B.E Electrical and Electronic Engineering

EE4050: Final Report

Project Name: Electrochemical Impedance Spectroscopy for Battery Measurement

Student Name	Leyi Huang
Student Number	121110602
Date	4/13/2024
Supervisor Name	Kevin McCathy

Declaration:

The report was written entirely by the author, except where stated otherwise. The source of any material not created by the author has been clearly referenced. The work described in this report was conducted by the author, except where stated otherwise.

Signature: ***Leyi Huang***

1.Table of content

Abstract— This study analyzes different types of batteries through Electrochemical Impedance Spectroscopy (EIS). The EIS approach incorporated complex elements like the Warburg element to reveal diffusion processes and the Constant Phase Element to indicate capacitive behavior and degradation. Data fitting was executed via the impedance.py package, providing an basic understanding of the batteries' performance.

Keywords—Li-ion batteries, Ni-MH batteries, Electrochemical Impedance Spectroscopy, Equivalent circuit

2.Summary of Project Achievements

The project has successfully utilized EIS as a core analytical technique. The project has made solid progress in understanding and working with two types of batteries: lithium-ion and nickel-metal hydride. For lithium-ion batteries, known for good energy density and cycle life, the focus was on working principal, which is mainly through lithium ions moving back and forth between two ends of the battery. Nickel-metal hydride batteries, which are more budget-friendly and not harmful to the environment, were also studied for their basic properties.

In our report, an overview of the foundational principles of electrochemical impedance spectroscopy (EIS) has introduced. Beginning with the fundamental definition of impedance, we elaborated on the concept as the opposition a circuit presents to the flow of alternating current. We further explained how impedance is a complex quantity with both magnitude and phase, leading into a discussion of Nyquist and Bode plots—essential tools for interpreting EIS data. The Nyquist plot, with its characteristic semicircular arcs, reveals information about the resistive and capacitive behavior of the battery. The Bode plot showing the frequency response of the impedance magnitude and phase angle. In the theoretical analysis, a various specific battery models was used to show how the imaginary part of impedance relates to the semicircle radius in Nyquist plots, a representation of capacitive effects and charge transfer resistance. For instance, the ohmic resistance $R_{b,}$ is represented by the x-axis intercept of the Nyquist plot. This comprehensive theoretical work provided the foundation for the investigations and simulations of equivalent battery circuits.

In the simulation phase, Google Colab was utilized to simulate circuit elements, effectively modelling two equivalent circuits that represent the behaviors of the batteries. This study went beyond simple models and used more detailed elements like the Warburg element, which is good at showing how particles inside the battery move. This is important for understanding how the battery performs at various levels of charge and use. The constant phase element was also used to get a better picture of how the batteries degrade within the effect of double layer capacitance grown.

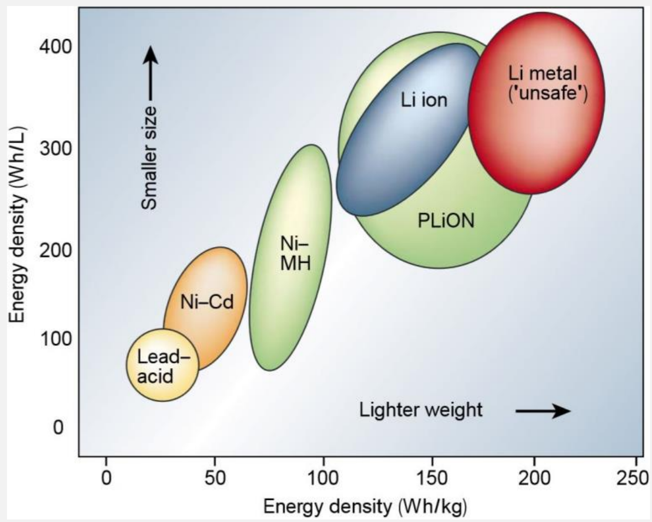
Following these simulations, real-world battery data have been proceeded. The ability to accurately acquire EIS measurements on 2 types of commercial battery cells has been established. The project has use the Analog Devices measurement system AD5941. Concurrently, the installation of data measuring software has been achieved as well as data preprocessing. Furthermore, an example of fitting data has been established using Python package, designated as impedance.py, enhance the basic understanding of the analytical capabilities of the project.

3.Acknowledgement

The research greatly benefited from the support provided by the project supervisor, Dr. Kevin McCarthy. His technical knowledge and clear explanations helped the student to develop a deep understanding of the subject matter. The student would like to thank Liam Riordan, Mohamed Khairy and Akila Marimuthu of Analog Devices for providing an EVAL-AD5941board for this project and for helpful support with the SensorPal software.

4.Introduction

The current battery market is witnessing a rapid adoption of rechargeable nickel-metal hydride (NiMH) and lithium-ion (Li-ion) batteries, primarily in hybrid and electric vehicles. Li-ion batteries stand out for being approximately 50% lighter than traditional lead-acid and nickel-cadmium (NiCd) batteries [1] as shown in figure 1.1, while also able to store up to three times more energy. This capacity allows for an impressive lifespan, typically reaching nearly 2000 charge cycles at a voltage of around 3.6V.



.

Figure 1.1. Different types of batteries material comparison in energy density[1].

They are also less expensive to produce, as they do not require cobalt, a costly and sometimes ethical material found in other Li-ion batteries [2]. Furthermore, Li-ion batteries have a very low self-discharge rate, typically less than 5% per month. This compares to favourably to other types of batteries that can have self-discharge rates of 20-30% per month [3].

On the other hand, NiMH batteries present a viable alternative with a better energy-to-weight ratio compared to lead-acid batteries, delivering double the power. They also have a reliable life cycle, proven to last for about 500 charges with a standard voltage of 1.2V [4]. The fundamental operation of a battery is based on the assembly of multiple electrochemical cells. These cells are linked in series or parallel to achieve the desired voltage and capacity. Each cell comprises a positive and a negative electrode, with an electrolyte solution filled with salts to facilitate ion movement between electrodes. When these electrodes are connected externally, a flow of electrons is generated because of the chemical reactions at both electrodes, enabling the battery to supply electrical current, as show in figure 1.2.

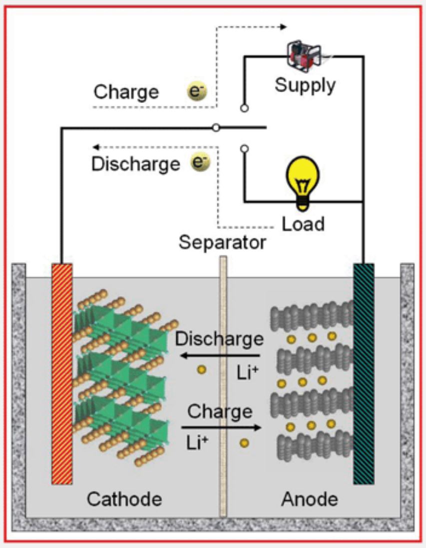


Figure 1.2. Basic components and operation principle of a Li-ion cell [5]

To have a better understanding of battery, the state of charge (SOC) indicates the remaining energy in a battery relative to its full capacity. Determining SOC can be problematic. The traditional approach requires fully discharging the battery, which is impractical for electric vehicles (EVs) since they cannot be fully depleted during regular use. Consequently, accurate estimation of SOC without complete discharge is a critical area of research in battery technology.

Among the various methods under investigation, AC impedance measurements[6], or as known as Electrochemical Impedance Spectroscopy (EIS) have emerged as a significant technique. This approach involves analysing the battery's response to an alternating current at different frequencies, providing insights into various battery parameters. These parameters can often correlate with the SOC. Utilizing EIS for SOC estimation is advantageous because it can potentially allow for continuous monitoring of a battery's charge state without the need for full discharge, which is especially beneficial in the management of EV batteries and other critical applications.

The primary focus of this report is the study of Electrochemical Impedance Spectroscopy (EIS) measurements on both ideal and real batteries.

