

Methods—Unexpected Effects in Galvanostatic EIS of Randles' Cells: Initial Transients and Harmonics Generated

To cite this article: Gökberk Katrc *et al* 2022 *J. Electrochem. Soc.* **169** 030527

View the [article online](#) for updates and enhancements.



 **244th Electrochemical Society Meeting**
October 8 – 12, 2023 • Gothenburg, Sweden
50 symposia in electrochemistry & solid
state science
Abstract submission deadline:
April 7, 2023

Read the call for
papers &
submit your abstract!



Methods—Unexpected Effects in Galvanostatic EIS of Randles' Cells: Initial Transients and Harmonics Generated

Gökberk Katırcı,¹ Mohammed Ahmed Zabara,^a and Burak Ülgüt^z

Bilkent University, Department of Chemistry, Ankara, Turkey

Non-linear EIS analysis is gaining wider attention and interest due to the deeper understanding that is provided especially when combined with linear EIS. The nonlinear part of the data can get corrupted due to a number of effects. One of these is the initial transient, which is the response right after excitation signal is applied before a steady-state is reached. In this study, we demonstrate this phenomenon through analyzing simplified Randles' cells via Kirchhoff's laws. To get rid of the effects of the initial transient, instrument manufacturers typically discard some fraction of the response, the effectiveness of which, as demonstrated here has to be checked.

© 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: [10.1149/1945-7111/ac5ad7](https://doi.org/10.1149/1945-7111/ac5ad7)]

Manuscript submitted December 30, 2021; revised manuscript received February 23, 2022. Published March 17, 2022.

In recent years, studies involving investigations on the non-linear response of Electrochemical Impedance Spectroscopy (EIS) measurements have been increasing. The physical phenomena behind the electrochemical processes in an electrochemical system is explained through nonlinear relations between current and voltage e.g., Butler-Volmer equation. Reflections of this non-linearity is observed in the impedance response, depending on the excitation signal applied. The investigation of the non-linear part of the response signal can lead to invaluable information, which can complement the information obtained from the linear part.¹

In non-linear EIS, distortions from linearity in the response signal are analyzed in the frequency domain by means of Fourier Transform. The appearance of higher harmonics above the noise level beside the fundamental signal is an indication of the presence of non-linearities in the response. These harmonics are studied and correlated to linear impedance response or directly to electrochemical processes. Recently, theoretical background along with some experimental examples were reviewed by Vidaković-Koch et al.² which highlighted the functionality of non-linear EIS for in-depth kinetic analysis of electrochemical systems. Murbach and Schwartz attributed nonlinear harmonic response to cell aging, thermodynamic and kinetic properties of commercial batteries.³ In addition, studies by Harting et al. compared aging process at different temperatures with EIS for lithium ion batteries.⁴⁻⁶ Furthermore, Liebhart and co-workers published their study about utilizing non-linear EIS in analyzing and modeling of lithium ion batteries at different temperatures and SoC's.⁷ In another study by Kiel et al., authors employed higher order harmonic analysis in order to investigate EIS errors, and built simple Randles circuit models for simulation to explain the error sources.⁸ Furthermore, Ernst et al. investigated non-linear EIS of lithium ion batteries under different SoC's and temperatures in terms of current and overpotentials.⁹ A review paper by Szekeres and co-workers thoroughly discussed advantages and drawbacks of the methods for initial transient correction.¹⁰ In the past, we have investigated the nonlinear harmonic analysis of Li/SOCl₂ batteries,¹¹ and demonstrated the passivation layer effect on harmonics. Specifically, our observations indicated that the increase in harmonics directly correlated with an increase in the passivation layer. The value of higher harmonics in EIS is clearly demonstrated.

Like with any characterization technique, negative controls have to be an integral part of nonlinear EIS analysis. Before analyzing the response of electrochemical system, one has to make sure that any observed non-linearities are originating from the studied systems and not due to other artifacts. An easy control experiment can be

achieved using dummy cells constructed from components with identical parameters to the studies system.

During such investigations, we measured several dummy cells that were constructed as models of simplified Randles' Cells (Fig. 1) as negative control experiments. We observed that the harmonics of the signals are not only significantly above the noise floor but also frequency dependent, and can be mistaken for the non-linearities due to the electrochemical processes. In the current manuscript, we will describe the fundamental reason behind the non-linear response and show that the experimental result perfectly matches a simple simulation based on Kirchhoff's laws (Fig. A-1). We will further show that the non-linearity observed is frequency dependent whenever a capacitor is involved and the cases where this frequency dependence is not observed are only due to the noise being higher than the non-linearities (Fig. A-2).

As we will show below, this issue is one of startup transients. As the sine wave starts being applied, the system response takes finite time before a steady-state response is established. This is the reason for a typical waiting period before the analyzed data is collected. However, the implementations across the manufacturers vary widely and mostly left to the experimenter to adjust (somewhat hidden under "advanced" sections). In the literature, we have been able to find two references that mention this effect. Firstly, JR Macdonald and Y Barsoukov the mode of measurement is not mentioned, but the recipe for solution is "adding *at least* one period delay after the sine-wave onset"(emphasis added).¹² In another study referenced by Orazem and Tribollet,¹ Pollard and Comte simply calculated the response to a single period of signal and estimated the error to be 4% when only a single sine wave is considered in potentiostatic mode for solid electrolytes.¹³ It is also worth noting that a methods have been developed for galvanostatic modulation that selects a frequency-dependent amplitude in maintaining a constant level of AC voltage.^{14,15} It is important to emphasize that our study specifically focuses on galvanostatic mode. The startup transients in potentiostatic mode are typically much shorter and beyond the scope of this manuscript.

We will show that even when galvanostatically measuring a dummy cell constructed in the simplified Randles' cell configuration, the frequency dependent non-linearity is clearly observable. The level of non-linearity is typically too low to be seen in the fundamental (typically less than 1%), however, when measuring the non-linear spectrum, this effect has to be taken into account and suppressed appropriately.

Experimental

Two dummy cells were built to test the effect. The first one (10 Hz) is made of 1 k Ω resistance (in series) connected to 1 μ F capacitor and 100 k Ω resistance in parallel. Similarly, the second one (100 Hz) is built with the same 1k Ω resistance (in series) linked with

^aPresent Address: Sabancı University, SUNUM, Istanbul, Turkey.

^zE-mail: ulgut@fen.bilkent.edu.tr

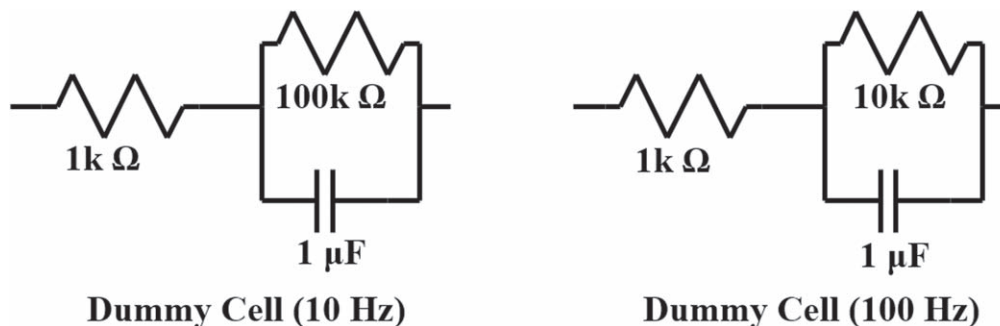


Figure 1. Two simulated and measured dummy cell diagrams with characteristic frequencies of 10 Hz (left) and 100 Hz (right).

1 μF capacitor and 100 $\text{k}\Omega$ resistance in parallel. The simulation parameters were also adjusted to these exact values.^b Series resistances are chosen such that a resistive response is observed at the high frequency limit of the experiments.

