Non-linear harmonics in EIS of batteries with lithium anodes: Proper controls and analysis

Mohammed Ahmed Zabara, Gökberk Katırcı, Burak Ülgüt

Department of Chemistry, Bilkent University, Ankara 06800, Turkey

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ABSTRACT

Non-linear Harmonic Analysis is used to investigate the distortions accompanying the Electrochemical Impedance Spectroscopy (EIS) measurements. The distortions emerge from non-linearity and non-stationarity due to the underlying redox reactions as well as the capacitance. Identifying each response and its source is crucial to correlate the obtained harmonics to their corresponding electrochemical processes. In this study, we identify the distortions of Galvanostatic-EIS measurements of Lithium Primary Batteries by means of comparing mathematical simulations and experimental measurements. The simulations were performed on RC-based equivalent circuit models, which showed the presence of certain distortions. The experimental measurements displayed distortions in the form of both non-linearity and non-stationarity in the case of batteries. The level of the harmonics in the measurements is either similar or higher than the harmonics simulated in the RC equivalent circuits at different frequencies. The obtained harmonics compared to simulations highlights the importance of control measurements before the analysis of non-linear harmonics of EIS measurements galvanostatically excited.

1. Introduction

Electrochemical Impedance Spectroscopy (EIS) has shown its applicability in characterizing different battery chemistries involving Lithium (Li) in various forms in detail [1–4]. Its non-invasive, non-destructive, and in-situ nature is important for batteries since their components are very reactive and hard to characterize except in sealed cells. On the flip side, EIS data is hampered by concerns of linearity and stationarity requirements of the measurement [5,6]. Failing to meet either of them leads to wrong conclusions regarding the studied systems. Different methods such as checking compatibility with Kramers-Kronig (KK) relations and monitoring Total Harmonic Distortion (THD) are used to assess the linearity and the stationarity of the data [7–10].

In THD, the alternating time-domain response signals are analyzed in the frequency-domain to search for the existence of high-order harmonics along with the fundamental response, which is assigned as distortions in the data [10,11]. To obtain the EIS data, the excitation parameters are adjusted while monitoring the level of the harmonics to fall below noise levels [12].

In the broadest sense, an electrochemical response is expected to be non-linear. None of the relations that explain the kinetics and thermodynamics of electrochemical systems are linear [13]. Further, any electrode/electrolyte interface leads to a double-layer capacitance. As shown in an earlier study [14], the existence of this capacitance leads to non-linear behavior during the startup phase of any frequency sine wave excitation.

Stationarity in electrochemical systems is difficult to achieve due to the complex dynamics of the electrochemical processes, which usually involve charge and mass transfer through various interfaces. The stationarity condition is satisfied by ensuring that the experimental timescale is shorter than any significant change in the system. In impedance measurement the linearity condition is satisfied through low AC amplitudes, which ensure that the higher order terms are negligible. In reverse, high amplitude AC excitations are applied to obtain non-linear/non-stationary harmonics.

Several studies have been made to correlate non-linear harmonic occurrence to kinetic and mechanistic properties in the literature. Early studies were done in the field of corrosion. Darowicki et al. published a review which described the application of the harmonic analysis to study activation reactions and diffusion processes in corrosion systems.

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Other studies used harmonic analysis to measure the rate of corrosion for different systems [16,17]. In the field of fuel cells, harmonic analysis was used for the diagnosis of dehydration, flooding and CO-poisoning processes as well as monitoring oxygen concentration and operation status of PEM fuel cells [18].

For batteries, harmonic analysis was used to study charge and mass transfer processes in Li-ion batteries. Krewer et al. investigated the relation of the excitation signal amplitude to the observed harmonics for different types of Li-ion batteries and showed its relation to Li plating process [19]. Murbach et al. studied the non-linear harmonic response for Li-NMC batteries at different States-of-Charge and showed the relation of the observed harmonics to the degradation of the batteries [20]. Ernst et al. reported the relation of the non-linear harmonics to the overpotential of the battery at charge and discharge [21] and Kim et al. showed how non-linear harmonics can be used to probe aging of Li-ion batteries [22].