5.Theoretical Aspects, Previous Work and Literature Review

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

The impedance Z(w) can be expressed in the form of voltage divided by current, which is:

$$\mathrm{Z}(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_m e^{j\omega t}}{I_m e^{j(\omega t-\varphi)}} \frac{V_m}{I_m} e^{j\varphi} \tag{1}$$

Where:

- $\mathrm{V}(\omega)$ *is the voltage*
- $\mathrm{I}\ (\omega)$ *is the current, and*
- ω is the angular frequency, given by $2\pi f$

Simplified using Euler's formula and divide into real and imaginary part:

$$\mathrm{Z}(\omega) = \frac{V_m}{I_m} e^{j\varphi} = \frac{V_m}{I_m}[\cos(\varphi) + j\sin(\varphi)] = Z_0[\cos(\varphi) + j\sin(\varphi)] \tag{2}$$

Where real part $Z_0[\cos(\varphi)]$: R(resistance),

Imaginary part $Z_0[\sin(\varphi)]$: C(capacitance) + L(inductance)

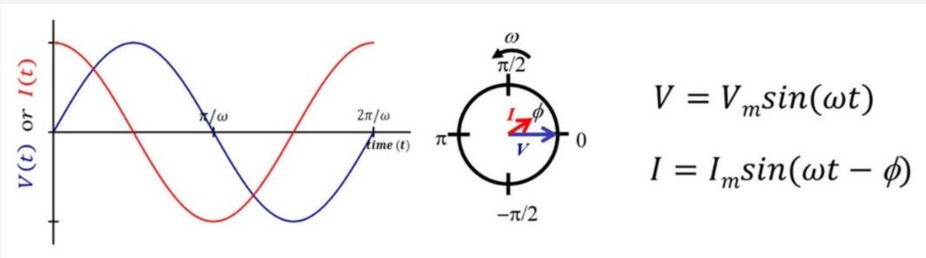


Figure 2.1: Illustration of relationship between the voltage and current when applying AC voltage with the angular frequency ω[7]

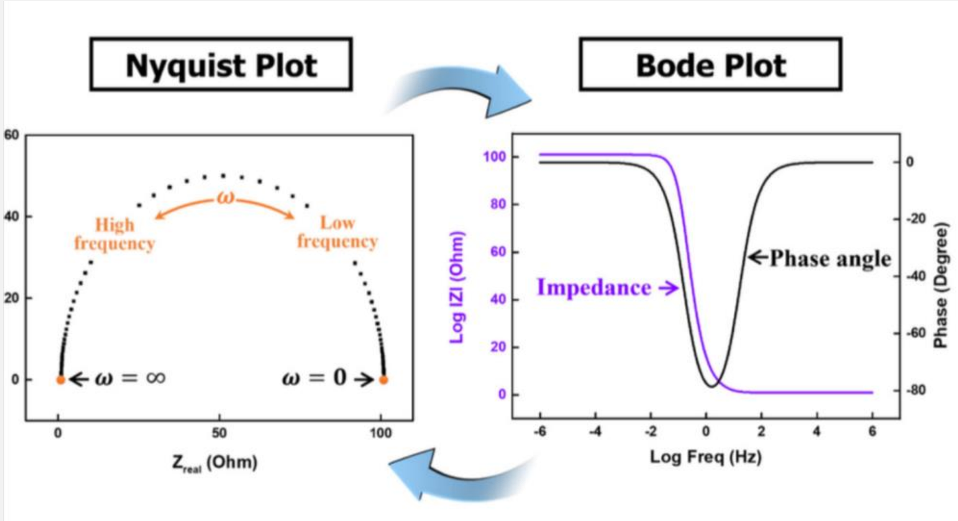


Figure 2.2: EIS representation by Nyquist and Bode plot [7]

Lithium ions (Li+) intercalating (inserting) into the active material of an electrode, which is a key process during charging and discharging of lithium-ion batteries. The active material particles are connected by conductive carbon black, which provides electronic conductivity within the electrode, figure 2.3 shows the movement of Li+ ions from the electrolyte into the active material (intercalation) is indicated, as well as the counter movement of electrons through the external circuit (current collector). Plot (c) indicating the complexities and potential overlap in interpreting real-world data. Most of the missing features can be retrieved using dedicated electrochemical experiments, as explained in the following text.

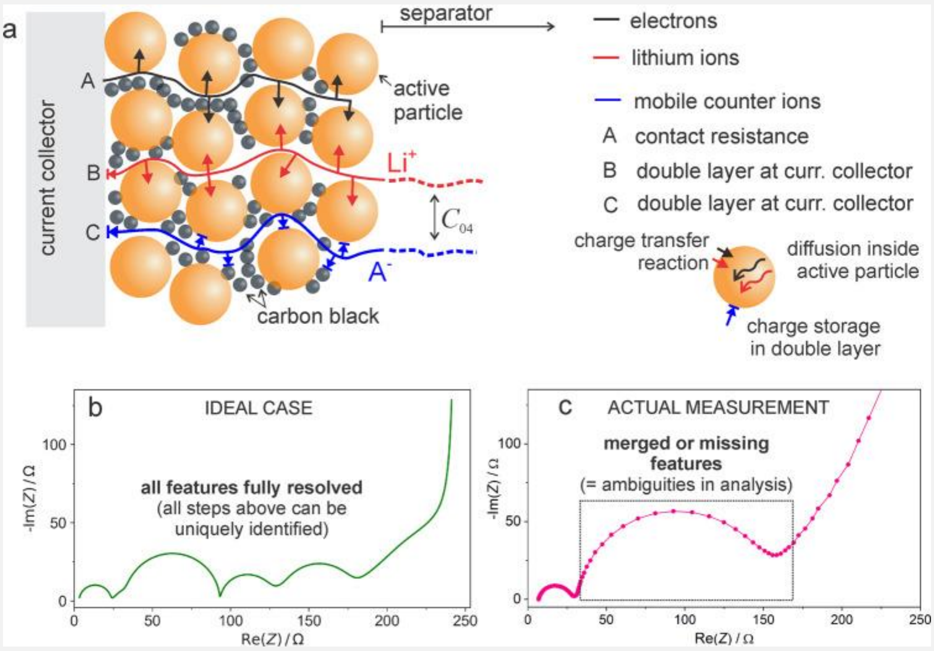


Figure 2.3: The basic scheme showing the electrode structure in panel[8]. a Diagram illustrate the movement of electrons intercalate into the graphite. b Theoretically impedance response c Practical EIS measurement where some of the predict feature is overlap due to the time constant.

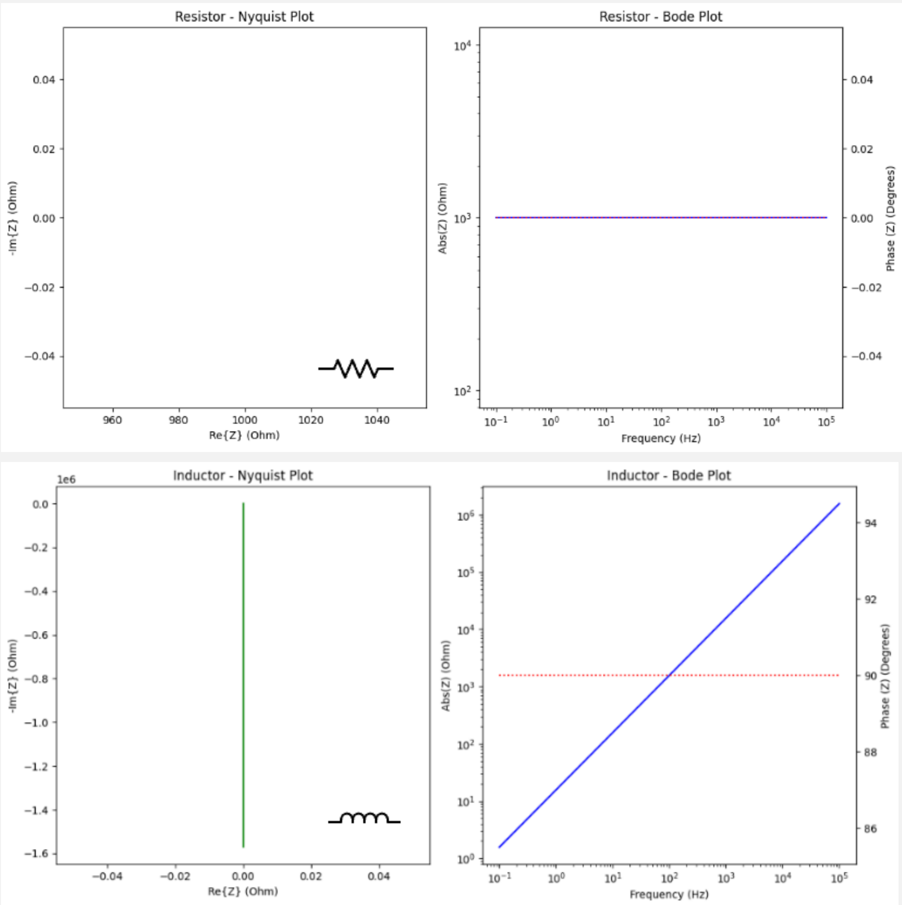
The impedance Z is complex and can be expressed as:

$$\mathrm{Z}(\omega) = R + \frac{1}{j\omega C} + j\omega L + Z_\omega \tag{3}$$

Where:

- R is the ohmic resistance
- C is the capacitance
- L is the inductance
- Z_ω *is the Warburg impedance, and* j *is the imgainaery unit* $(j^2 = -1)$

The impedance of relevant circuit element as shown below as table 1, and the corresponding bode plot and Nyquist plot as shown in figure 2.4.