Measurements with dummy cells were made with Gamry Instruments® Reference 3000 potentiostat/galvanostat/ZRA, coupled with Gamry's Framework (version 7.8.6). The data collection employed a modified version of the measurement script. Details of this modification was published in a previous publication.¹¹ The modification to the standard script applies a sinusoidal signal of fixed five periods and measures the voltage response. This time-domain signal is then saved in a separate file for each frequency. The fundamental response and its overtones (harmonics) were calculated in a post-processing step. Unless otherwise mentioned, the Fourier transform input is the voltage signal from 4 periods of the applied frequency. The first cycle is discarded, as was the default in our instrument.

Throughout the experiments, 10 μA AC current was employed on both dummy cells, with zero as the DC current setpoint.

The simulations were done in Python's Spyder (Anaconda) IDE, with importing Matplotlib, NumPy and SciPy libraries.^{16–18} The complete code is available in the [Appendix](#).

Results and Discussion

Measurement.—The results of the measurement on two different dummy cells are shown in Fig. 2, where the impedance is shown along with the voltage amplitude of the second, third and fourth harmonics. For both dummy cells, the harmonics clearly show a frequency-dependent signal that reaches a maximum around the time constant of the respective cell that is slowly decreasing with increasing harmonic order. This observation has to be properly explained before any further analysis of nonlinearities in the studied system.

Simulation.—In order to investigate the issue in more detail, a simple simulation is carried out. The voltage across the cell under arbitrary current can be calculated as the sum of the voltage across the series resistor (R_s) and the voltage across the capacitor (C) or equivalently the voltage across the parallel resistor (R_p).

To calculate the voltage across the parallel part of the circuit, the current distribution across the two parallel arms must be calculated, based on the fact that the voltage across the parallel resistor and the capacitor will be equal. Therefore:

$$i_R \times R_p = \frac{\int_0^t i_C dt}{C} \quad [1]$$

where i_R is the current through the parallel resistor, and i_C is the current through the capacitor. Further, the two currents must sum up to the total current:

$$i_R + i_C = i \quad [2]$$

where i is the total current. By substituting Eq. 2 in Eq. 1 and reorganizing, an equation regarding i_C as a function of C , R_p and i can be obtained:

$$i_C = i - \frac{1}{C \times R_p} \times \int_0^t i_C dt \quad [3]$$

For a discrete time series, this equation may be rewritten as:

$$i_C[j] = i[j] - \frac{1}{C \times R_p} \times \sum_{k=0}^{index-1} i_C[k] \times t_s \quad [4]$$

Where t_s is the sampling time and j is the index used for the current arrays. This equation can be used iteratively to calculate the current through the capacitor. It is important that there are no assumptions regarding the current in this equation. This is critical in being able to simulate arbitrary current sequences. This way, a sine wave starting after a zero current period, as well as what is happening after the signal is stopped can be simulated.

Once the current through the capacitor (and therefore the current through the resistor) is calculated, the voltage across the whole cell can be written as:

$$E = i[j] \times R_s + \sum_{k=0}^{index} i_C[k] \times t_s / C \quad [5]$$

or equivalently

$$E = i[j] \times R_s + (i[j] - i_C[j]) \times R_p \quad [6]$$

It is worth noting that these equations are developed with no assumptions regarding the waveform of the current. An analytical solution to Eq. 3 can be achieved by assuming sinusoidal signal for the current. However, the numerical method can be employed to calculate the voltage progression after the sine wave is turned off, or as a response to ill-defined sine waves during the digital-to-analog conversion. This issue effects the amount of time required between frequencies which is an issue that is reserved for a future study.

For each frequency of interest, the time-domain simulations were carried out before a Fourier Transform calculation in order to simulate the impedance response along with the harmonics of the voltage. These results are summarized in Fig. 3 in the same format as Fig. 2. In these simulations, 5 periods of the signal were applied and the first cycle was discarded before the Fourier Transform just like the experimental procedure. In addition, a random noise of 0.1% can be added to the voltage in the time-domain, to generate a perfectly matching response as shown in Fig. A-1. The simulations and the experiments show a remarkable similarity indicating that the background phenomena resulting in the signal is simply explained by the above fundamental framework.

^bThe relevant characteristic frequency can be calculated by $(1/(C \times R_p))$ since the series resistance is only additive in the galvanostatic mode.

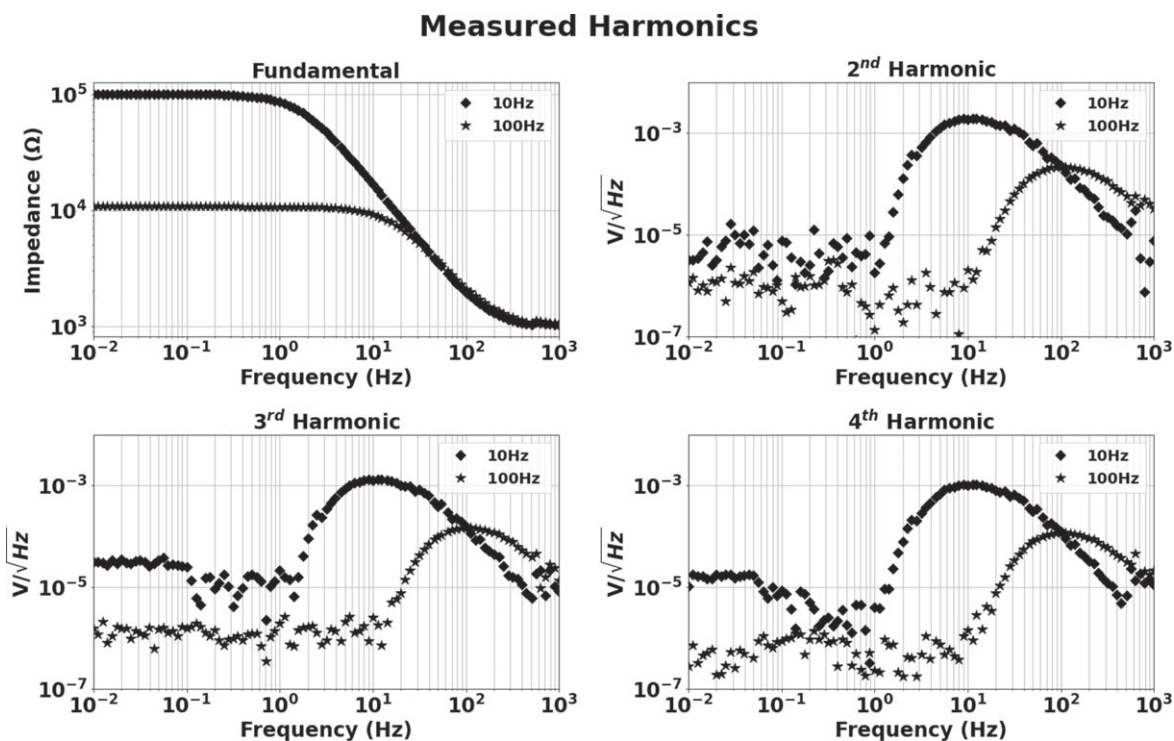


Figure 2. Impedance and Non-linear Harmonic Analysis of the voltage response obtained from Galvanostatic-EIS measurements for dummy cells with characteristic frequencies of 10 Hz and 100 Hz.

