot(FUDS['T'],FUDS['Im'], 'b-')
    ax2.set_xlabel('Time (s)', fontsize = 20)
    ax2.set_ylabel('Current (A)', fontsize = 20)
    plt.title(graphtitle, fontsize = 24)
    plt.show(True)
return()

def VDifference(graphtitle, FUDS, impedance, st,DCEvsDisCharge):
#graphtitle: general title of the whole graphs, it should include state of
charge of the battery and sampling time of the measurement

```

```

#FUDS: FUDS measurement array, the file should be imported.
#impedance: impedance measurement result, array, the measurement done by
gamry.
#st: it corresponds to sampling time of the measurement.

#sampling time check: the imported sampling time is compared to the actual
one that measurement has.
    if st != FUDS['T'][99]/100:
        print "Given sampling time and the actual one belonging to data do
            not match. Check your data!"
    else:
        print "Sampling time of this data is %s sec." % st

#Current data are transfered into frequency domain.
#The size of the Voltage array that will be calculated is determined.
#Frequency values are calculated.
    currentfftarray = scipy.fft(FUDS['Im'])
    voltagefftarray = np.ndarray(shape =len(currentfftarray) , dtype =
        'complex128')
    freqs = scipy.fftpack.fftfreq(len(FUDS), st)

#For each value of i this loop checks whether each ith value of freq meet
the given condition with impedance freq.
#Current and impedance values corresponding to the ith values meeting the
condition are taken and written in voltagefftarray.
#By complex multiplication voltage values in frequency domain are
obtained.
    for i in np.arange(1,len(currentfftarray)):
        j=MatchAbsNearest(impedance['Freq'],freqs[i])
        voltagefftarray[i]=np.complex(currentfftarray[i].real*
            impedance['Zreal'][j]- currentfftarray[i].imag*
            impedance['Zimag'][j], currentfftarray[i].real*
            impedance['Zimag'][j]+ currentfftarray[i].imag*
            impedance['Zreal'][j])

#By inverse fast fourier transform voltage values are transfered into time
domain.
    calculatedvoltagearray = scipy.fftpack.ifft(voltagefftarray)

    charge = 0.0
    for i in np.arange(1,len(calculatedvoltagearray)):
        charge = charge + FUDS['Im'][i]*(FUDS['T'][i]-FUDS['T'][i-1])
        nearest = MatchNearest(DCEvsDisCharge['Q'],charge)
        calculatedvoltagearray[i] = calculatedvoltagearray[i]+
            DCEvsDisCharge['V'][nearest]
        #print ('charge=%f'%charge, ' DCV=%f'%DCEvsDisCharge['V'][nearest])

#Calculated voltage values are subtracted from measured voltage values.
    difference = []

    for j in range(len(FUDS['Vf'])):
        difference.append(FUDS['Vf'][j] - calculatedvoltagearray[j].real-
            FUDS['Vf'][0])

#Time vs Voltage difference graph is plotted.
    pylab.plot(FUDS['T'], difference)
    pylab.xlabel('Time', fontsize = 14)

```

```

pylab.ylabel('Voltage Difference', fontsize = 14)
pylab.title(graphtitle, fontsize = 15)
pylab.show(True)

return()

def FrequencyDomain(graphtitle, FUDS, impedance, st):
#graphtitle: general title of the whole graphs, it should include state of
charge of the battery and sampling time of the measurement
#FUDS: FUDS measurement array, the file should be imported.
#impedance: impedance measurement result, array, the measurement done by
gamry.
#st: it corresponds to sampling time of the measurement.

#sampling time check: the imported sampling time is compared to the actual
one that measurement has.
    if st != FUDS['T'][99]/100.0:
        print "Given sampling time and the actual one belonging to data do
            not match. Check your data!"
    else:
        print "Sampling time of this data set is %s second" % st

#Voltage and Current data are transfered into frequency domain.
#The size of the Voltage array that will be calculated is determined.
#Frequency values are calculated.
    measuredvoltagefft = scipy.fftpack.fft(FUDS['Vf'])
    currentfftarray = scipy.fftpack.fft(FUDS['Im'])
    voltagefftarray = np.ndarray(shape = len(currentfftarray) , dtype =
        'complex128')
    freqs = scipy.fftpack.fftfreq(len(FUDS), st)