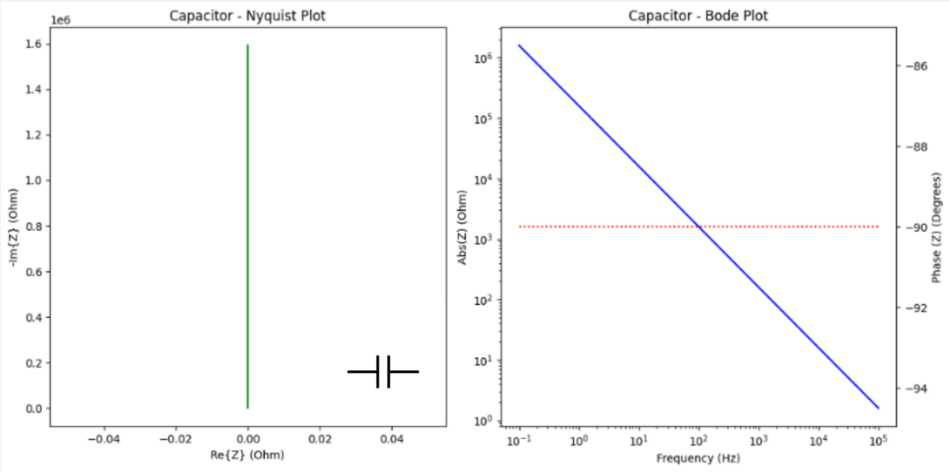


Figure 2.4. Basic circuit component Nyquist and Bode plot simulations result.

Table 1: Impedance of the circuit element

Equivalent Element	Impedance
R (Resistance)	R
C (Capacitance)	$\frac{1}{j\omega C}$
L (Inductance)	$j\omega L$
W (Warburg Impedance)	$\sigma(1-j)\omega^{-\frac{1}{2}}$
	σ: Warburg coefficient
CPE (Constant Phase Element)	$\frac{1}{Q(j\omega)^{\alpha}}$
	$\alpha = 1\ for\ ideal\ capacitor$

The electrical equivalent circuit of a battery is a schematic representation of the electrochemical processes taking place at the positive and negative electrodes. These processes are depicted through various circuit elements, as explained in Figure 2.5 (A).

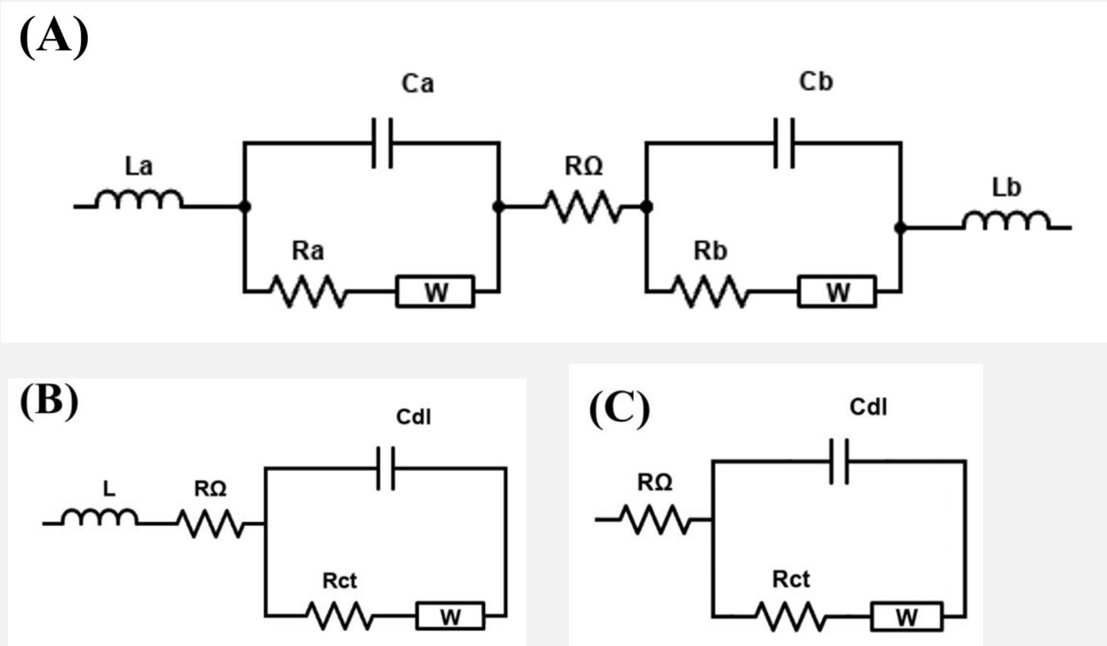


Figure 2.5. Simplified progress of battery circuit model[6]

Battery electrodes are typically porous in nature, a feature that leads to impedance have an inductive behavior at high frequencies[9]. This inductiveness is represented by inductors in the circuit diagram. The resistance (R_Ω) within the circuit represents the ohmic resistance of the electrode material and the electrolyte.

Furthermore, the circuit includes elements such as the charge transfer resistance R_{ct}, double-layer capacitance C_{dl}, and Warburg impedance W for both the anode and cathode. These elements capture the resistance to electron flow at the electrode/electrolyte interface, the capacitive behavior due to the electrode surface electrostatic energy storage, and the diffusion-related impedance[9], respectively.

A simplified version of this circuit is presented in Figure 2.5 (b). This simplification is often necessary because the impedance of the entire cell is typically very low, making it practical to represent the cell with a reduced circuit that focuses on one electrode. However, given that inductance presents a significant reactance in EIS measurements and experiments carried out at low frequencies can minimize overall contribution of cell, the inductor element may be excluded.

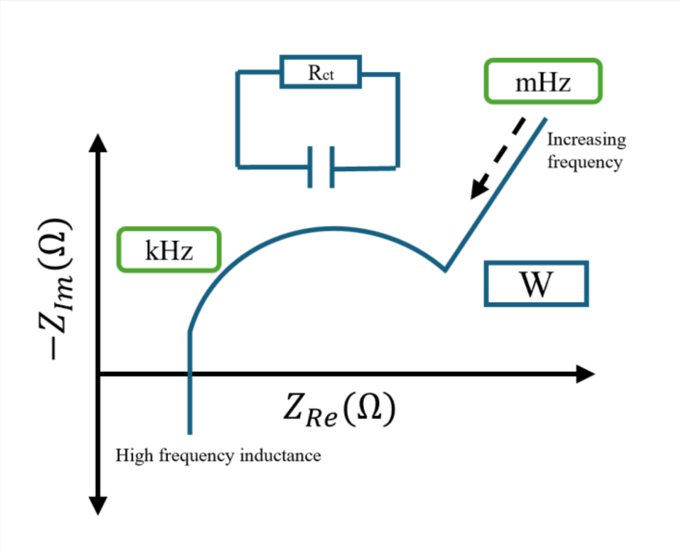


Figure 2.6. EIS of battery circuit model[10]

6.Electrochemical Circuit model

Simple Randles Circuit

The circuit below illustrates a fundamental Randles circuit, a schematic representation commonly used to model the electrochemical impedance of a cell. It features a resistor R_0 in series with a parallel combination of another resistor R_1 and a capacitor C_1. The total impedance Z of the circuit can be mathematically described by the sum of R_0 and the complex impedance resulting from the R_1 - C_1 parallel branch.

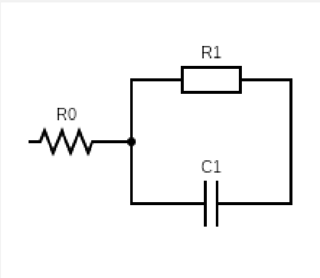


Fig. 3.1 Simple Randle Cell Model

The overall impedance is defined as Z

$$Z = R_0 + \frac{R_0\left(\frac{1}{jwC_1}\right)}{R_1 + \frac{1}{jwC_1}} = R_0 + \frac{R_1}{1 + jwR_1C_1} \tag{4}$$

We make $\omega_1 = \frac{1}{R_1C_1}$

Where ω_1 is the angular frequency at which the imaginary part of the impedance is maximized. This frequency, often referred to as the 'corner frequency,' marks the transition point in the Nyquist plot, where the capacitive behavior of the system starts to dominate over the resistive behavior.

So that equation gets into

$$Z = R_0 + \frac{R_1}{1 + j\frac{\omega}{\omega_1}} = R_0 + \frac{R_1}{1 + (\frac{\omega}{\omega_1})^2} - \frac{R_1\frac{\omega}{\omega_1}}{1 + (\frac{\omega}{\omega_1})^2}j \tag{5}$$

Now, the real part is:

$$Z' = R_0 + \frac{R_1}{1 + (\frac{\omega}{\omega_1})^2} \tag{6}$$

And the imaginary part is:

$$Z'' = -\frac{R_1\frac{\omega}{\omega_1}}{1 + (\frac{\omega}{\omega_1})^2} \tag{7}$$

When $\omega \ll \omega_1$

$$Z \approx R_0 + R_1 \tag{8}$$

This indicate that the impedance at lower frequency is equal to the sum of resistance.