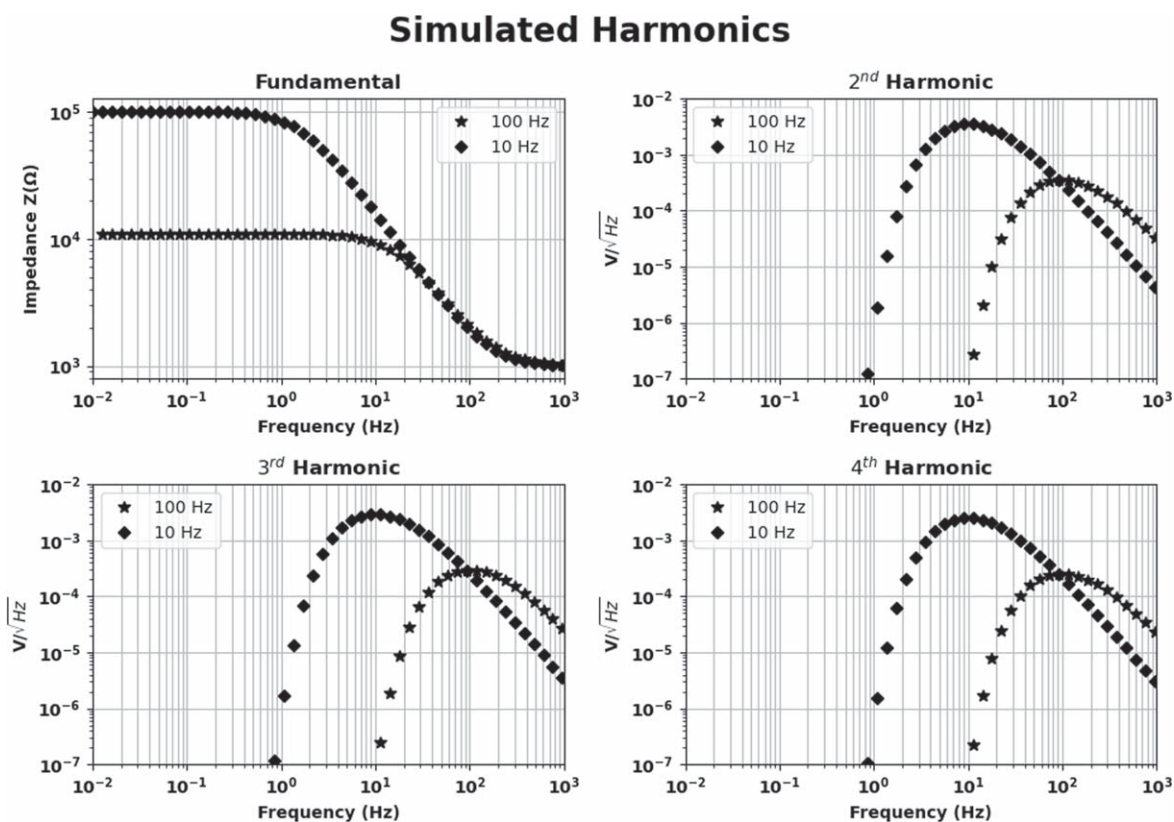


Figure 3. Modulus Impedance and Non-linear Harmonic Analysis of the voltage response obtained from Galvanostatic-EIS simulations for dummy cells with characteristic frequencies of 10 Hz and 100 Hz.

In order to understand the response in more detail, the time-domain response of the cell was inspected deeper. Figure 4 shows examples from the three domains of the response. The middle panel

in each domain shows the applied current, with the top panel showing the breakdown of the current to the parallel resistor and capacitor. The bottom panel in each shows the total voltage across

Table I. The information was obtained from the following software and personal communication [REF-3000 Gamry Software v7.8.6, Dr. Iosif Fromondi (Product Manager & Head of Marketing—Metrohm Autolab), Dr. Nicolas Murer (Research Scientist—BioLogic), Mr. Luca Pini (Territory Manager MEA-LATAM—Ametek Advanced Measurement Technologies), Dr. Antonie Baars (Manager-Ivium Technologies)].

Manufacturer	Default	Remarks
Gamry	1 Full Period	Adjustable with a script edit
Metrohm-Autolab	10 cycles or 1 s, whichever is faster	Editable under the advanced group (Newer software is faster with more dynamic selection)
BioLogic	10% of the period	Editable in the standard dialog box
PAR-Solartron	0 s	User specifiable as an amount of time
Ivium	Half sine period, minimum 0.2 s	User specifiable, number of periods and absolute time can be chosen, depending on which is longer

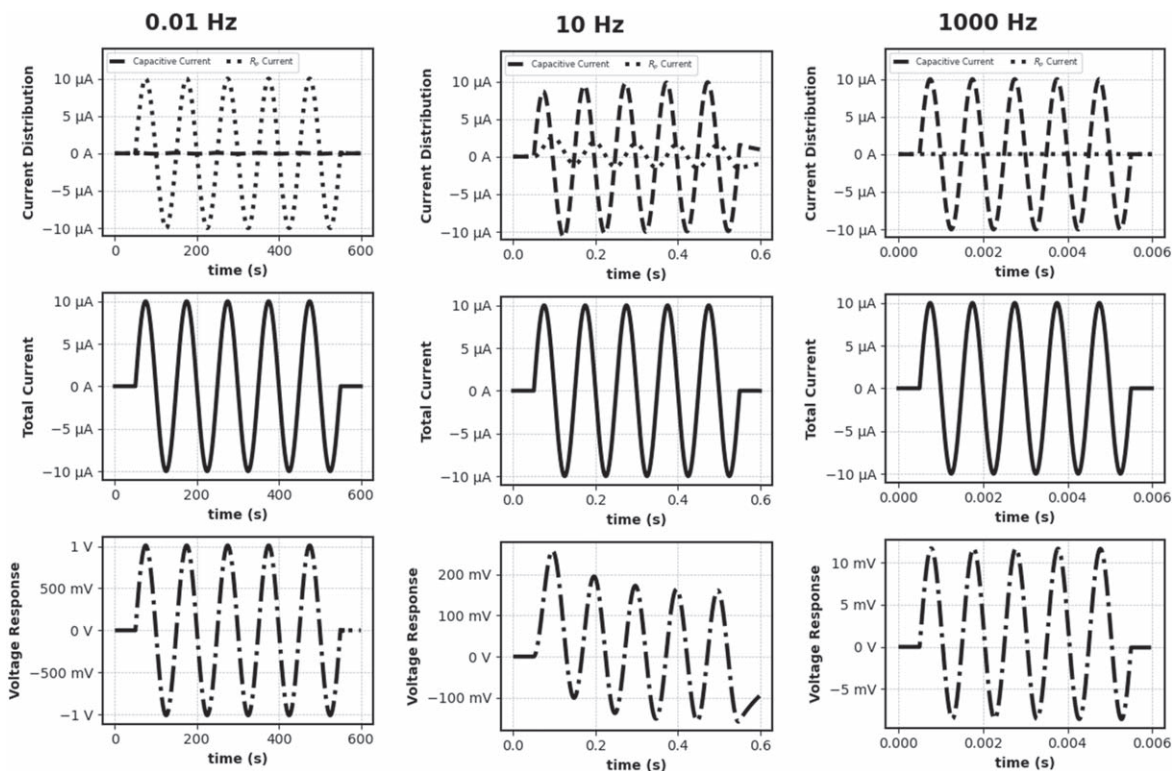


Figure 4. Excitation currents and response voltages of simulated 10 Hz dummy cell. Frequencies are 0.01 Hz, 10 Hz and 1000 Hz respectively.

the total cell. From the current breakdown, the intuitive assumption of low frequency current mostly passing through the resistor and high frequency current mostly passing through the capacitor in the parallel section is confirmed. Around the critical frequency, the current passing through both arms of the parallel section is of the same order of magnitude in amplitude, but different in phase. The voltage in the low frequency exhibits an in-phase response as expected for a resistive response. In the high frequency region, the total voltage is mostly dictated by the series resistor and therefore is still an in-phase signal. However, the capacitance manifests itself as a non-zero DC level, since a pure capacitor always exhibits a non-zero voltage as shown in Fig. A-6. Around the critical frequency, the short time response appears to have some DC offset, which ultimately settles to no DC offset in the voltage. This transient response is responsible for the nonlinearity that is shown above.