#For each value of i this loop checks whether each ith value of freq meet
the given condition with impedance freq.
#Current and impedance values corresponding to the ith values meeting the
condition are taken.
#By complex multiplication voltage values in frequency domain are
obtained.
    for i in np.arange(1,len(currentfftarray)):
        j=MatchAbsNearest(impedance['Freq'],freqs[i])
        voltagefftarray[i]=np.complex(currentfftarray[i].real*
            impedance['Zreal'][j]- currentfftarray[i].imag*
            impedance['Zimag'][j], currentfftarray[i].real*
            impedance['Zimag'][j]+ currentfftarray[i].imag*
            impedance['Zreal'][j])

#Frequency vs imaginary part of both calculated and measured voltage, and
Frequency vs Real part of both measured and calculated voltage are
plotted.
    pylab.subplot(211)
    plt.semilogx(freqs[1:], voltagefftarray[1:].imag, 'r-', label =
        "Calculated Voltage")
    plt.semilogx(freqs[1:], measuredvoltagefft[1:].imag, 'b-', label =
        "Measured Voltage")
    # plt.semilogx(freqs[1:],
    measuredvoltagefft[1:].imag/voltagefftarray[1:].imag, 'k-', label =
    "Measured/Calculated Voltage")
    pylab.xlabel('Frequency', fontsize=12)

```

```

pylab.ylabel('Imaginary part of Voltage', fontsize=12)
pylab.title(graphtitle, fontsize=16)
pylab.legend()
pylab.subplot(212)
plt.semilogx(freqs[1:], voltagefftarray[1:].real, 'r-', label =
              "Calculated Voltage")
plt.semilogx(freqs[1:], measuredvoltagefft[1:].real, 'b-', label =
              "Measured Voltage")
# plt.semilogx(freqs[1:],
measuredvoltagefft[1:].real/voltagefftarray[1:].real, 'k-', label =
"Measured/Calculated Voltage")
pylab.xlabel('Frequency', fontsize=12)
pylab.ylabel('Real part of Voltage', fontsize=12)
pylab.legend()
pylab.show(True)

#to plot Zmod/phase graph follow the scripts below
"""modreal_calculated = voltagefftarray.real**2
modimag_calculated = voltagefftarray.imag**2
Vmod_calculated = []
for k in range (len(voltagefftarray)):
    Vmod_calculated.append(math.sqrt(modreal_calculated[k] +
modimag_calculated[k]))
phase_calculated = []
for i in range(len(voltagefftarray)):
    phase_calculated.append(math.atan2(voltagefftarray.imag[i],
voltagefftarray.real[i]))
modreal_measured = measuredvoltagefft.real**2
modimag_measured = measuredvoltagefft.imag**2
Vmod_measured = []
for t in range (len(measuredvoltagefft)):
    Vmod_measured.append(math.sqrt(modreal_measured[t] +
modimag_measured[t]))
phase_measured = []
for j in range(len(measuredvoltagefft)):
    phase_measured.append(math.atan2(measuredvoltagefft.imag[j],
measuredvoltagefft.real[j]))
pylab.subplot(211)
plt.loglog(freqs[1:], Vmod_calculated[1:], 'r-', label = "Calculated
Voltage")
plt.loglog(freqs[1:], Vmod_measured[1:], 'b-', label = "Measured
Voltage")
pylab.xlabel('log(Frequency)', fontsize = 14)
pylab.ylabel('log(Zmod)', fontsize = 14)
pylab.title(graphtitle, fontsize = 18)
pylab.legend()
pylab.subplot(212)
plt.semilogx(freqs[1:], phase_calculated[1:], 'r-', label = "Calculated
Voltage")
plt.semilogx(freqs[1:], phase_measured[1:], 'b-', label ="Measured
Voltage")
pylab.xlabel('log(Frequency)', fontsize = 14)
pylab.ylabel('Phase (radians)', fontsize = 14)
pylab.legend()
pylab.show()
"""
return()

```

```

def freqDomainVdifference (graphtitle, FUDS, impedance, st):
#graphtitle: general title of the whole graphs, it should include state of
charge of the battery and sampling time of the measurement
#FUDS: FUDS measurement array, the file should be imported.
#impedance: impedance measurement result, array, the measurement done by
gamry.
#st: it corresponds to sampling time of the measurement.