When $\omega \gg \omega_1$

$$Z \approx R_0 \tag{9}$$

This indicate that the impedance at higher frequency is equal to R_0 itself, and the corresponding response for a simple Randles circuit is shown in figure 3.2, the parameter value used as specify in table 2.

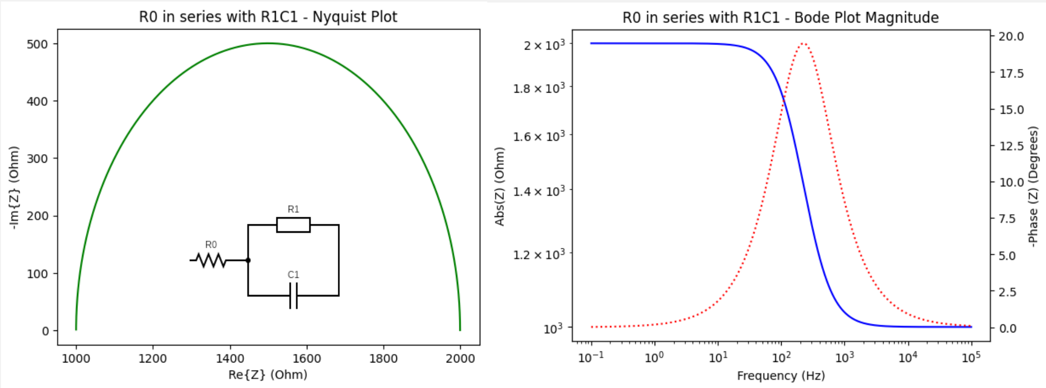


Fig. 3.2 Simple Randle Cell Model

Table 2: Simple Randle Cell Model parameters

Equivalent Element	Impedance
R_0	1000
R_1	1000
C_1	$1\mu f$

Advanced Randles Circuit

The presence of two Randle's cells in series, as shown in fig.3.4, suggests a more complex system where two different electrochemical processes with different characteristic time constants are occurring. This is reflected in the Nyquist plot by two semicircles, the diameter of each semicircle can be related to the charge transfer resistance in that part of the circuit. and in the Bode plot by two peaks in impedance magnitude, each corresponding to one of the Randle's cells. The Bode plot shows two peaks in impedance magnitude, again corresponding to the frequency response of each Randle's cell. The phase plot (Bode phase plot) should show two distinct phase shifts at frequencies where each semicircle dominates the impedance response.

The total impedance is defined as Z:

$$\mathrm{Z} = R_0 + Z_1 + Z_2 = R_0 + R_1 + \frac{1}{jwC_1} + R_2 + \frac{1}{jwC_2} \tag{10}$$

The table3 provides the values for the elements of this advanced model. For instance, R_0 is the ohmic resistance of the battery, R_1 and R_2 are the charge transfer resistances, and C_1 and C_2 are the double layer capacitances for the respective cell.

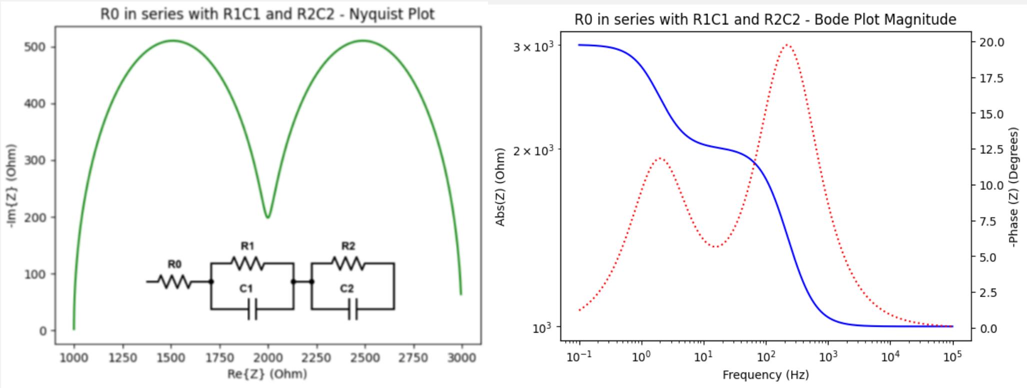


Fig. 3.3 Advanced Randle Cell Model

Table 3: Advanced Randle Cell Model parameters

Equivalent Element	Impedance
R_0	1000
R_1	1000
R_2	1000
C_1	$1\mu f$
C_2	$10mf$

Constant phase element and Warburg impedance

In Li-ion battery, the constant phase element and the Warburg element are used to describe non-ideal capacitive behavior of electrochemical interfaces. Due to surface roughness, leakage capacitance, and nonuniform distribution[11], the non-ideal behavior are presented by the use of CPE. The Warburg element is used to describe the diffusion behavior of the slow process in the battery. The model is evaluated by the creator J.E.B Randles[12]

The impedance of the CPE is expressed as:

$$Z_{CPE} = \frac{1}{Q(jw)^{\alpha}} \qquad (11)$$

Where α parameter reflects the extent to which the interface deviates from the ideal capacitive behavior, while the Q parameter is related to the effective capacitance of the electrode surface, The units of Q° are S•sn [13].

The impedance of the Warburg can be determined as：

$$Z_w = \sigma(1-j)\omega^{-\frac{1}{2}} \tag{12}$$

Where Z_w is the Warburg impedance, σ is the Warburg coefficient.

The presence of Warburg impedance in an electrochemical system's EIS spectrum is indicative of a semi-infinite diffusion process.

The circuit diagram below shows the EIS Nyquist plot and Bode plot for a more realistic half-cell battery system that includes Constant Phase Element (CPE) and Warburg impedance to mimic non-ideal capacitive behavior and diffusion processes, respectively.

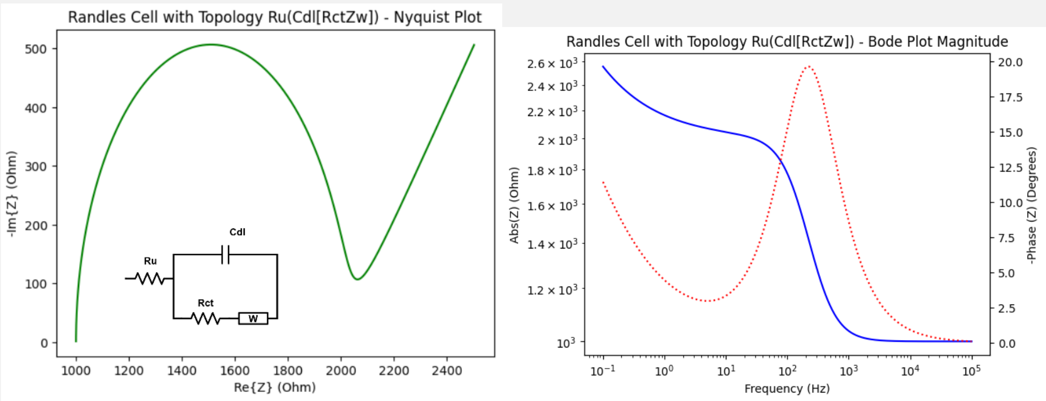


Fig. 3.4 Half-Cell Model contains CPE and Warburg elements.

In Nyquist plot, the presence of the Warburg element typically shows as a 45-degree inclined line at low frequencies, indicative of diffusion-controlled processes. This Warburg behavior often appears after the semicircle at mid-frequencies, which is due to charge transfer resistance in parallel with the CPE, representing double-layer capacitance.

The circuit (figure 3.4) above presented is a basic Randles model used in Electrochemical Impedance Spectroscopy (EIS) for educational purposes and to study EIS principles. Real battery systems, however, are more complex and vary based on the specific chemistry and construction, cell type, storage and cycling condition. For example, Matto Galeotti et al[14] conduct a research on how EIS will changed with cycle period. In hence, tailored models are needed for accurate representation. This report will therefore focus on foundational aspects of EIS, recognizing that it does not cover all battery types.