As mentioned in the introduction, it is commonplace among the instrument manufacturers to get rid of the some of the signal before doing the Fourier Transform. The amount of time varies greatly as the time used by manufacturers to minimize nonlinearity associated with transients is shown in Table I. This is considered as a protection against the type of startup-transient as shown around the critical frequency. In the case of potentiostatic EIS, there is at least one literature example justifying this practice,¹³ however, in galvanostatic EIS, as shown by the middle bottom panel, this period needs to be carefully selected. It is important to note that for the linear impedance measurement, the effect does not cause any problems for the selected levels of resistance and capacitance as the fundamental signal appears to be minimally affected. As can be seen in Fig. A-5, the fundamental voltage response has about 100 times higher amplitude than the second, third and fourth harmonics. However, the nonlinear part of the measurement is significantly affected. To observe the effect of the number of cycles that are discarded during measurement, we have adjusted the parameters in our simulation code. As can be seen in Fig. A-3 in Appendix, measuring without discarding any cycles with a total of 5 cycles lead to a drastic

increase in harmonic amplitudes. On the other hand, another scenario was adopted with discarding first 35 cycles of a total of 40 cycles, as seen in the Fig. A-4. Even in this case, the nonlinearity is still present, though with drastically reduced second, third and fourth harmonics of below 10^{-10} V amplitudes. These results explain why many instrument manufacturers employ different scenarios for measuring and wisely allow the user to modify these periods without limits. It is clear that there is no way to completely get rid of the effect, however, it will get below the noise floor after waiting long enough.

Conclusions

We have shown that even in the most ideal of cases, galvanostatic EIS displays non-zero harmonic response in the presence of capacitors. This is simply from the response of the capacitor to a current signal that starts being applied after a period of no signal.

This nonlinear response has a decay time of $C \times R_p$ only at frequencies that are around the critical frequency. Proper waiting period for this effect would be the necessary multiple of this time constant that pushes this response to below the noise level (i.e., $5 \times C \times R_p$ would be enough to push it below 1%).

Further, issues such as small DC offsets in the applied current, range and/or filter setting changes are all reasons for concern that were not discussed within this manuscript. Nonlinear measurements undoubtedly can provide insightful information; however, they should always be accompanied by control measurements with a dummy cell that mimics the impedance characteristics of the cell in question. Only then, the nonlinear response can be attributed to the electrochemical processes inside the battery.

Acknowledgments

BU would like to acknowledge useful discussions with Mr. Abe Krebs of Gamry Instruments in the original discovery stage.

Appendix

In the script we were able to add a noise, generated by a NumPy random function, to get the same result as our measurement. The rest of the parameters were the same as our measurement.

Further control experiments with a simple resistor and capacitor are conducted as shown in Fig. A.2. The resistor only shows the noise floor, whereas the capacitor shows a linearly increasing nonlinear signal (in the loglog scale) as frequency decreases. In Fig. A.2, only a resistance and a capacitor measured.

The scenario for Fig. A.3 was analyzing all of the 5 cycles without discarding any of them. By doing so, it can be deduced that discarding a portion of the response signal is beneficial.

In Fig. A.4, a total of 30 cycles were simulated and first 25 of these cycles were discarded. This figure demonstrates the presence of non-linearity still exist even after 25 cycles.

Figure A.5 is the exact same figure as Fig. 2, only with the fundamental response is plotted as voltage response instead of impedance.

Figure A.6 emphasizes the voltage response of pure capacitor, where a 1 μF capacitor is simulated with 10 μA AC, at 100 Hz and 1000 Hz. Only positive voltage response is observed at high frequencies.

It is worth investigating the response of the pure capacitor analytically as well. The voltage across a capacitor can simply be written as:

$$V = \frac{\int_0^t i dt}{C} \quad [\text{A.1}]$$

Where t is the time, i is the current, V is the voltage and C is the capacitance. Assuming an applied current waveform is a sinusoidal current with zero phase shift:

$$i = i_0 \sin(\omega t) \quad [\text{A.2}]$$

Where i_0 is the amplitude and ω is the angular frequency. By substituting Eqs. A.2 into A.1 and integration, the voltage can be written as:

$$V = \frac{-i_0 \cos(\omega t)}{\omega C} + \hat{c} \quad [\text{A.3}]$$

Where \hat{c} is the integration constant. Noticing that the voltage is zero when time is zero, the integration constant can be calculated:

$$\hat{c} = \frac{i_0}{\omega C} \quad [\text{A.4}]$$

Substituting A4 back into A3:

$$V = \frac{-i_0 \cos(\omega t)}{\omega C} + \frac{i_0}{\omega C} \quad [\text{A.5}]$$

This equation clearly shows that there is a frequency-dependent offset which manifests itself as the nonlinearity when the response is capacitive.

Simulation Code for Randles Cell:

```
# -*- coding: utf-8 -*-
"""
```

Created on Tue Nov 2 09:39:50 2021

@author: Burak Ülgüt & Gökberk Katurcı

```
"""
```

```
import numpy as np
```

```
import math
```

```
import matplotlib.pyplot as pylab
```

```
import scipy.fftpack
```

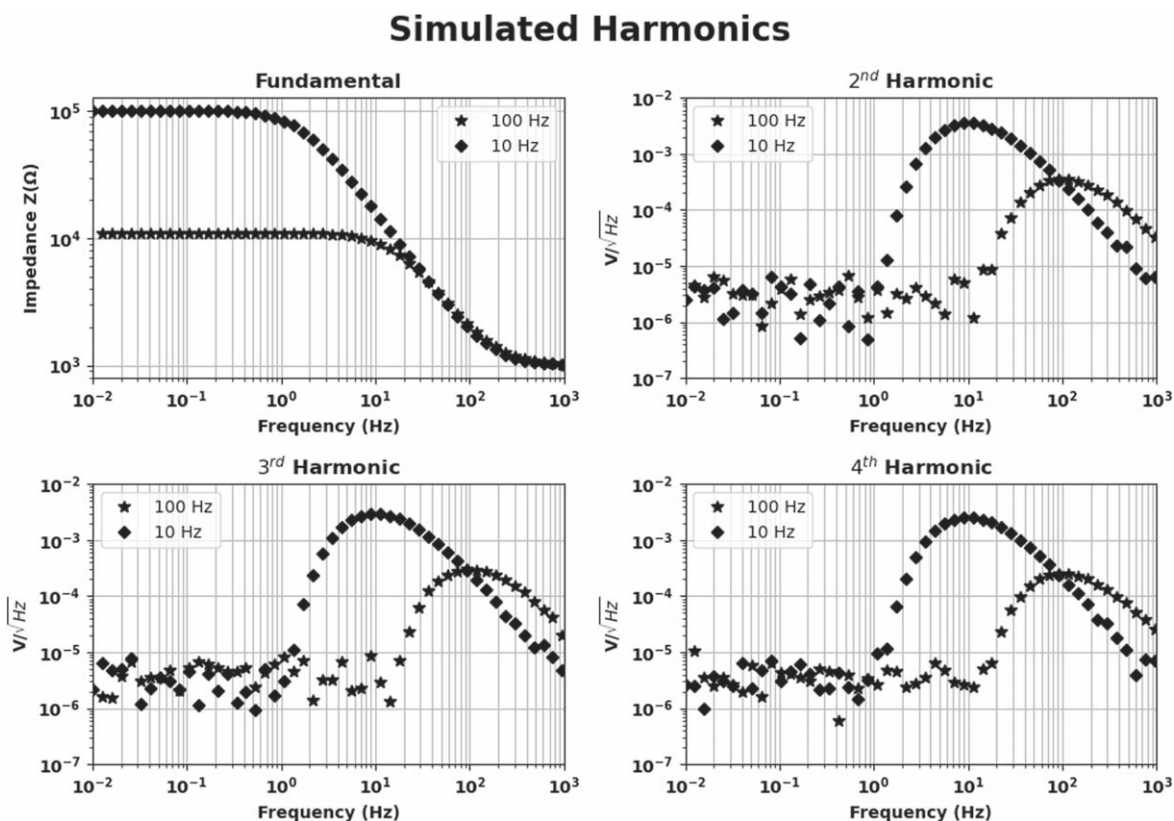


Figure A.1. Modulus Impedance and Non-linear Harmonic Analysis of the voltage response obtained from Galvanostatic-EIS simulations for dummy cells with characteristic frequencies of 10 Hz and 100 Hz with 0.1% added noise.