#sampling time check: the imported sampling time is compared to the actual
one that measurement has.
    if st != FUDS['T'][99]/100.0:
        print "Given sampling time and the actual one belonging to data do
            not match. Check your data!"
    else:
        print "Sampling time of this data set is %s second" % st

#Voltage and Current data are transfered into frequency domain.
#The size of the Voltage array that will be calculated is determined.
#Frequency values are calculated.
    measuredvoltagefft = scipy.fft(FUDS['Vf'])
    currentfftarray = scipy.fft(FUDS['Im'])
    voltagefftarray = np.ndarray(shape =len(currentfftarray) , dtype =
                                'complex128')
    freqs = scipy.fftpack.fftfreq(len(FUDS), st)
#For each value of i this loop checks whether each ith value of freq meet
the given condition with impedance freq.
#Current and impedance values corresponding to the ith values meeting the
condition are taken.
#By complex multiplication voltage values in frequency domain are
obtained.
    for i in np.arange(1,len(currentfftarray)):
        j=MatchAbsNearest(impedance['Freq'],freqs[i])
        voltagefftarray[i]=np.complex(currentfftarray[i].real*
            impedance['Zreal'][j]- currentfftarray[i].imag*
            impedance['Zimag'][j], currentfftarray[i].real*
            impedance['Zimag'][j]+ currentfftarray[i].imag*
            impedance['Zreal'][j])
#Calculated voltage values are subtracted from the measured one in
frequency domain.
#Since voltage values in frequency domain are complex numbers, real and
imaginary part are subtracted separately.
    differenceReal = []
    differenceImag = []
    for k in range(len(measuredvoltagefft)):
        differenceReal.append(measuredvoltagefft.real[k]-
                                voltagefftarray.real[k])
        differenceImag.append(measuredvoltagefft.imag[k]-
                                voltagefftarray.imag[k])

#Frequency vs imaginary part of voltage difference, and Frequency vs Real
part of voltage difference are plotted.
    pylab.subplot(211)
    plt.semilogx(freqs[1:], differenceImag[1:])
    pylab.xlabel('Frequency', fontsize=12)
    pylab.ylabel('Imaginary part of Voltage Difference', fontsize=12)
    pylab.title(graphtitle, fontsize=16)
    pylab.subplot(212)

```

```
plt.semilogx(freqs[1:], differenceReal[1:])
pylab.xlabel('Frequency', fontsize=12)
pylab.ylabel('Real part of Voltage Difference', fontsize=12)
pylab.show()

return()
```

9.1.2. Curve fitting using various functions and background subtraction:

```
import numpy as np
import scipy
from scipy.optimize import curve_fit
import pylab
import matplotlib.pyplot as plt
import matplotlib as mpl

#for changing the font of the graphs
mpl.rc('font', family = 'Georgia')

dataarray = np.genfromtxt(r'.\FUDS_measurement_#1_27Oct2015_1E-1.DTA',
    skiprows = 3, dtype = [('Pt','i8'), ('T','i8'), ('Vf','f8'),
    ('Im','f8'), ('Vu','f8'), ('Sig','f8'), ('Ach','f8'),
    ('IERange','i8'), ('Over','S12')])

time = np.array(dataarray['T'][:1372], dtype = int)
voltage = np.array(dataarray['Vf'][:1372], dtype = float)
current = np.array(dataarray['Im'][:1372], dtype = float)

#these arrays are formed in order to get fitted curve subtracted from
original voltage.
backsubt = np.zeros(1372)
backsubt1 = np.zeros(1372)
backsubt2 = np.zeros(1372)
backsubt3 = np.zeros(1372)
backsubt4 = np.zeros(1372)
backsubt5 = np.zeros(1372)
backsubt6 = np.zeros(1372)

def func0(time, a, b, c):
    f0 = a * np.exp(-b * time) + c
    return f0
def func1(time, a, b, c, d, f):
    f1 = a * np.exp(-b * time) + d * np.exp(-f * time) + c
    return f1

def func2 (time, a, b, c, d):
    f2 = a * (time**b) - c * (time**(d/2))
    return f2

def func3 (time, a, b):
    f3 = a * time**b
    return f3
```

```

def func4 (time, a, b):
    f4 = a * time**(b/2)
    return f4

def func5 (time, a, b, c, d):
    f5 = a * time**b - c * time**(d/3)
    return f5

def func6 (time, a, b, c, d):
    f6 = a * time**b - np.exp(-c*time) + d
    return f6

plt.plot(time, voltage, label = 'Original Voltage Response')

popt, pcov = curve_fit(func0, time, voltage)
#plt.plot(time, func0(time, *popt), label = '$y = a.e^{-b.x} + c$')

popt1, pcov1 = curve_fit(func1, time, voltage)
plt.plot(time, func1(time, *popt1), label = '$y = a.e^{-b.x} + d.e^{-f.x} + c$')

popt2, pcov2 = curve_fit(func2, time, voltage)
plt.plot(time, func2(time, *popt2), label = '$y = a.x^b - c.x^{d/2}$')