7.Experimental techniques

Intro of Analog Device Batz System AD5941

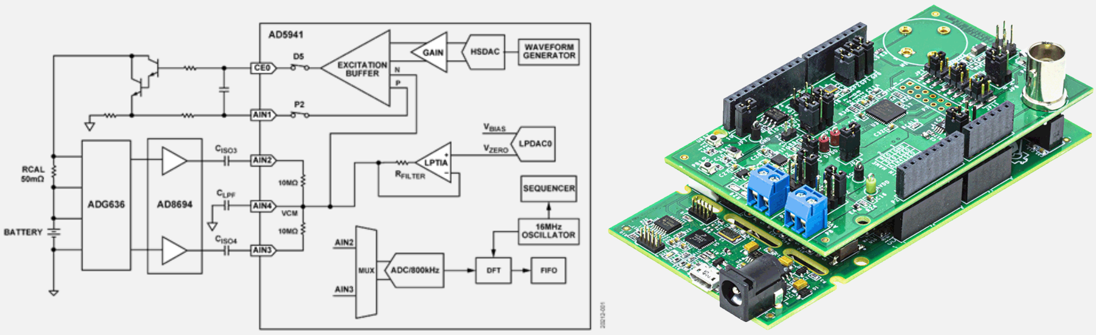


Figure 4.1: Evaluation kits. Left: Block Diagram Right: Evaluation Board contains AD5941 and CN0510 [15]

The experiment utilizes a kit developed by Analog Devices, which includes their SensorPal software. This platform processes impedance data and exports it in CSV format. The system connects to the battery from four BNC cables, ensuring a stable and reliable interface for the measurement signals. The measured EIS data is then achieved to a laptop.

To get the impedance from an battery, an AC current signal is applied to the known resistor R_{CAL}(calibration resistor), and response voltage V_{CAL}, is then measured. Same, measured the voltage of the impedance Vz_{unknow}. The unknown impedance can be calculated using the following equation:

$$Z_{unknown} = \frac{V_{Zunknown}}{V_{cal}} \times R_{cal} \tag{13}$$

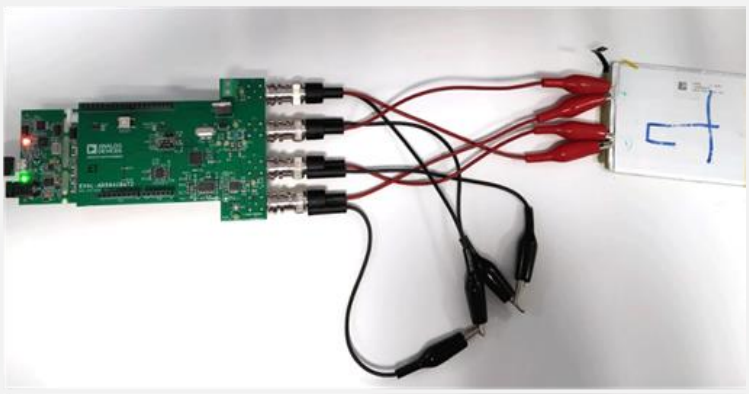


Figure 4.2 Complete EIS Battery System[15]

8.Results

The results section presents data from EIS measurements performed on various commercial batteries: Duracell Non-Rechargeable battery, as well as Energizer Rechargeable battery, under alternating current (AC) and direct current (DC) bias, as indicated in the figure titles. The data align with theoretical expectations, showing an inductive behavior at higher frequencies, which is typical for many electrochemical cells.

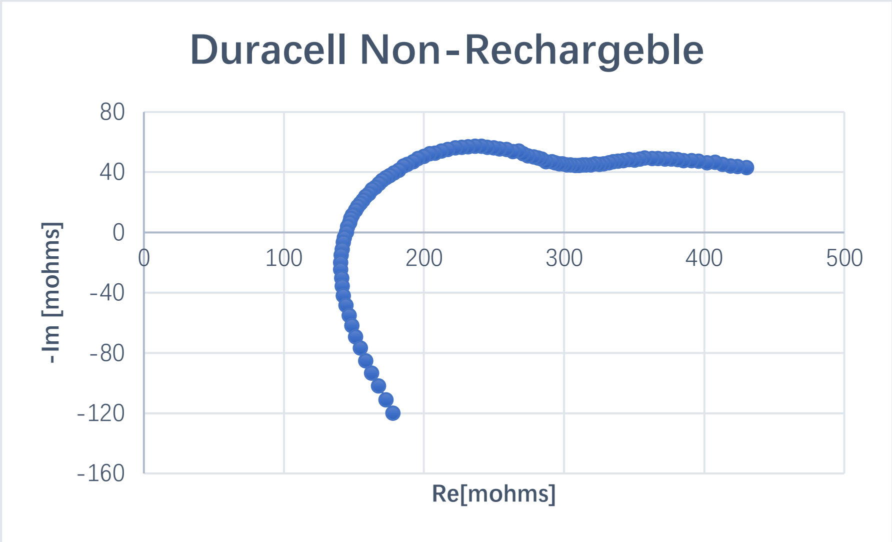


Figure 5.1 Duracell Ni-MH Non-Rechargeable battery. Frequency Sweep: 1-50 kHz. AC:300mV DC:1V

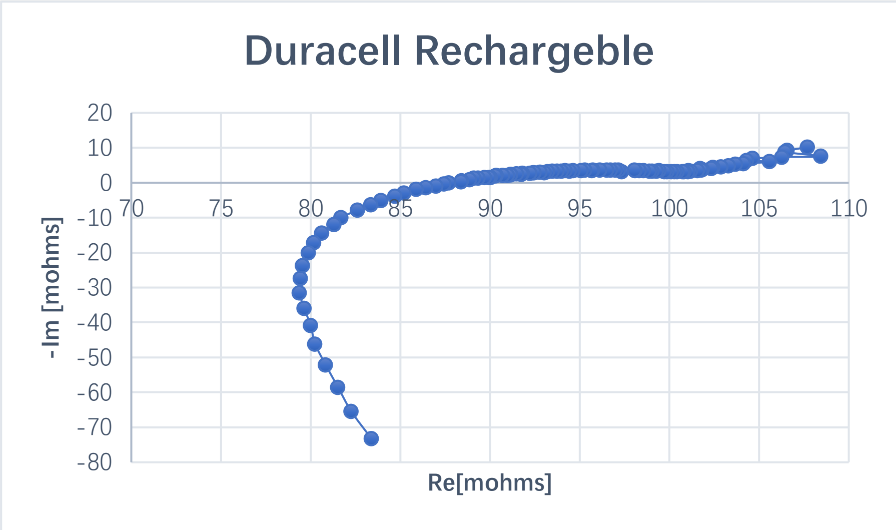


Figure 5.2 Duracell Ni-MH Rechargeable battery. Frequency Sweep: 1-50 kHz. AC:300mV DC:0.9V

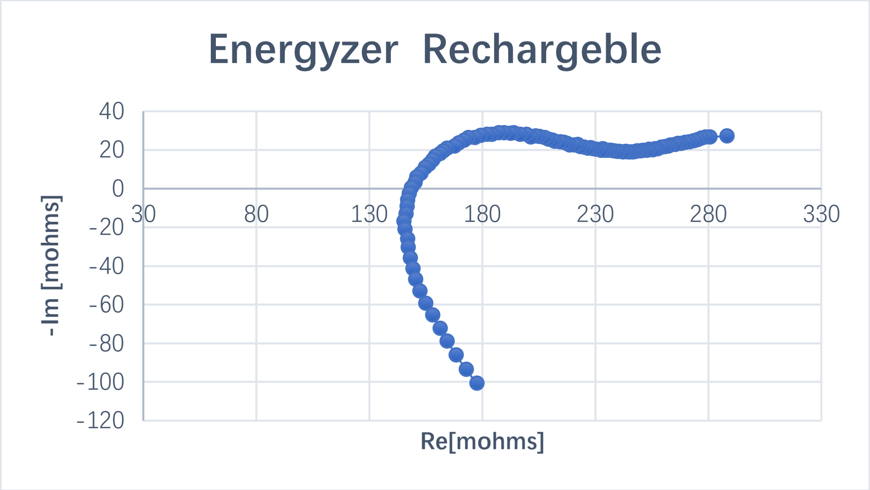


Figure 5.3 Energizer Ni-MH Rechargeable battery. Frequency Sweep: 1-50 kHz. AC:300 mV DC:1V

At high frequencies, inductive effects in EIS data become noticeable. However, for cells with overall low impedance, these effects may be negligible and not require an inductor in the equivalent circuit model for a high-frequency range. In hence the following results remove the inductive part, which is at very high frequency, for the purpose for focusing on the effective impedance of the cell.

The following results further conducted a study on characterize the impedance behavior and extract pertinent electrical parameters via equivalent circuit models, thereby assessing each battery's electrochemical attributes. The EIS data was modelled and fitted using the methodology described in [16], which outlines a Python tool for circuit model fitting of impedance data. This package offers a systematic approach to EIS data fitting, enabling the extraction of equivalent circuit parameters that provide insights into the battery's charge transfer, ohmic resistance, double-layer capacitance, and diffusion processes.

The equivalent circuit model fitting was executed in a Google Colab environment. The models and the parameters used to generate the plot were selected based on the fitting results. Impedance measurements were obtained for each battery type across a frequency range from 1 kHz to 50 kHz under a regulated AC voltage. Ideal fit were obtained for each battery type as well as validation.