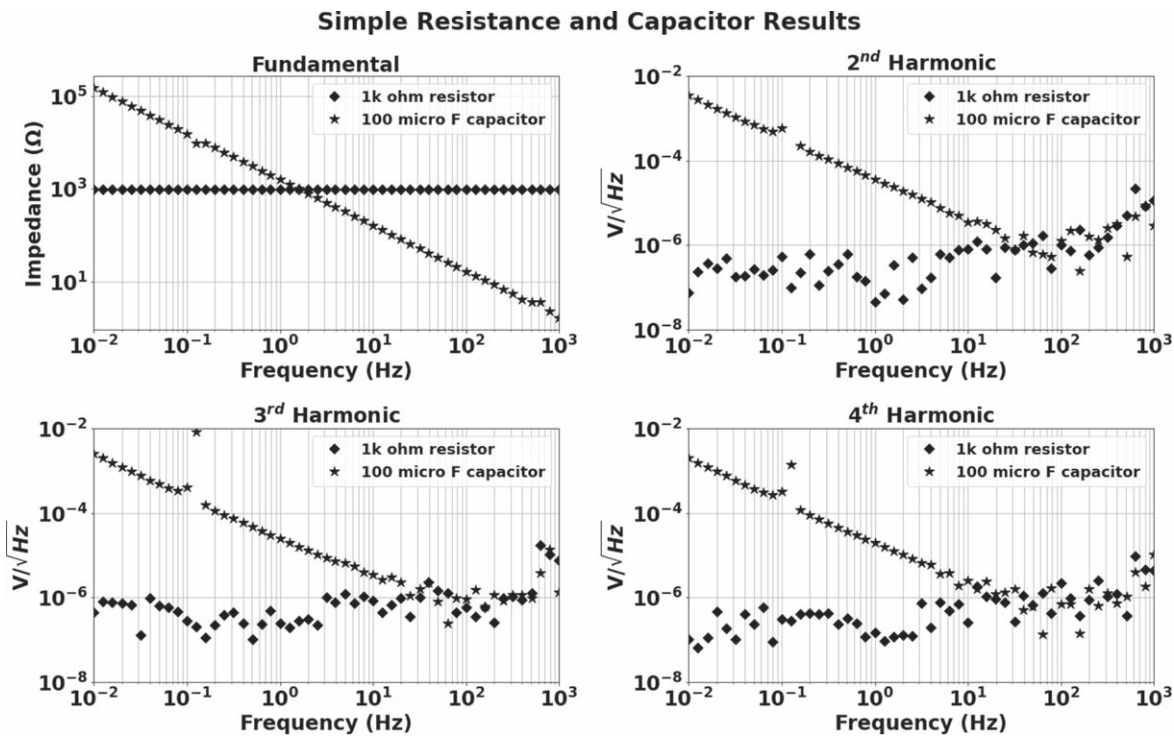


Figure A-2. Modulus Impedance and Non-linear Harmonic Analysis of the voltage response obtained from Galvanostatic-EIS measurements for 1 k Ω resistor and 100 μ F capacitor.

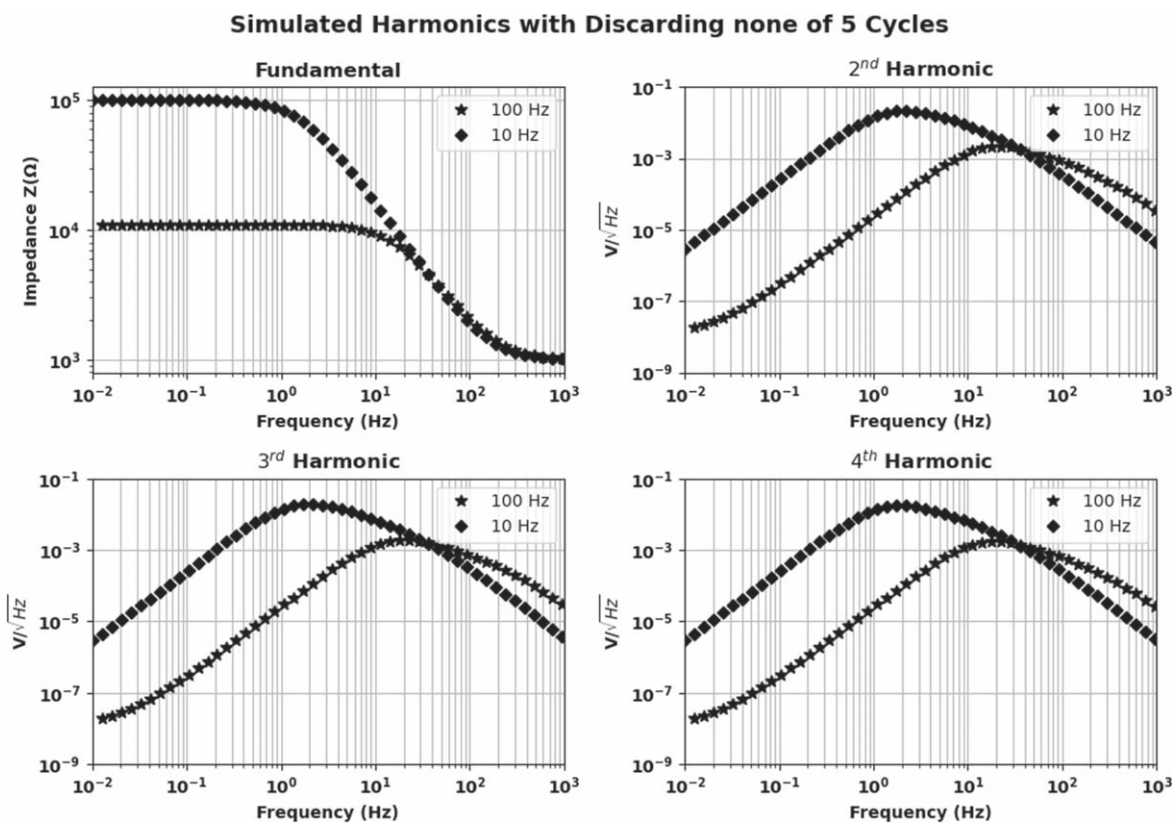


Figure A-3. Simulations for dummy cells without discarding any cycles.