popt3, pcov3 = curve_fit(func3, time, voltage)
plt.plot(time, func3(time, *popt3), label = '$y = a.x^b$')

popt4, pcov4 = curve_fit(func4, time, voltage)
plt.plot(time, func4(time, *popt4), label = '$y = a.x^{b/2}$')

popt5, pcov5 = curve_fit(func5, time, voltage)
plt.plot(time, func5(time, *popt5), label = '$y = a.x^b - c.x^{d/3}$')

popt6, pcov6 = curve_fit(func6, time, voltage)
plt.plot(time, func6(time, *popt6), label = '$y = a.x^b - c.x^{d/3}$')

plt.figure()
ax = plt.subplot(111)

for i in range(0,1371):
    backgsubt[i] = voltage[i]-func0(time[i], *popt)
    ax.plot(time, backgsubt, label = '$y = a.e^{-b.x} + c$')

for i in range(0,1371):
    backgsubt1[i]=voltage[i]-func1(time[i], *popt1)
    ax.plot(time, backgsubt1, label = '$y = a.e^{-b.x} + d.e^{-f.x} + c$')

for i in range(0,1371):
    backgsubt2[i]=voltage[i]-func2(time[i], *popt2)
    ax.plot(time, backgsubt2, label = '$y = a.x^b - c.x^{d/2}$')

for i in range(0,1371):
    backgsubt3[i]=voltage[i]-func3(time[i], *popt3)
    ax.plot(time, backgsubt3, label = '$y = a.x^b$')

for i in range(0,1371):
    backgsubt4[i]=voltage[i]-func4(time[i], *popt4)

```

```

ax.plot(time, backgsubt4, label = '$y = a.x^{b/2}$')

for i in range(0,1371):
    backgsubt5[i]=voltage[i]-func5(time[i], *popt5)
ax.plot(time, backgsubt5, label = '$y = a.x^b - c.x^{d/3}$')

for i in range(0,1371):
    backgsubt6[i]=voltage[i]-func6(time[i], *popt6)
ax.plot(time, backgsubt6, label = '$y = a.x^b - c.x^{d/3}$')

pylab.xlabel('Time (sec)', fontsize = 18)
pylab.ylabel('Voltage (V)', fontsize = 18)
pylab.title('Curves After Each Fitted Functions Subtracted from Original
            Voltage Response', fontsize = 20)

plt.legend()
pylab.show()
plt.show()

```

9.1.3. Background subtraction by using piecewise linear approximation:

```

import scipy
import numpy as np
import scipy.fftpack
import pylab
import matplotlib.pyplot as plt
import matplotlib as mpl
from scipy import signal

#for changing font of the graphs
mpl.rc('font', family = 'Georgia')

def signaldetrend(response, response1, response2, response3, response4,
response5, soc1V35=False, soc1V25=False, imp1V35=False, imp1V25=False,
curr1V35=False, curr1V25=False, pot1V25=False):

#sorting time, voltage and current data from the other data embedded in
the profile measurement of all three sampling time
    time = np.array(response['T'][:1371], dtype = float)
    voltage = np.array(response['Vf'][:1371], dtype = float)
    current = np.array(response['Im'][:1371], dtype = float)

    time1 = np.array(response1['T'][:1371], dtype = float)
    voltage1 = np.array(response1['Vf'][:1371], dtype = float)
    current1 = np.array(response1['Im'][:1371], dtype = float)

    time2 = np.array(response2['T'][:1371], dtype = float)
    voltage2 = np.array(response2['Vf'][:1371], dtype = float)
    current2 = np.array(response2['Im'][:1371], dtype = float)

    time3 = np.array(response3['T'][:1371], dtype = float)

```

```

voltage3 = np.array(response3['Vf'][:1371], dtype = float)
current3 = np.array(response3['Im'][:1371], dtype = float)

time4 = np.array(response4['T'][:1371], dtype = float)
voltage4 = np.array(response4['Vf'][:1371], dtype = float)
current4 = np.array(response4['Im'][:1371], dtype = float)

time5 = np.array(response5['T'][:1371], dtype = float)
voltage5 = np.array(response5['Vf'][:1371], dtype = float)
current5 = np.array(response5['Im'][:1371], dtype = float)

allvoltage = np.ndarray([6,time.size], dtype = float)
allvoltage = (voltage, voltage1, voltage2, voltage3, voltage4,
              voltage5)
detrendeddataarray = np.ndarray([6, time.size], dtype = float)

alltime = np.ndarray([6, time.size], dtype = float)
alltime = (time, time1, time2, time3, time4, time5)

allcurrent = np.ndarray([6, time.size], dtype = float)
allcurrent = (current, current1, current2, current3, current4,
              current5)