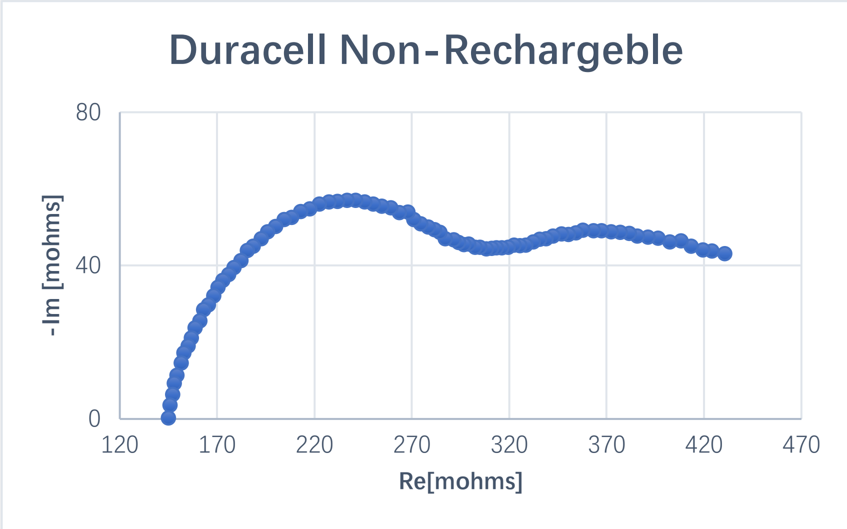


Figure 5.4 Duracell Ni-MH Non-Rechargeable battery. Frequency Sweep: 1-50kHz. AC:300mV DC:1V

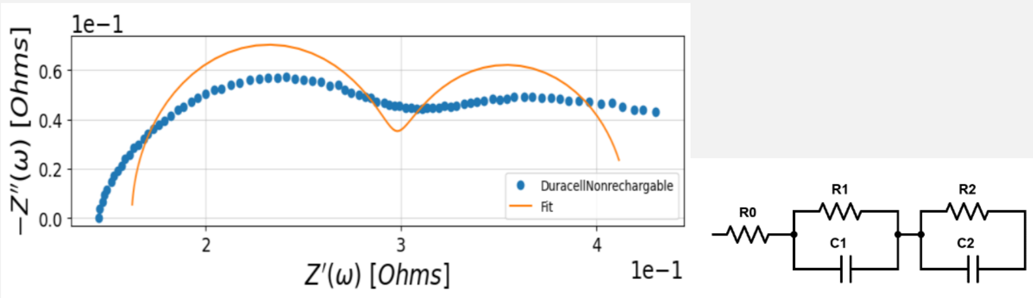


Figure 5.5 Left: Fitting result. Right: Equivalent circuit

Table 4: Duracell Ni-MH Non-Rechargeable battery Fitting parameters.

Equivalent Element	Value
R_0	162[mOhms]
R_1	119[mOhms]
R_2	136[mOhms]
C_1	$270[mF]$
C_2	$4.74[mF]$

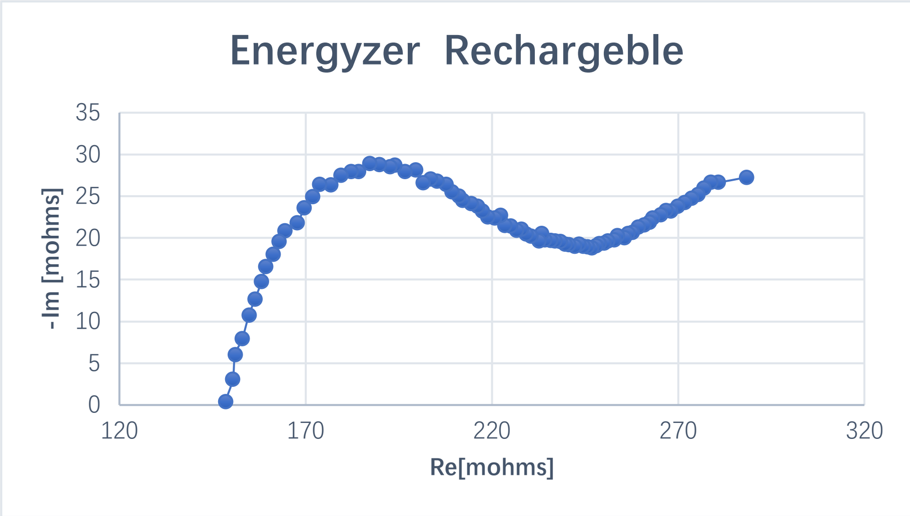


Figure 5.6 Energizer Ni-MH Rechargeable battery. Frequency Sweep: 1-50kHz. AC:300 mV DC:1V

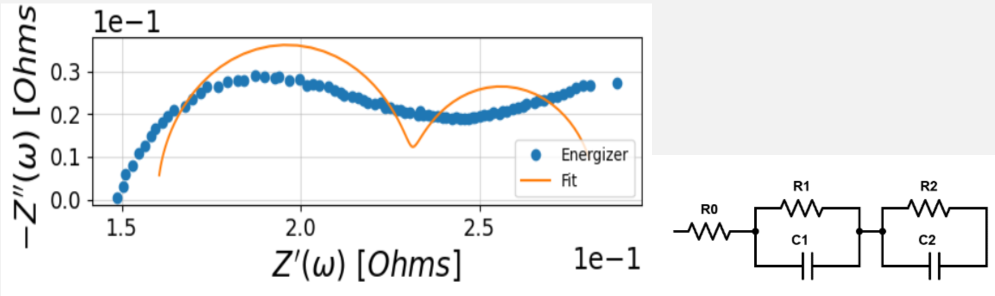


Figure 5.7 Left: Fitting result. Right: Equivalent circuit

Table 5: Energizer Ni-MH Rechargeable battery Fitting Parameters.

Equivalent Element	Value
R_0	160[mOhms]
R_1	51.3[mOhms]
R_2	71.2[mOhms]
C_1	$0.582[F]$
C_2	$4.45mF$

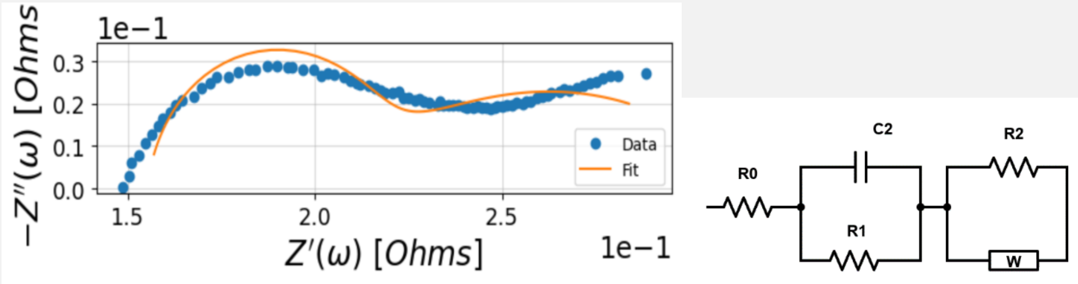


Figure 5.8 Left: Fitting result. Right: Equivalent circuit

Table 6: Energizer Ni-MH Rechargeable battery Fitting Parameters.

Equivalent Element	Value
R_0	154[mOhms]
R_1	55.2[mOhms]
R_2	109[mOhms]
C_1	$3.99[F]$
W	$372[Ohm \times s^{-\frac{1}{2}}]$

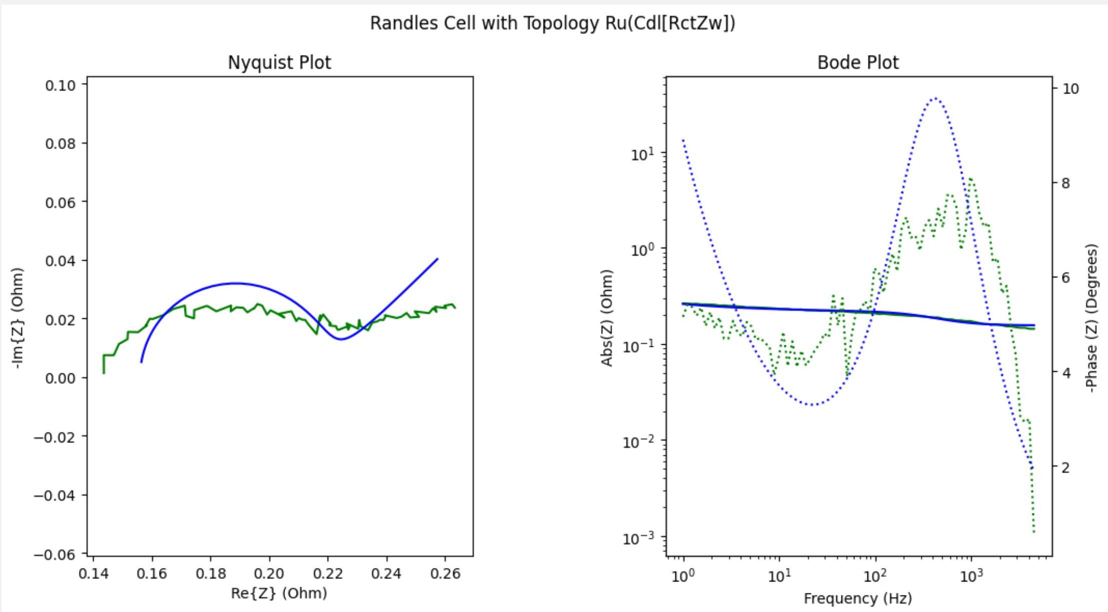


Figure 5.9 Validation result based on Colab.