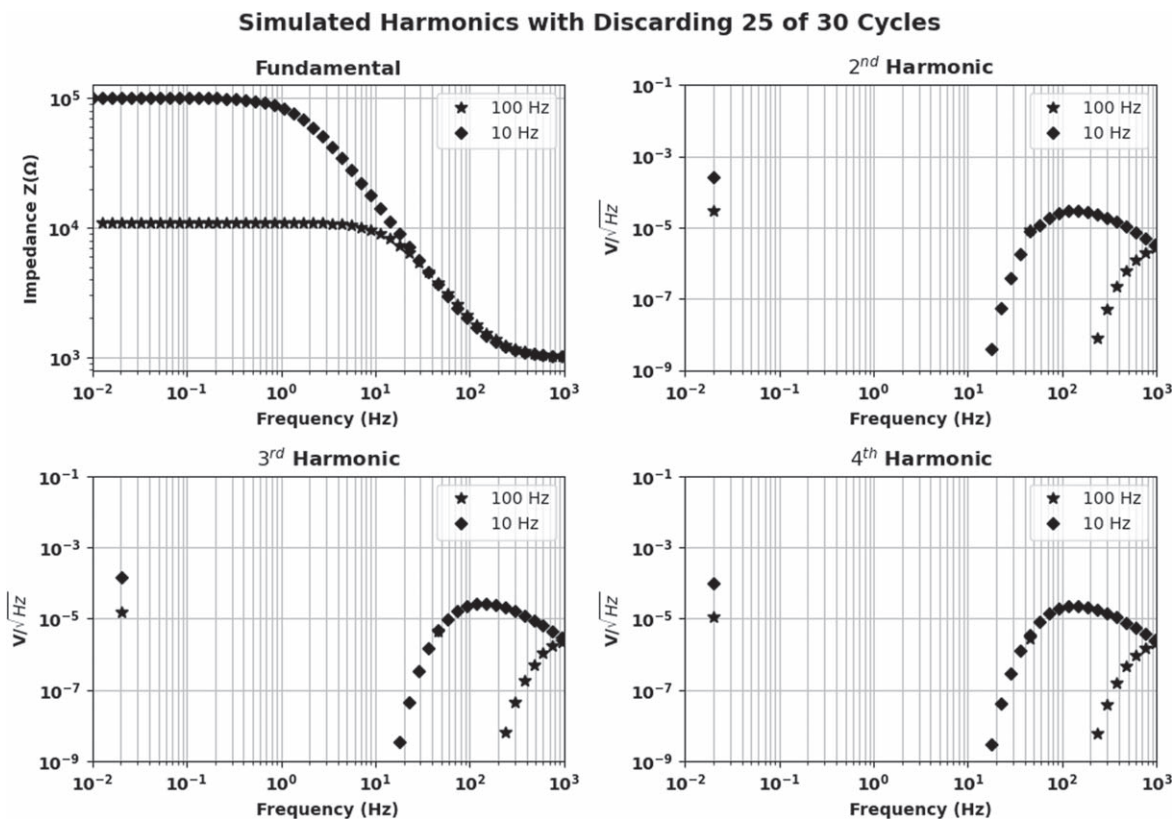


Figure A-4. Simulations for dummy cells with discarding 25 cycles of 30 cycles.

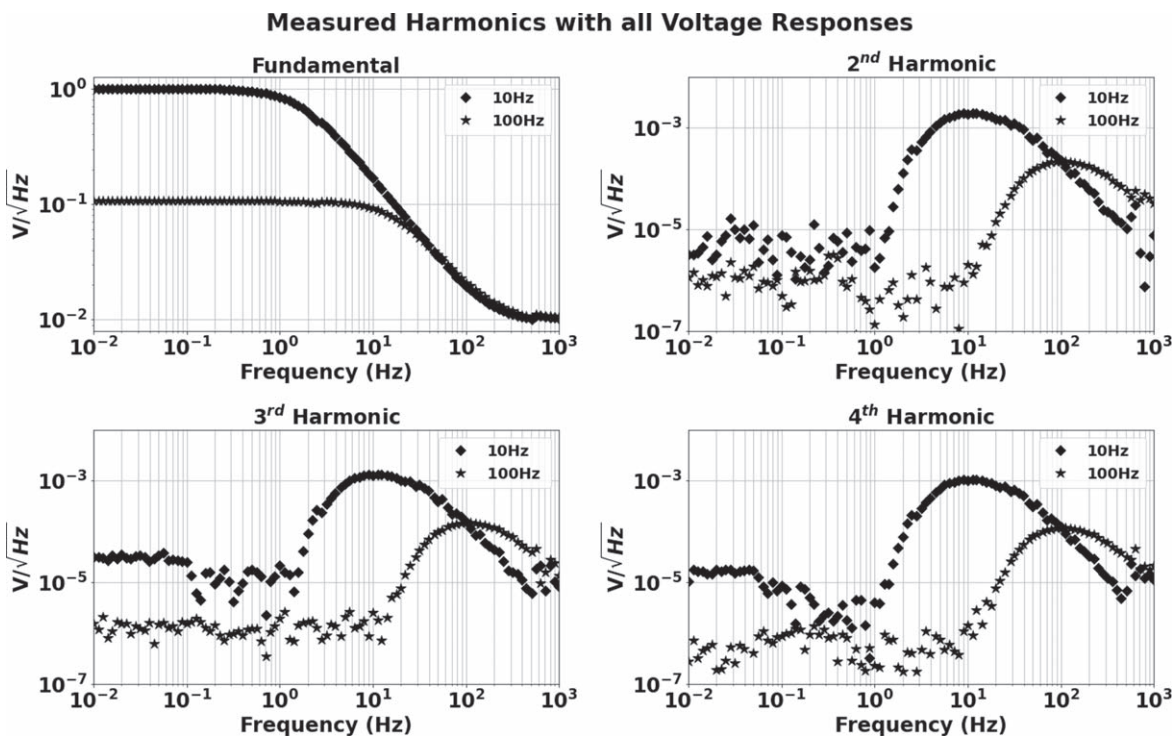


Figure A-5. Modulus Impedance and Non-linear Harmonic Analysis of the voltage response obtained from Galvanostatic-EIS measurements for dummy cells with characteristic frequency of 10 Hz and 100 Hz Harmonics with all Response Voltages

```
import random
# Class Definition #####BEGIN#####
class galvanostaticrandles:
```

```
def __init__(self,sigalfrequency,amplitude,R = 1.0,C = 1.0,Rp
= 10, no_of_periods = 5,pointsperperiod = 128,offsetratio = 0.01,
sigaldelayratio = 0.5,noiselevel = 0.01):
```