#equal segment lengths, namely one fourth of the profile and half of the
profile
segmentlength = np.array([343, 686])

for i in range(len(segmentlength)):
    for m in range(0,6):
        detrendeddataarray[m][:] = signal.detrend(allvoltage[m][:],
        bp = np.arange(0, len(allvoltage[m][:]), segmentlength[i]))
        #detrendeddataarray[m][:] = signal.detrend(allvoltage[m][:],
        bp = (100,300,600,1200))

fftcurrent = np.ndarray([6,time.size], dtype = complex)
fftvoltage = np.ndarray([6,time.size], dtype = complex)
impedance = np.ndarray([6,time.size], dtype = complex)
st = alltime[0][99]/100

fftcurrent[0][:] = (scipy.fftpack.fft(allcurrent[0][:]))
fftvoltage[0][:] = (scipy.fftpack.fft(detrendeddataarray[0][:]))
freqs = scipy.fftpack.fftfreq((time.size), st)
impedance[0][:] = fftvoltage[0][:]/fftcurrent[0][:]

st = alltime[1][99]/100
fftcurrent[1][:] = (scipy.fftpack.fft(allcurrent[1][:]))
fftvoltage[1][:] = (scipy.fftpack.fft(detrendeddataarray[1][:]))
freqs1 = scipy.fftpack.fftfreq((time1.size), st)
impedance[1][:] = fftvoltage[1][:]/fftcurrent[1][:]

st = alltime[2][99]/100
fftcurrent[2][:] = (scipy.fftpack.fft(allcurrent[2][:]))
fftvoltage[2][:] = (scipy.fftpack.fft(detrendeddataarray[2][:]))
freqs2 = scipy.fftpack.fftfreq((time2.size), st)
impedance[2][:] = fftvoltage[2][:]/fftcurrent[2][:]

st = alltime[3][99]/100

```

```

fftcurrent[3][:] = (scipy.fftpack.fft(allcurrent[3][:]))
fftvoltage[3][:] = (scipy.fftpack.fft(detrendeddataarray[3][:]))
freqs3 = scipy.fftpack.fftfreq((time3.size), st)
impedance[3][:] = fftvoltage[3][:]/fftcurrent[3][:]

st = alltime[4][99]/100
fftcurrent[4][:] = (scipy.fftpack.fft(allcurrent[4][:]))
fftvoltage[4][:] = (scipy.fftpack.fft(detrendeddataarray[4][:]))
freqs4 = scipy.fftpack.fftfreq((time4.size), st)
impedance[4][:] = fftvoltage[4][:]/fftcurrent[4][:]

st = alltime[5][99]/100
fftcurrent[5][:] = (scipy.fftpack.fft(allcurrent[5][:]))
fftvoltage[5][:] = (scipy.fftpack.fft(detrendeddataarray[5][:]))
freqs5 = scipy.fftpack.fftfreq((time5.size), st)
impedance[5][:] = fftvoltage[5][:]/fftcurrent[5][:]

if segmentlength[i] == 343:
    if(curr1V35):
        fig, ax = plt.subplots(nrows=3,ncols=2)
        plt.subplot(3,2,1)
        st = alltime[0][99]/100
        plt.loglog(freqs, abs(fftcurrent[0][:]), '-r', label =
                    'sampling time %s s' % st)
        pylab.ylabel('Current in f-domain', fontsize = 14)
        pylab.legend()
        pylab.title('Current in f-domain, SOC = 1.35 V', fontsize
                    = 20)

        st = alltime[1][99]/100
        plt.subplot(3,2,3)
        plt.loglog(freqs1, abs(fftcurrent[1][:]), '-b', label =
                    'sampling time %s s' % st)
        pylab.ylabel('Current in f-domain', fontsize = 14)
        pylab.legend()

        st = alltime[2][99]/100
        plt.subplot(3,2,5)
        plt.loglog(freqs2, abs(fftcurrent[2][:]), '-m', label =
                    'sampling time %s s' % st)
        pylab.ylabel('Current in f-domain', fontsize = 14)
        pylab.xlabel('Frequency (Hz)', fontsize = 16)
        pylab.legend()