9.Discussion of results

Duracell Non-Rechargeable Battery

The Nyquist plot (Figure 5.4) displays a capacitive semicircle at mid-frequencies. The diameter of the semicircle is generally associated with charge transfer resistance, while the intercept with the real axis at high frequency is related to the ohmic resistance of the electrolyte, electrodes, and separators. The corresponding equivalent circuit model included a parallel RC circuit provided an appropriate fit, as corroborated by visual comparison in the Nyquist representation.

The absence of a perfect fit at low frequencies might be due to several factors, including limitations in the data, where the Warburg characteristic is not captured, or inaccuracies in the equivalent circuit model.

Energizer Rechargeable Battery

The Nyquist plot (Figure 5.6) showcases a behavior typical for rechargeable batteries, with a clear semicircle at mid to high frequencies which suggests charge transfer resistance, and a straight sloped line at lower frequencies indicative of diffusion processes, often modelled by a Warburg impedance.

The fitted results are plotted on the Nyquist plot (Figure 5.7, Left), providing a visual validation of the equivalent circuit model's ability to represent the battery's impedance characteristics. Using Google Colab, the fitted parameters can be used to simulate the impedance spectrum and validate the model further. This involves generating a complex impedance curve across the same frequency sweep used for the measurements. The simulated data can then be plotted to ensure it matches the experimental data points closely.

Two distinct equivalent circuit models were applied to fit the EIS data of the Energizer Ni-MH Rechargeable battery. The chosen model appears to capture the primary electrochemical characteristics of the battery. However, to find the most accurate representation of the battery’s, a comparison of these models is needed.

10.Ethics, Health, and safety

During the course of this project, health and safety protocols were implemented to ensure a safe environment. A specialized battery box as shown in figure 6.1 was constructed, to hold the battery during measurement procedures. This safety measure was crucial in avoid risks such as overheating or potential battery failure, providing an additional layer of protection against the unlikely event of a battery exploding. The measure process is following BATZ board user guide, such as power up the BATZ board prior to connecting any batteries. This step is essential to avoid the short-circuiting of the battery.

The ethical considerations of this project were following the standards set by the University College Cork (UCC). All sources of background information, hardware, and software utilized within the project were properly cited. The use of images in reports, seminar presentations, and open-day posters was conducted under guidelines. The entirety of the research and written material in the report is the original work of the student. To ensure transparency, no measurements or model fits were altered; all data presented is the actual data obtained from battery measurements and simulations.

Figure 6.1 Battery holder box built special for this project.

11.Summary and Conclusion

The project aimed to enhance the understanding and analysis of battery performance using Electrochemical Impedance Spectroscopy (EIS). We investigated the working principles of lithium-ion batteries, including the significance of lithium ions' movement and how it affects energy density and cycle life. Additionally, we conducted thorough basic introduction on nickel-metal hydride batteries, credit to their environmentally friendly attributes and cost-effectiveness.

By exploring the fundamental principles of EIS, starting with the very definition of impedance as a complex quantity that characterizes the opposition to alternating current in an electrochemical system. Through Nyquist and Bode plots, we demonstrated the resistive and capacitive behaviors of batteries, with a theoretical exploration of various battery models, noting the correspondence between the imaginary impedance part and Nyquist plots' semicircular radius.

One of the highlights of our project was the successful utilization of the Analog Devices BATZ measurement system. This sophisticated piece of equipment allowed us to capture precise EIS measurements, which can capture as low as milli Ohms for accurate analysis. Real-world battery data was then measured and collected, followed by fitting this data to the equivalent circuits to interpret battery performance. The theoretical models and simulations came to life as we observed that the measured results from the batteries generally aligned with the behavior predicted by theory. This not only validated our understanding and application of EIS but also reinforced the reliability of our modeling approach. The work accomplished in this project has not only enforce our understanding of EIS but has also proven instrumental in assessing and predicting the performance of different battery types.

12.Suggestions for future work

The current analysis has provided valuable insights into the electrochemical characteristics of different types of battery. Future studies should aim to include a wider variety of battery chemistries, such as Lithium-ion, Lead-acid, and newer solid-state batteries. While the study utilized specific ECMs that were appropriate for the given battery types, other models may offer better insights for different battery configurations or states of health. Research should be directed towards evaluating a broader range of circuit models, including those with additional RC elements, or incorporating elements to account for inductive behaviors at higher frequencies.

13.Bibliography

[1] J.-M. Tarascon and M. Armand, “Issues and challenges facing rechargeable lithium batteries,” *Nature*, vol. 414, no. 6861, Art. no. 6861, Nov. 2001, doi: 10.1038/35104644.

[2] C. Frank, “Ford Downsizes Plan for Battery Factory, Citing Slower EV Demand,” CF.ORG. Accessed: Dec. 03, 2023. [Online]. Available: https://www.cf.org/news/ford-downsizes-plan-for-battery-factory-citing-slower-ev-demand/

[3] D. Deng, “Li-ion batteries: basics, progress, and challenges,” *Energy Sci. Eng.*, vol. 3, no. 5, pp. 385–418, Sep. 2015, doi: 10.1002/ese3.95.

[4] Y. Zhu, W. H. Zhu, Z. Davis, and B. J. Tatarchuk, “Simulation of Ni-MH Batteries via an Equivalent Circuit Model for Energy Storage Applications,” *Adv. Phys. Chem.*, vol. 2016, pp. 1–11, Mar. 2016, doi: 10.1155/2016/4584781.

[5] D. Deng, M. G. Kim, J. Y. Lee, and J. Cho, “Green energy storage materials: Nanostructured TiO2 and Sn-based anodes for lithium-ion batteries,” *Energy Environ. Sci.*, vol. 2, no. 8, pp. 818–837, Jul. 2009, doi: 10.1039/B823474D.

[6] S. Rodrigues, N. Munichandraiah, and A. K. Shukla, “A review of state-of-charge indication of batteries by means of a.c. impedance measurements,” *J. Power Sources*, vol. 87, no. 1, pp. 12–20, Apr. 2000, doi: 10.1016/S0378-7753(99)00351-1.

[7] T. Momma, M. Matsunaga, D. Mukoyama, and T. Osaka, “Ac impedance analysis of lithium ion battery under temperature control,” *J. Power Sources*, vol. 216, pp. 304–307, Oct. 2012, doi: 10.1016/j.jpowsour.2012.05.095.

[8] J. Moškon and M. Gaberšček, “Transmission line models for evaluation of impedance response of insertion battery electrodes and cells,” *J. Power Sources Adv.*, vol. 7, p. 100047, Feb. 2021, doi: 10.1016/j.powera.2021.100047.

[9] N. A. Hampson, S. A. G. R. Karunathilaka, and R. Leek, “The impedance of electrical storage cells,” *J. Appl. Electrochem.*, vol. 10, no. 1, pp. 3–11, Jan. 1980, doi: 10.1007/BF00937331.

[10] A. Guha and A. Patra, “Online Estimation of the Electrochemical Impedance Spectrum and Remaining Useful Life of Lithium-Ion Batteries,” *IEEE Trans. Instrum. Meas.*, vol. 67, no. 8, pp. 1836–1849, Aug. 2018, doi: 10.1109/TIM.2018.2809138.

[11] W. Choi, H.-C. Shin, J. M. Kim, J.-Y. Choi, and W.-S. Yoon, “Modeling and Applications of Electrochemical Impedance Spectroscopy (EIS) for Lithium-ion Batteries,” *J. Electrochem. Sci. Technol.*, vol. 11, no. 1, pp. 1–13, Feb. 2020, doi: 10.33961/jecst.2019.00528.

[12] J. E. B. Randles, “Kinetics of rapid electrode reactions,” *Discuss. Faraday Soc.*, vol. 1, pp. 11–19, Jan. 1947, doi: 10.1039/DF9470100011.

[13] “Impedance spectroscopy,” *Impedance Spectrosc.*.

[14] M. Galeotti, C. Giammanco, L. Cinà, S. Cordiner, and A. Di Carlo, “Synthetic methods for the evaluation of the State of Health (SOH) of nickel-metal hydride (NiMH) batteries,” *Energy Convers. Manag.*, vol. 92, pp. 1–9, Mar. 2015, doi: 10.1016/j.enconman.2014.12.040.