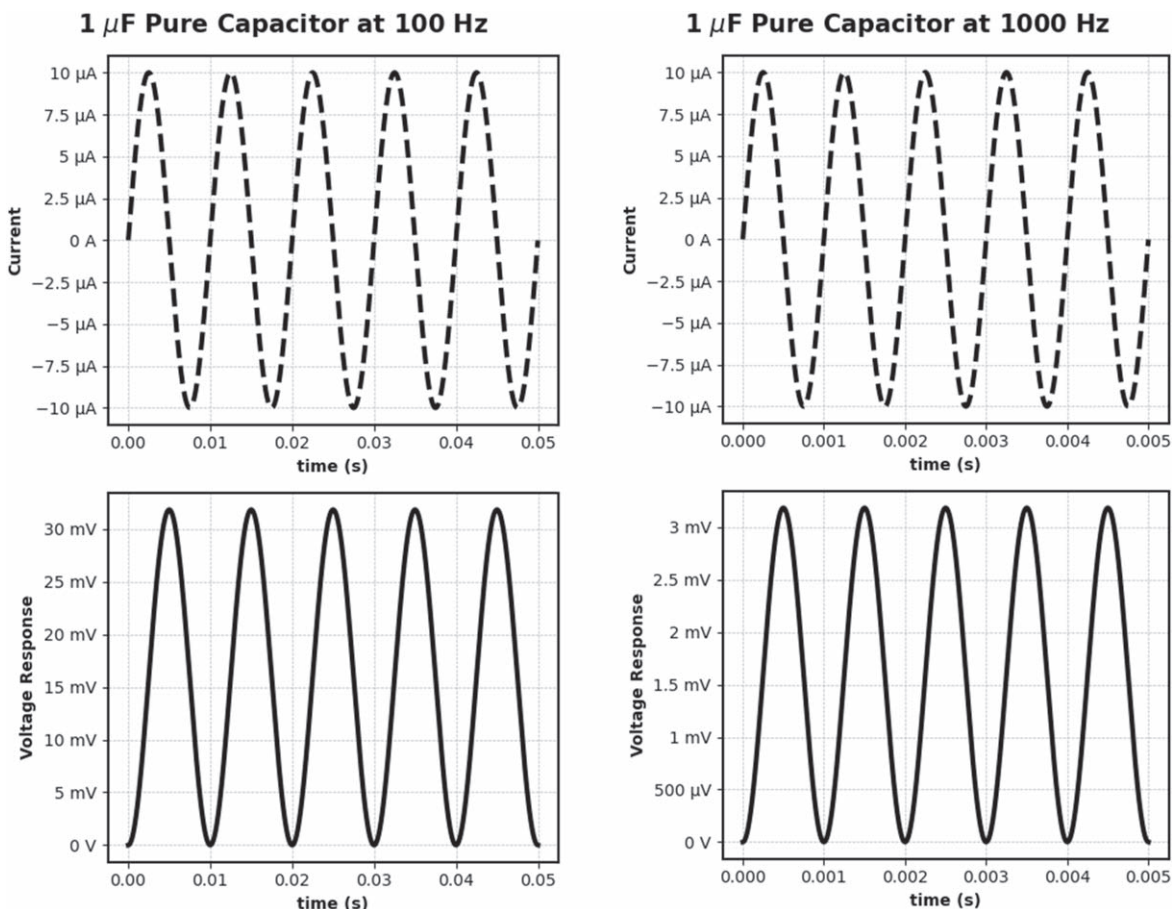


Figure A-6. Simulated voltage response of a pure capacitor.

```

self.samplingfrequency = 1000000
pointsperperiod = signalfrequency#Hz
self.signalfrequency = signalfrequency
offset = offsetratio * amplitude
self.signaldelayratio = signaldelayratio
signaldelay = self.signaldelayratio/signalfrequency#seconds
signallengthtime = 2*signaldelay+no_of_periods/signalfrequency
self.time = np.arange(0,signallengthtime,1/self.samplingfrequency)
signallengthpoints = len(self.time)
self.signal = np.zeros(int(signallengthpoints))
self.voltage = np.zeros(int(signallengthpoints))
self.capcurrent = np.zeros(int(signallengthpoints))
self.sinebegin = int(signaldelay * self.samplingfrequency)
self.sineend = int((signaldelay+no_of_periods/signalfrequency) * self.samplingfrequency)

for i in range(int(signallengthpoints)):
    if i > self.sinebegin and i < self.sineend:
        self.signal[i] = offset + amplitude*math.sin(2*math.pi*signalfrequency*(float(i)/self.samplingfrequency - signaldelay))

charge = 0.0

for i in range (int(signallengthpoints)):
    charge = charge + self.capcurrent[i-1]/self.samplingfrequency
    self.capcurrent[i] = self.signal[i] - charge/(Rp*C)
    #print(charge/(Rp*C))
    self.voltage[i] = R*self.signal[i]+Rp*(self.signal[i]-self.capcurrent[i])+noiselevel*random.random()

```

```

def plottimedomain(self):
    pylab.subplot(221)
    pylab.scatter(self.time,self.signal,label = 'Tot. Current')
    pylab.scatter(self.time,self.capcurrent,label = "C Current")
    pylab.scatter(self.time,self.signal-self.capcurrent,label = "Rp Current")
    pylab.ylabel("Current")
    pylab.subplot(222)
    pylab.scatter(self.time,self.voltage)
    pylab.ylabel("Voltage")
    pylab.xlabel("Time")
    pylab.subplot(223)
    pylab.scatter(self.time[self.sinebegin:self.sineend],self.signal[self.sinebegin:self.sineend],label = 'Tot. Current')
    pylab.scatter(self.time[self.sinebegin:self.sineend],self.capcurrent[self.sinebegin:self.sineend],label = "C Current")
    pylab.scatter(self.time[self.sinebegin:self.sineend],self.signal[self.sinebegin:self.sineend]-self.capcurrent[self.sinebegin:self.sineend],label="Rp Current")
    pylab.ylabel("Current")
    pylab.subplot(224)
    pylab.scatter(self.time[self.sinebegin:self.sineend],self.voltage[self.sinebegin:self.sineend])
    pylab.ylabel("Voltage")
    pylab.xlabel("Time")
    pylab.show(block = True)
    return True

def gettimedomain(self):
    return self.time[self.sinebegin:self.sineend],self.signal[self.sinebegin:self.sineend],self.voltage[self.sinebegin:self.sineend]

def getfreqdomain(self,waitingperiods = 0):

```

```

begin = int(self.sinebegin + waitingperiods * self.sampling-
frequency/ self.signalfrequency)
length = self.sineend -begin
self.fdomaincurrent = 2*scipy.fft.fft(self.signal[begin:self.si-
neend]):int(length/2))/length
self.fdomainvoltage = 2*scipy.fft.fft(self.voltage[begin:self.
sineend]):int(length/2))/length
self.freq = scipy.fftpack.fftfreq(int(length),1/self.sampling-
frequency)[:int(length/2)]

    return self.freq,self.fdomaincurrent,self.fdomainvoltage
# Class Definition#####END#####
initfreq = 10000.0
finalfreq = 0.01
ptsperdec = 10
no_of_decades = int(abs(math.log10(initfreq/finalfreq)))
ACAmplitude = 0.00001 #in Amps
no_of_periods = 5
WaitingPeriods = 1
freqrange = np.logspace(math.log10(initfreq), math.log10(final-
freq),num=ptsperdec*no_of_decades)
zfund = np.ndarray(shape=len(freqrange),dtype=np.com-
plex128)
vfund = np.zeros(len(freqrange))
vsecond = np.zeros(len(freqrange))
vthird = np.zeros(len(freqrange))
vfourth = np.zeros(len(freqrange))
for freq in freqrange:
    simulation = galvanostaticandles(freq,ACAmplitude,R =
1000.0,C = 0.000001,Rp=10000.0,signdelayratio=0.0,offse-
tratio=0.0,no_of_periods=no_of_periods,pointsperperiod=8192,
noiselevel=0.000)
    f,fdomi,fdomv = simulation.getfreqdomain
(waitingperiods=WaitingPeriods)
    position = no_of_periods - WaitingPeriods
    freqindex = np.where(freq==freqrange)[0]
    vfund[freqindex] = abs(fdomv[position])
    vsecond[freqindex] = abs(fdomv[position+1])
    vthird[freqindex] = abs(fdomv[position+2])
    vfourth[freqindex] = abs(fdomv[position+3])
    zfund[freqindex]=fdomv[position]/fdomi[position]
pylab.subplot(221)
pylab.loglog(freqrange,abs(zfund))
pylab.subplot(222)
pylab.loglog(freqrange,abs(vsecond))
pylab.subplot(223)
pylab.loglog(freqrange,abs(vthird))
pylab.subplot(224)
pylab.loglog(freqrange,abs(vfourth))
pylab.show(True)
Simulation Code for Pure Capacitor:
# -*- coding: utf-8 -*-
'''
Created on Tue Nov 2 09:39:50 2021
@author: Burak Ülgüt & Gökberk Katurcı
'''

import numpy as np
import math
import matplotlib.pyplot as pylab
import scipy.fftpack
import random
# Class Definition #####BEGIN#####
class galvanostaticcap:
    def __init__(self,signalfrequency,amplitude, C = 1.0, no_of_-
periods=5,pointsperperiod=128,offsetratio=0.01,signdelayr-
atio=0.5,noiselevel=0.01):
    self.samplingfrequency=pointsperperiod*signalfrequency#Hz