        plt.subplot(3,2,2)
        st = alltime[0][99]/100
        plt.loglog(freqs, abs(fftvoltage[0][:]), '-r', label =
                    'sampling time %s s' % st)
        pylab.ylabel('Voltage in f-domain', fontsize = 14)
        pylab.ylim(10**(-5),10**(2))
        pylab.legend()
        pylab.title('Detrended Voltage in f-domain -
                    Segmentlength: % s, SOC = 1.35 V' %
                    segmentlength[i], fontsize = 16)

        st = alltime[1][99]/100
        plt.subplot(3,2,4)

```

```

plt.loglog(freqs1, abs(fft voltage[1][:]), '-b', label =
            'sampling time %s s' % st)
pylab.ylabel('Voltage in f-domain', fontsize = 14)
pylab.ylim(10**(-5),10**(2))
pylab.legend()

st = alltime[2][99]/100
plt.subplot(3,2,6)
plt.loglog(freqs2, abs(fft voltage[2][:]), '-m', label =
            'sampling time %s s' % st)
pylab.ylabel('Voltage in f-domain', fontsize = 14)
pylab.xlabel('Frequency (Hz)', fontsize = 16)
pylab.ylim(10**(-5),10**(2))
pylab.legend()
pylab.show(True)

if(curr1V25):
    pylab.subplot(311)
    st = alltime[3][99]/100
    pylab.loglog(freqs, abs(fft current[3][:]), '-r', label =
                'sampling time %s s' % st)
    pylab.ylabel('Current in f-domain', fontsize = 14)
    pylab.legend()
    pylab.title('Current in f-domain, SOC = 1.25 V',
                fontsize=22)
    st = alltime[4][99]/100
    pylab.subplot(312)
    pylab.loglog(freqs1, abs(fft current[4][:]), '-b', label =
                'sampling time %s s' % st)
    pylab.ylabel('Current in f-domain', fontsize = 14)
    pylab.legend()
    st = alltime[5][99]/100
    pylab.subplot(313)
    pylab.loglog(freqs2, abs(fft current[5][:]), '-m', label =
                'sampling time %s s' % st)
    pylab.ylabel('Current in f-domain', fontsize = 14)
    pylab.xlabel('Frequency (Hz)', fontsize = 16)
    pylab.legend()
    pylab.show(True)

if(pot1V25):
    pylab.subplot(311)
    st = alltime[3][99]/100
    pylab.loglog(freqs, abs(fft voltage[3][:]), '-r', label =
                'sampling time %s s' % st)
    pylab.ylabel('Voltage in f-domain', fontsize = 14)
    pylab.ylim(10**(-5),10**(2))
    pylab.legend()
    pylab.title('Detrended Voltage in f-domain -
                Segmentlength:%s, SOC = 1.25 V' %
                segmentlength[i], fontsize = 22)
    st = alltime[4][99]/100
    pylab.subplot(312)
    pylab.loglog(freqs1, abs(fft voltage[4][:]), '-b', label =
                'sampling time %s s' % st)
    pylab.ylabel('Voltage in f-domain', fontsize = 14)
    pylab.ylim(10**(-5),10**(2))

```

```

pylab.legend()
st = alltime[5][99]/100
pylab.subplot(313)
pylab.loglog(freqs2, abs(fftvoltage[5][:]), '-m', label =
              'sampling time %s s' % st)
pylab.ylabel('Voltage in f-domain', fontsize = 14)
pylab.xlabel('Frequency (Hz)', fontsize = 16)
pylab.ylim(10**(-5),10**(2))
pylab.legend()
pylab.show(True)

if(imp1V35): #add segmentlength[i]==343 to prevent loop two times
    if segment is [100,300,600,1200]
        #impedance for both 1.35 and 1.25 soc
        fig, ax = plt.subplots(nrows=3,ncols=2)
        plt.subplot(3,2,1)
        st = alltime[0][99]/100
        plt.loglog(freqs, abs(impedance[0][:]), 'or', label =
                  'sampling time %s s' % st)
        pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
        pylab.ylim(10**(-5),10**(2))
        pylab.legend()
        pylab.title('Impedance of Detrended Voltage-
                    Segments=[100,300,600,1200], SOC=1.35V', fontsize = 14)
#pylab.title('Impedance of Detrended Voltage-Segmentlength:%s, SOC= 1.35V'
% segmentlength[i], fontsize = 17)

        st = alltime[1][99]/100
        plt.subplot(3,2,3)
        plt.loglog(freqs1, abs(impedance[1][:]), 'ob', label =
                  'sampling time %s s' % st)
        pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
        pylab.ylim(10**(-5),10**(2))
        pylab.legend()