However, when assigning the non-linearity from the obtained harmonics, a distinction should be made between the non-stationarity which results from the change in the system during the measurements and the non-linearity of the electrochemical response. The separation of non-stationarity from non-linearity in the response is hard to achieve especially for complicated systems such as batteries. In a recent review, Szekeres et al. summarized the existing methods for the non-stationarity determination in EIS measurements [23] which in essence include altering the way of excitation [24–26], acquisition [27,28] and impedance calculations [29,30] to help in differentiating the non-stationarity in the data.

Further, some of the non-linear response due to the double layer capacitance (mainly the startup transient) can be mistakenly assigned to the redox events in the batteries. This manuscript will clearly show that the only way to distinguish the two is to set up a dummy cell that is as close as possible to the battery in the AC response. The measurements then can be performed on both the dummy cell and the device-under-test under the same conditions in order to properly assign the various features to the proper processes.

We perform our investigation by first identifying the experimentally-observed non-idealities in a simple electrochemical system that is as close to ideal as possible, $\text{Fe}^{3+}/\text{Fe}^{2+}$ on glassy carbon electrode. Second, we use simulations based on the RC equivalent circuits fitted to KK-transformable EIS data of different Li primary batteries to observe the distortions in the response of the Galvanostatic-EIS (G-EIS) data under possible non-stationary conditions. Third, we analyze the experimental non-linear/non-stationary response of different Li primary batteries with comparisons of the distortions observed for the RC circuits.

Fig. 1. (a) Frequency domain analysis for primary Li battery showing the excitation signal containing one fundamental signal while the response signal contains multiple harmonics with the fundamental signals. (b) Formation of the Non-linear Harmonic Spectrum from several frequencies.
2. Experimental

**Batteries:** all measurements were performed on commercial Li primary batteries of different chemistries. Four different primary battery chemistries were used from different manufacturers: i) Lithium Thionyl Chloride (Li/SOCl$_2$) primary battery from Saft (LS14500) AA-size with 2600mAh capacity and 3.6 V nominal voltage ii) Lithium Manganese Dioxide (Li/MnO$_2$) primary battery from Power-Xtra (CR17450SL/ 151P) AA-size with 2600mAh capacity and 3.0 V nominal voltage iii) Lithium PolyCarbon Monofluoride (Li/PolyC) from Panasonic (BR-A) D-size with 13000mAh capacity and 3.6 V nominal voltage iv) Lithium Thionyl Chloride (Li/SOCl$_2$) primary battery from Saft (LSH20) D-size with 13000mAh capacity and 3.6 V nominal voltage. All the cells were measured as fresh as possible and they are at >99% State-of-Charge during the measurements.

**Instruments:** Gamry Interface 5000 and Interface 1000 were used with an adjusted Galvanostatic-EIS script. The script was adjusted to record the time domain response signal in separate file at each frequency after the regular EIS measurement. Sinusoidal current excitation signals of five cycles were applied after each harmonic EIS measurement and the response voltage signal was recorded. The duration of data record was the sum of the regular EIS measurement and the duration of excitation of five-cycle at each frequency. The frequency range used was between 1 kHz and 50mHz for typical measurement. The frequency of excitation of five-cycle at each frequency was applied after the regular EIS measurement. Sinusoidal current excitation signals were then drawn versus the frequency, which gives non-linear harmonic spectrum for the studied frequency range, as shown in Fig. 1(b). This analysis is performed for all the time domain signals at various frequencies. The harmonics are then drawn versus the frequency, which gives non-linear harmonic spectrum for the studied frequency range, as shown in Fig. 1(b).