```

```

    self.signalfrequency = signalfrequency
    offset = offsetratio * amplitude
    self.signdelayratio = signdelayratio
    signdelay=self.signdelayratio/signalfrequency#seconds
    signtime=2*signdelay+no_of_periods/signalfre-
quency
    self.time = np.arange(0,signtime,1/self.samplingfre-
quency)
    signtimepoints=len(self.time)
    self.signal = np.zeros(int(signtimepoints))
    self.voltage=np.zeros(int(signtimepoints))
    self.sinebegin = int(signdelay * self.samplingfrequency)
    self.sineend = int((signdelay+no_of_periods/signalfre-
quency) * self.samplingfrequency)

    for i in range(int(signtimepoints)):
        if i > self.sinebegin and i < self.sineend:
            self.signal[i]=offset + amplitude*math.sin(2*math.pi*-
signalfrequency*(float(i)/self.samplingfrequency - signdelay))

    charge = 0.0
    for i in range (int(signtimepoints)):
        charge = charge + self.capcurrent[i-1]/self.samplingfre-
quency
        self.voltage[i]= charge/C

    def plottimedomain(self):
        pylab.subplot(221)
        pylab.scatter(self.time,self.signal,label = 'Tot. Current')
        pylab.ylabel("Current")
        pylab.subplot(222)
        pylab.scatter(self.time,self.voltage)
        pylab.ylabel("Voltage")
        pylab.xlabel("Time")
        pylab.subplot(223)
        pylab.scatter(self.time[self.sinebegin:self.sineend],self.signal
[self.sinebegin:self.sineend],label = 'Tot. Current')
        pylab.ylabel("Current")
        pylab.subplot(224)
        pylab.scatter(self.time[self.sinebegin:self.sineend],self.vol-
tage[self.sinebegin:self.sineend])
        pylab.ylabel("Voltage")
        pylab.xlabel("Time")
        pylab.show(block = True)
    return True

    def gettimedomain(self):
    return self.time[self.sinebegin:self.sineend],self.signal[self.
sinebegin:self.sineend],self.voltage[self.sinebegin:self.sineend]

    def getfreqdomain(self,waitingperiods = 0):
    begin = int(self.sinebegin + waitingperiods * self.sampling-
frequency/ self.signalfrequency)
    length = self.sineend -begin
    self.fdomaincurrent = 2*scipy.fft.fft(self.signal[begin:self.si-
neend]):int(length/2))/length
    self.fdomainvoltage = 2*scipy.fft.fft(self.voltage[begin:self.
sineend]):int(length/2))/length
    self.freq = scipy.fftpack.fftfreq(int(length),1/self.sampling-
frequency)[:int(length/2)]

    return self.freq,self.fdomaincurrent,self.fdomainvoltage
# Class Definition#####END#####
initfreq = 10000.0
finalfreq = 0.01
ptsperdec = 10
no_of_decades = int(abs(math.log10(initfreq/finalfreq)))

```

```

ACAmplitude = 0.00001 #in Amps
no_of_periods = 5
WaitingPeriods = 1
freqrange = np.logspace(math.log10(initfreq), math.log10(final-
freq), num = ptsperdec*no_of_decades)
zfund = np.ndarray(shape = len(freqrange), dtype = np.com-
plex128)
vfund = np.zeros(len(freqrange))
vsecond = np.zeros(len(freqrange))
vthird = np.zeros(len(freqrange))
vfourth = np.zeros(len(freqrange))
for freq in freqrange:
    simulation = galvanostaticandles(freq,ACAmplitude, C =
0.000001, signaldelayratio = 0.0,offsetratio = 0.00,no_of_periods
= no_of_periods,pointsperperiod = 8192,noiselevel = 0.000)
    f,fdomi,fdomv = simulation.getfreqdomain(waitingperiods =
WaitingPeriods)
    position = no_of_periods - WaitingPeriods
    freqindex = np.where(freq==freqrange)[0]
    vfund[freqindex] = abs(fdomv[position])
    vsecond[freqindex] = abs(fdomv[position+1])
    vthird[freqindex] = abs(fdomv[position+2])
    vfourth[freqindex] = abs(fdomv[position+3])
    zfund[freqindex] = fdomv[position]/fdomi[position]
pylab.subplot(221)
pylab.loglog(freqrange,abs(zfund))
pylab.subplot(222)
pylab.loglog(freqrange,abs(vsecond))
pylab.subplot(223)
pylab.loglog(freqrange,abs(vthird))
pylab.subplot(224)
pylab.loglog(freqrange,abs(vfourth))
pylab.show(True)

```

ORCID

Gökberk Katırcı  <https://orcid.org/0000-0003-1716-5947>
 Mohammed Ahmed Zabara  <https://orcid.org/0000-0002-4195-6258>
 Burak Ülgüt  <https://orcid.org/0000-0002-4402-0033>

References

1. M. E. Orazem and B. Tribollet, *Electrochemical Impedance Spectroscopy*. (Wiley, New York, NY) 2nd ed. (2017).
2. T. Vidaković-Koch, T. Miličić, L. A. Živković, H. S. Chan, U. Krewer, and M. Petkovska, "Nonlinear frequency response analysis: a recent review and perspectives." *Curr Opin Electrochem.*, **30**, 100851 (2021).
3. M. D. Murbach, V. W. Hu, and D. T. Schwartz, "Nonlinear electrochemical impedance spectroscopy of lithium-ion batteries: experimental approach, analysis, and initial findings." *J. Electrochem. Soc.*, **165**, A2758 (2018).
4. N. Harting, N. Wolff, F. Röder, and U. Krewer, "Nonlinear frequency response analysis (NFRA) of lithium-ion batteries." *Electrochim Acta [Internet].*, **248**, 133 (2017).
5. N. Harting, N. Wolff, and U. Krewer, "Identification of Lithium Plating in Lithium-Ion Batteries using Nonlinear Frequency Response Analysis (NFRA)." *Electrochim Acta [Internet].*, **281**, 378 (2018).
6. N. Wolff, N. Harting, M. Heinrich, F. Röder, and U. Krewer, "Nonlinear frequency response analysis on lithium-ion batteries: a model-based assessment." *Electrochim. Acta*, **260**, 614 (2018).
7. B. Liebhart, M. Satzke, L. Komsijska, and C. Endisch, "Application of nonlinear impedance spectroscopy for the diagnosis of lithium-ion battery cells under various operating conditions." *J Power Sources [Internet].*, **480**, 228673 (2020).
8. M. Kiel, O. Bohlen, and D. U. Sauer, "Harmonic analysis for identification of nonlinearities in impedance spectroscopy." *Electrochim. Acta*, **53**, 7367 (2008).
9. S. Ernst, T. P. Heins, N. Schlüter, and U. Schröder, "Capturing the current-overpotential nonlinearity of lithium-ion batteries by nonlinear electrochemical impedance spectroscopy (NLEIS) in charge and discharge direction." *Front Energy Res.*, **7**, 1 (2019).
10. K. J. Szekeres, S. Vesztergom, M. Ujvári, and G. G. Láng, "Methods for the determination of valid impedance spectra in non-stationary electrochemical systems: concepts and techniques of practical importance." *ChemElectroChem.*, **8**, 1233 (2021).
11. M. A. Zabara, C. B. Uzundal, and B. Ulgut, "Linear and nonlinear electrochemical impedance spectroscopy studies of Li/SOCl₂ 2 batteries." *J. Electrochem. Soc.*, **166**, A811 (2019).
12. Y. Barsukov, Ross, and J. Macdonald, "Electrochemical impedance spectroscopy." *Charact Mater.*, **2**, 898 (2012).
13. R. Pollard and T. Comte, "Determination of transport properties for solid electrolytes from the impedance of thin layer cells." *J. Electrochem. Soc.*, **136**, 3734 (1989).
14. P. T. Wojcik and M. E. Orazem, "Variable amplitude galvanostatically modulated impedance spectroscopy as a non-invasive tool for assessing reactivity at the corrosion potential." *NACE - Int Corros Conf Ser.*, **1997**, 289 (1997).
15. P. T. Wojcik, P. Agarwal, and M. E. Orazem, "A method for maintaining a constant potential variation during galvanostatic regulation of electrochemical impedance measurements." *Electrochim. Acta*, **41**, 977 (1996).
16. J. D. Hunter, "MATPLOTLIB: A 2D graphics environment." *Comput. Sci. Eng.*, **9**, 90 (2007).
17. C. R. Harris et al., "Array programming with NumPy." *Nature*, **585**, 357 (2020).
18. P. Virtanen et al. SciPy 1.0 Contributors, "SciPy 1.0: fundamental algorithms for scientific computing in Python." *Nat. Methods*, **17**, 261 (2020).