        st = alltime[2][99]/100
        plt.subplot(3,2,5)
        pylab.loglog(freqs2, abs(impedance[2][:]), 'om', label =
                  'sampling time %s s' % st)
        pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
        pylab.xlabel('Frequency (Hz)', fontsize = 16)
        pylab.ylim(10**(-5),10**(2))
        pylab.legend()

        plt.subplot(3,2,2)
        st = alltime[3][99]/100
        plt.loglog(freqs3, abs(impedance[3][:]), 'or', label =
                  'sampling time %s s' % st)
        pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
        pylab.ylim(10**(-5),10**(3))
        pylab.legend()
        pylab.title('Impedance of Detrended Voltage-
                    Segments=[100,300,600,1200], SOC=1.25V', fontsize = 14)
#pylab.title('Impedance of Detrended Voltage-Segmentlength:%s, SOC= 1.25V'
% segmentlength[i], fontsize = 17)

        st = alltime[4][99]/100

```

```

plt.subplot(3,2,4)
plt.loglog(freqs4, abs(impedance[4][:]), 'ob', label =
            'sampling time %s s' % st)
pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
pylab.ylim(10**(-5),10**(2))
pylab.legend()

st = alltime[5][99]/100
plt.subplot(3,2,6)
pylab.loglog(freqs5, abs(impedance[5][:]), 'om', label =
            'sampling time %s s' % st)
pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
pylab.ylim(10**(-5),10**(4))
pylab.xlabel('Frequency (Hz)', fontsize = 16)
pylab.legend()
pylab.show(True)

if(imp1V25): #impedance for 1.25 soc
    pylab.subplot(311)
    st = alltime[3][99]/100
    pylab.loglog(freqs3, abs(impedance[3][:]), 'or', label =
                'sampling time %s s' % st)
    pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
    pylab.ylim(10**(-5),10**(3))
    pylab.legend()
    #pylab.title('Impedance of Detrended Voltage - Segments =
    [100,300,600,1200], SOC = 1.25 V', fontsize = 22)
    pylab.title('Impedance of Detrended Voltage -
    Segmentlength:%s, SOC = 1.25 V' % segmentlength[i],
    fontsize = 22)
    st = alltime[4][99]/100
    pylab.subplot(312)
    pylab.loglog(freqs4, abs(impedance[4][:]), 'ob', label =
                'sampling time %s s' % st)
    pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
    pylab.ylim(10**(-5),10**(2))
    pylab.legend()
    st = alltime[5][99]/100
    pylab.subplot(313)
    pylab.loglog(freqs5, abs(impedance[5][:]), 'om', label =
                'sampling time %s s' % st)
    pylab.ylabel('Impedance (Magnitude)', fontsize = 14)
    pylab.ylim(10**(-5),10**(4))
    pylab.xlabel('Frequency (Hz)', fontsize = 16)
    pylab.legend()
    pylab.show(True)

if(soc1V35): #detrended voltage with both 1.35 and 1.25 V
    fig, ax = plt.subplots(nrows=3,ncols=2)
    plt.subplot(3,2,1)
    #sampling time of the data
    st = alltime[0][99]/100
    pylab.plot(alltime[0][:], detrendeddataarray[0][:], '-r',
                label = 'sampling time %s s' % st)
    pylab.ylabel('Voltage (V)', fontsize = 16)
    pylab.legend()

```

```

pylab.title('Detrended Voltage-Segments=[100,300,600,1200],
            SOC= 1.35V', fontsize = 17)
#pylab.title('Detrended Voltage - Segmentlength:%s at 0.01, 1
and 10 s Sampling Time, SOC = 1.35 V' % segmentlength[i],
            fontsize = 22)

st = alltime[1][99]/100
plt.subplot(3,2,3)
pylab.plot(alltime[1][:], detrendeddataarray[1][:], '-b',
            label = 'sampling time %s s' % st)
pylab.ylabel('Voltage (V)', fontsize = 16)
pylab.legend()

st = alltime[2][99]/100
plt.subplot(3,2,5)
pylab.plot(alltime[2][:], detrendeddataarray[2][:], '-m',
            label = 'sampling time %s s' % st)
pylab.ylabel('Voltage (V)', fontsize = 16)
pylab.xlabel('Time (sec)', fontsize = 16)
pylab.legend()