**Simulations:** The simulations were done by using Spyder IDE of Anaconda with importing NumPy, Matplotlib, and SciPy libraries. This simulation is a modified version of the code we used in our previous publication [14]. The code builds a class for generating the simulations with all the resistance and capacitance values. The current method creates 3 RC elements connected in series, whereas in the previous publication, it was only 1 (simplified Randles’ Cell). Details of the mathematics are provided in Appendix.

3. Non-linear harmonic spectrum

The method for performing Non-linear Harmonic analysis during G-EIS measurement is shown in Fig. 1. The harmonics are obtained by transforming the time-domain response signals to the frequency-domain. For that aim, Fast Fourier Transform (FFT) is used (details of the used method are explained in Appendix). In the case of a linear response, the frequency response is composed of only one signal called the fundamental signal. This response is demonstrated by the FFT of the excitation signal in Fig. 1(a). For the non-linear case, the response contains multiple signals along with the fundamental signal and is in the frequencies that are integer multiples of the fundamental signal, as shown in the response voltage signal in Fig. 1(a). This analysis is performed for all the time domain signals at various frequencies. The harmonics are then drawn versus the frequency, which gives non-linear harmonic spectrum for the studied frequency range, as shown in Fig. 1(b).

The non-linear harmonic spectra demonstrate different trends and values at different frequency ranges. This is dependent on the type of the distortion in the response signal at the frequencies studied. The distortions obtained in such spectrum are the combination of two types, non-linearity, and non-stationarity. Non-linearity is any deviation from the linear relation between the excitation and response [31,32]. Non-stationarity is identified as the change in the impedance of the studied system during the course of the measurement [19]. This change is observed either at the beginning of the excitation in a case called Initial Transient which is reduced by repetitive cycles [33] or throughout the measurement as a voltage drift which shows constant increase/decrease in the voltage.

The distortion types discussed above are demonstrated in Fig. 2 which shows harmonic spectra obtained from analyzing the voltage
response of G-EIS measurement of three simplified Randles’ dummy cells connected in series $R_u$: $0.1 \Omega$, $(R_1: 0.1 \Omega, C_1:2200 \mu F)$, $(R_2: 0.1 \Omega, C_2:1F)$, $(R_3: 1.5 \Omega, C_3:16F)$. Fig. 2 (a) shows linear harmonic spectrum composed of the fundamental signal with other harmonics at the noise level of the measurement.

Fig. 2 (b) shows the type of distortions obtained from non-stationary responses of two scenarios. The first is the non-stationarity by the initial transient of the response, which appears as a change in the voltage level of response signal at the first cycles of the response, which is then stabilized to a constant level, see Fig. 2 (b)(i). The harmonic spectrum shows increase in the higher order harmonics at the time constant of the electrochemical response. We have shown through simulating with Randles’ cell that this behavior is from the capacitive contribution of the electrochemical process, which shows highest harmonic response at the time constant of the cell [14]. The second is the result of the continuous change in the voltage level of the system (Voltage drift) see Fig. 2 (b)(ii). The harmonic spectrum here shows high level of harmonic at almost constant level which is dominant over other responses.

Finally, a mixed non-linear/non-stationary distortion response is shown in Fig. 3(c) which is the typical response obtained from exciting Li primary battery with high AC excitation. The separation of non-linear response from the non-stationary response is hard, if not impossible since any attempt at mathematical correction for the DC level will result in variation in the nature of the response signal, which will result in losing some component of the response data.

4. Non-linear harmonic analysis of one electron redox system

Prior to Non-linear Harmonic analysis of G-EIS measurements on Li batteries, we performed the analysis of G-EIS data to simple redox system of $Fe^{2+}/Fe^{3+}$ on glassy carbon working electrode with Ag/AgCl reference and graphite carbon counter electrodes. The aim of this analysis is to observe the type of non-linear response resulting from increasing the AC amplitude of the G-EIS measurements in as standard an electrochemical system as possible. This type of analysis serves as a control and helps in distinguishing the type of distortions for more complex systems. To ensure the stability of the system we used a solution of 0.1 M NaClO$_4$ with 1 mM of both Fe$^{2+}$ and Fe$^{3+}$ ions. The linear KK-transformable G-EIS data of the system are shown in Fig. 3 (a) which demonstrates a distorted semicircle representing the charge transfer processes along the double layer capacitance. Non-linear Harmonics were analyzed at three different AC excitations around 0 DC current (i.e. open circuit potential). Three excitation AC amplitudes applied are 8, 40 and 200 nA.