[15] “CN0510 Circuit Note | Analog Devices.” Accessed: Dec. 14, 2023. [Online]. Available: https://www.analog.com/en/design-center/reference-designs/circuits-from-the-lab/CN0510.html#rd-description

[16] “impedance.py — impedance.py 1.7.1 documentation.” Accessed: Apr. 11, 2024. [Online]. Available: https://impedancepy.readthedocs.io/en/latest/index.html

Appendix I: Python code for EIS Simulation (developed on Google Colab)

```
# This programme simulates some EIS curves for simple circuits.

# The circuits are mainly taken from "Electrochemical Impedance Sprectroscopy

# - A Tutorial" by Lazanas and Prodromodis", ACS Meas. Sci. Au 2023,3, 162-193.

import numpy as np

import matplotlib.pyplot as plt


# First define a function that will be used to draw the Nyquist and Bode plots.

def drawZplots(Zarray,PlotTitle):


# Thus function draws a Nyquist and a Bode plot from the impedance data in Zarray with
a title in PlotTitle

  fig, (nyquist,bode) = plt.subplots(1,2)


#  Draw the Nyquist plot

  nyquist.plot(np.real(Zarray),-np.imag(Zarray),color='green')

  nyquist.set_xlabel("Re{Z} (Ohm)")

  nyquist.set_ylabel("-Im(Z) (Ohm)")

  nyquist.set_title("Nyquist Plot")


#  Draw the Bode plot magnitude

  bode.plot(Freq,np.abs(Zarray),color='blue')

  bode.set_xscale('log')

  bode.set_yscale('log')

  bode.set_xlabel("Frequency (Hz)")

  bode.set_ylabel("Abs(Z) (Ohm)")
```

```
    bode.set_title("Bode Plot")
#  Draw the Bode plot phase as a second y-axis
    bode2 = bode.twinx()
    bode2.plot(Freq,np.rad2deg(-np.angle(Zarray)),color='red',linestyle='dotted')
    bode2.set_ylabel("-Phase (Z) (Degrees)")

    plt.subplots_adjust(wspace = 0.5)
    fig.suptitle(PlotTitle)
    plt.show()

# End of function to draw the plots
# Set up a suitable frequency range for the simulations
# and claculate some frequency dependent quantities for use later
Fstart = 0.1 # Lowest frequency in Hz
Fstop =  1e5 # Highest frequency in Hz
Nfreq = 1001 # Number of frequencies
Ftemp = np.linspace(np.log10(Fstart),np.log10(Fstop),Nfreq)
Freq = 10**Ftemp
w = 2*np.pi*Freq
sqrt_w = np.sqrt(w)
on_sqrt_w = 1/sqrt_w
jw = 1j*w

# Simulate a single resistor
R1 = 1000
ZRes = R1 + 0*jw
drawZplots(ZRes,"Resistor")

# Simulate a single capacitor
```

```
C1 = 1.0e-6

ZCap = 0 +  1/(jw*C1)

drawZplots(ZCap,"Capacitor")


# Simulate a single inductor

L1 = 2.5

ZInd = 0 + jw*L1

drawZplots(ZInd,"Inductor")


# Simulate a resistor and capacitor in series

R1 = 1000

C1 = 1.0e-6

ZRCseries = R1 +  1/(jw*C1)

drawZplots(ZRCseries,"Resistor and Capacitor in Series")


# Simulate a resistor and capacitor in parallel

R1 = 1000

C1 = 1.0e-6

ZRCparallel = R1/(1 + jw*R1*C1)

drawZplots(ZRCparallel,"Resistor and Capacitor in Parallel")


# Simulate a resistor R0 in series with a parallel combination of R1,C1

R0 = 1000

R1 = 1000

C1 = 1.0e-6

ZR0_R1C1 = R0 + R1/(1 + jw*R1*C1)

drawZplots(ZR0_R1C1,"R0 in series with R1C1")
```

```
# Simulate a resistor R0 in series with a parallel combination of R1,C1 followed by another parallel combination of R2,C2

R0 = 1000

R1 = 1000

R2 = 1000

C1 = 1.0e-6

C2 = 1.0e-4

ZR0_R1C1_R2C2 = R0 + R1/(1 + jw*R1*C1) + R2/(1 + jw*R2*C2)

drawZplots(ZR0_R1C1_R2C2,"R0 in series with R1C1 and R2C2")


# Simulate a Warburg impedance on its own

Sigma = 400

ZWar = Sigma*on_sqrt_w*(1 - 1j)

drawZplots(ZWar,"Warburg Impedance (Zw)")


# Simulate a Randles cell containing a Warburg impedance

# The cell consists of a resistance Rct in series with a Warburg impeance Zw

# all in parallel with a capacitor Cdl and all of this is series with a

# resistance Ru. The cell notation is Ru(Cdl[RctZw]).


Ru = 1000

Rct = 1000

Cdl = 1e-6

Sigma = 400

ZWar = Sigma*on_sqrt_w*(1 - 1j)

ZRctZWar = Rct + ZWar

ZCdl = 0 +  1/(jw*Cdl)

ZRand = Ru + (ZCdl*ZRctZWar)/(ZCdl + ZRctZWar)

drawZplots(ZRand,"Randles Cell with Topology Ru(Cdl[RctZw])")
```

```
# Simulate a Constant Phase Element on its own

Alpha = 0.9

Q = 1.0e-6

ZCPE = 1/(Q*(jw**Alpha))

drawZplots(ZCPE,"Constant Phase Element")


# Simulate a resistor Ru in series with a Constant Phase Element Q1

Ru = 1000

Q1 = 1.0e-6

Alpha1 = 0.9

ZCPE1 = 1/(Q1*(jw**Alpha1))

ZRuZCPE1 = Ru + ZCPE1

drawZplots(ZRuZCPE1,"Resistor in Series with Constant Phase Element")


# Simulate a resistor Ru in series with a parallel combination of resistor

# Rct and Constant Phase Element Q1

Ru = 1000

Rct = 1000

Q1 = 2.0e-6

Alpha1 = 0.9

ZCPE1 = 1/(Q1*(jw**Alpha1))

ZRu_RctCPE1 = Ru + Rct*ZCPE1/(Rct + ZCPE1)

drawZplots(ZRu_RctCPE1,"Randles Cell with Topology Ru(RctCPE)")
```

Appendix II: Python code for fitting developed on Jupyter notebook

```
#For R0-p(R1,C1)-p(R2,W)
import impedance as imp
from impedance.models.circuits import Randles, CustomCircuit
from impedance import preprocessing

# Load data from the example EIS data
frequencies, Z = preprocessing.readCSV('./EnergizerDC1AC300m.csv')

# keep only the impedance data in the first quandrant
frequencies, Z = preprocessing.ignoreBelowX(frequencies, Z)
from impedance.models.circuits import CustomCircuit

circuit = 'R0-p(R1,C1)-p(R2,W)'
initial_guess = [45e-3,.1,5e-3,.1,0.02]
#constants={'R0': 45e-3}

circuit = CustomCircuit(circuit, initial_guess=initial_guess)
circuit.fit(frequencies, Z)
Z_fit = circuit.predict(frequencies)
print(circuit)
import matplotlib.pyplot as plt
from impedance.visualization import plot_nyquist

fig, ax = plt.subplots()
plot_nyquist(Z, fmt='o', scale=10, ax=ax)
```

```
plot_nyquist(Z_fit, fmt='-', scale=10, ax=ax)


plt.legend(['Data', 'Fit'])
plt.savefig('nyquist_plot.png', dpi=300)
plt.tight_layout()

plt.show()



#For R0-p(R1,C1)-p(R2,C2)
import impedance as imp
from impedance.models.circuits import Randles, CustomCircuit
from impedance import preprocessing

# Load data from the example EIS data
frequencies, Z = preprocessing.readCSV('./EnergizerDC1AC300m.csv')
#Note here the Duracell csv can be use here as well
# keep only the impedance data in the first quandrant
frequencies, Z = preprocessing.ignoreBelowX(frequencies, Z)

from impedance.models.circuits import CustomCircuit

circuit = 'R0-p(R1,C1)-p(R2,C2)'
initial_guess = [45e-3,1,5,0.02,0.05]
#constants={'R0': 45e-3}

circuit = CustomCircuit(circuit, initial_guess=initial_guess)
circuit.fit(frequencies, Z)
Z_fit = circuit.predict(frequencies)
```

```
print(circuit)

import matplotlib.pyplot as plt
from impedance.visualization import plot_nyquist
# Set a larger figure size
fig, ax = plt.subplots(figsize=(10, 8))
plot_nyquist(Z, fmt='o', scale=10, ax=ax)
plot_nyquist(Z_fit, fmt='-', scale=10, ax=ax)
plt.legend([Energizer', 'Fit'])
plt.show()
```

Appendix III:Logbook