plt.subplot(3,2,2)
#sampling time of the data
st = alltime[3][99]/100
pylab.plot(alltime[3][:], detrendeddataarray[3][:], '-r',
            label = 'sampling time %s s' % st)
pylab.ylabel('Voltage (V)', fontsize = 16)
pylab.legend()
pylab.title('Detrended Voltage-Segments=[100,300,600,1200],
            SOC= 1.25V', fontsize = 17)
#pylab.title('Detrended Voltage - Segmentlength:%s at 0.01, 1 and 10 s
Sampling Time, SOC = 1.25 V' % segmentlength[i], fontsize = 22)

st = alltime[4][99]/100
plt.subplot(3,2,4)
pylab.plot(alltime[4][:], detrendeddataarray[4][:], '-b',
            label = 'sampling time %s s' % st)
pylab.ylabel('Voltage (V)', fontsize = 16)
pylab.legend()
st = alltime[5][99]/100
plt.subplot(3,2,6)
pylab.plot(alltime[5][:], detrendeddataarray[5][:], '-m',
            label = 'sampling time %s s' % st)
pylab.ylabel('Voltage (V)', fontsize = 16)
pylab.xlabel('Time (sec)', fontsize = 16)
pylab.legend()
pylab.show(True)

```

9.1.4. Applying Singular Value Decomposition:

```
import numpy as np
import scipy.linalg as linalg
import matplotlib.pyplot as pylab

dataarray1 =
    np.genfromtxt(r'.\FUDS_(A)_12May2016_st(0.01)_chrg(1.35V).DTA',
        skiprows = 3, dtype = [('Pt','i8'), ('T','f8'), ('Vf','f8'),
            ('Im','f8'), ('Vu','f8'), ('Sig','f8'), ('Ach','f8'),
            ('IERange','i8'), ('Over','S12')])
dataarray2 = np.genfromtxt(r'.\FUDS_(A)_12May2016_st(1)_chrg(1.35V).DTA',
        skiprows = 3, dtype = [('Pt','i8'), ('T','i8'), ('Vf','f8'),
            ('Im','f8'), ('Vu','f8'), ('Sig','f8'), ('Ach','f8'),
            ('IERange','i8'), ('Over','S12')])
dataarray3 = np.genfromtxt(r'.\FUDS_(A)_12May2016_st(10)_chrg(1.35V).DTA',
        skiprows = 3, dtype = [('Pt','i8'), ('T','i8'), ('Vf','f8'),
            ('Im','f8'), ('Vu','f8'), ('Sig','f8'), ('Ach','f8'),
            ('IERange','i8'), ('Over','S12')])
dataarray4 = np.genfromtxt(r'.\OCP_(A)_12May2016_st(0.01)_chrg(1.35).DTA',
        skiprows = 45, dtype=[('Pt','i8'), ('T','f8'), ('Vf','f8'),
            ('Vm','f8'), ('Ach','f8'), ('Over','S12')])
dataarray5 =
    np.genfromtxt(r'.\OCP_(A)_26July2016_st(1s)_chg(1.35V)_debug.DTA',
        skiprows = 45, dtype=[('Pt','i8'), ('T','i8'), ('Vf','f8'),
            ('Vm','f8'), ('Ach','f8'), ('Over','S12')])
dataarray6 =
    np.genfromtxt(r'.\OCP_(A)_26July2016_st(10s)_chg(1.35V)_debug.DTA',
        skiprows = 45, dtype=[('Pt','i8'), ('T','i8'), ('Vf','f8'),
            ('Vm','f8'), ('Ach','f8'), ('Over','S12')])

Fullarray = np.ndarray([6,1372])
Fullarray = (dataarray1['Vf'], dataarray2['Vf'], dataarray3['Vf'],
    dataarray4['Vf'], dataarray5['Vf'], dataarray6['Vf'])

U,s,Vh = linalg.svd(Fullarray[:6])
pylab.subplot(211)
pylab.plot(Fullarray[0],label = '0')
pylab.plot(Fullarray[1],label = '1')
pylab.plot(Fullarray[2],label = '2')
pylab.plot(Fullarray[3],label = '3')
pylab.plot(Fullarray[4],label = '4')
pylab.plot(Fullarray[5],label = '5')
pylab.xlabel('Point', fontsize = 14)
pylab.ylabel('Voltage', fontsize = 14)
pylab.title("Singular Value Decomposition of Voltage Values belonging to
    FUDS and OCP data", fontsize = 20)
pylab.legend()
pylab.subplot(212)
for i in range(6):
    Vh[i][i] = 0.0
    pylab.plot(Vh[i],label=i)
pylab.legend()
pylab.xlabel('Point', fontsize = 14)
pylab.show(True)
```