At low AC amplitude (8 nA), we can observe the linear response where only the fundamental signal is present with higher harmonics at the noise level of $10^{-5}$ V with no structure or trend in the harmonics. Increasing the AC amplitude to (40 nA) results in two things. First, the appearance of a peak-like structure between 5 and 0.5 Hz highlighted with gray in Fig. 3b(ii). Second, the continuous increase of the harmonics level, especially 2nd and 3rd, as the frequency decreases highlighted with blue in Fig. 3b(ii). These two behaviors are believed to be

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2 We should differentiate the sudden changes observed at 2.5Hz and between 0.1Hz to 0.2Hz as instrumental artifacts. The first is related to the change in the filters of the used potentiostat at this specific frequency. The second is also instrumental in nature which is the result of the signal generation method at this small range of frequencies. These jumps will be observed in all the harmonic spectra shown in this study.
related to non-stationarity in the measurements resembling the behaviors discussed above for the dummy cells which can be mistakenly thought to result from some sort of non-linearity in the system. The first is due to the initial transient of the electron transfer process which shows the highest level at its time constant, 0.9 Hz. This behavior is the result of the distortion caused by the large AC amplitude which causes initial drift at the first cycles of the G-EIS measurement that vanishes for the rest of cycles. This is related to the double layer capacitance and can be expected to appear in every electrochemical system [14]. The second, is the voltage-dependent capacitive behavior which is expected to increase the value of the higher harmonics as the frequency decreases.

Increasing the AC amplitude to (200 nA) results in increasing the harmonics level but does not change the structure of the spectrum. By increasing the AC amplitude, the peak-like structure resulting from the initial transient is more obvious (highlighted with gray in Fig. 3b(iii)) followed by the capacitive charging increase of the harmonics (highlighted with blue in Fig. 3b(iii)). This analysis showed that higher order harmonics resulting from increasing the AC amplitude is the result of non-stationary behavior in the G-EIS measurements and not related to the non-linearity of the process. This conclusion is made by the similar behaviors observed in the dummy cells shown in section 3. Observing such behavior for batteries indicates that it is measurement artifact and not related to the non-linear behaviors of the battery processes.

5. Kramers-Kronig transformable EIS of Li primary battery chemistries

Proceeding to batteries, linear EIS were obtained to distinguish the different mass and charge transfer processes with their time constants. Four different Li primary battery chemistries were used with metallic Li as the anode. The batteries differ in the type of the electrolyte and the cathode active material. Linearity and stability of the data were confirmed by performing KK-compatibility tests for all the data, which are shown in Fig. 4. EIS shows similarities in the linear impedance response. In the Nyquist, a semicircle in the high frequency region for all the batteries between 10 kHz and 100 Hz is observed. In the literature, for Li batteries, this region is assigned to the Solid Electrolyte Interface (SEI) processes. This SEI impedance response is then followed by small semicircle which can be assigned to the anodic charge transfer (Li oxidation) and a large semicircle below 1 Hz assigned to either mass transfer or cathodic processes [1,31,35,36]. These linear impedance responses are used as guidance to identify the changes in the non-linear/non-stationary harmonic spectra of the batteries. However, we expect at least three separate regions in the non-linear harmonic spectra.

The simulation method is based on obtaining the high order harmonics for linear RC circuits representing the processes of the batteries. Though at least three RC circuits are required to represent the three regions of the linear impedance response. To obtain the RC parameters for the three regions, each distorted semicircle was fitted with a resistance connected in parallel with a Constant Phase Element (CPE). The CPE was used instead of capacitor to compensate for the distortion in the semicircles which is known to be mostly the results of geometric heterogeneity [37]. The equation governing the CPE impedance is as follows:

$$Z_{CPE} = \frac{1}{Y(\omega)^{\alpha}}$$

where $Y$ is the CPE term, $\omega$ is the frequency, $i$ is the complex number and
\( \alpha \) is the CPE coefficient.

The compensation is done by including the alpha value (\( \alpha \)) which in our model was ranging from 0.85 to 0.95. For the simulations, the capacitance was calculated from the CPE Y value as \( \frac{1}{Y \omega} \). Due to the similarity in the impedance response, the linear EIS between (1 kHz and 10mHz) were fitted with the same equivalent circuit model, which Table 1

<table>
<thead>
<tr>
<th>Battery Chemistry</th>
<th>( R_s (\Omega) )</th>
<th>( R_1 (\Omega) )</th>
<th>( CPE_1 (\text{mF}) )</th>
<th>( \alpha_1 )</th>
<th>( R_2 (\Omega) )</th>
<th>( CPE_2 (\text{mF}) )</th>
<th>( \alpha_2 )</th>
<th>( R_3 (\Omega) )</th>
<th>( CPE_3 (\text{mF}) )</th>
<th>( \alpha_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/SOCl(_2)</td>
<td>1.4</td>
<td>0.9</td>
<td>0.2</td>
<td>0.9</td>
<td>0.6</td>
<td>60</td>
<td>0.9</td>
<td>3.7</td>
<td>( 2 \times 10^3 )</td>
<td>0.9</td>
</tr>
<tr>
<td>Li/MnO(_2)</td>
<td>0.08</td>
<td>0.3</td>
<td>2</td>
<td>0.85</td>
<td>0.2</td>
<td>( 1.8 \times 10^3 )</td>
<td>0.85</td>
<td>7.3</td>
<td>( 3.6 \times 10^3 )</td>
<td>0.85</td>
</tr>
<tr>
<td>Li/PolyC</td>
<td>0.2</td>
<td>3.7</td>
<td>1</td>
<td>0.9</td>
<td>0.1</td>
<td>( 2 \times 10^3 )</td>
<td>0.99</td>
<td>9.2</td>
<td>( 4 \times 10^3 )</td>
<td>0.95</td>
</tr>
<tr>
<td>Li/FeS(_2)</td>
<td>0.1</td>
<td>0.04</td>
<td>13</td>
<td>0.85</td>
<td>0.05</td>
<td>( 6.5 \times 10^3 )</td>
<td>0.85</td>
<td>1.2</td>
<td>( 9.2 \times 10^3 )</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Fig. 5. Non-linear Harmonic Spectra for Li/SOCl\(_2\) battery AA-size at (a) Open Circuit potential with 0.5 mA AC excitation signal and (b) with AC excitation of 0.5 mA and DC-offset of 1 mA.

Fig. 6. Simulated Non-linear Harmonic Spectra for (a) Lithium Thionyl Chloride (Li/SOCl\(_2\)) (b) Lithium Manganese Dioxide (Li/MnO\(_2\)) (c) Lithium PolyCarbon Monofluoride (Li/PolyC) (d) Lithium Iron Sulfide (Li/FeS\(_2\)) primary battery chemistries at open circuit potential between 1 kHz and 10mHz.
contains a series combination of three parallelly connected resistance, CPE as shown in Fig. 4 (e). The high frequency region represents the SEI processes. The middle frequency region is assumed to be for the anodic charge transfer and the low frequency region is assumed to be for the cathodic charge/mass transfer [31,38,39]. The obtained resistance and CPE parameters are summarized in Table 1 and used as RC circuit to simulate the non-linear harmonics under non-stationary scenarios. It should be noted that although CPE model was used to fit the linear impedance data, the capacitive values used for the simulations are taken from the CPE-Y value along with the resistances obtained. The values of the parameters show variation with the chemistry employed. For example, the electrolyte resistance for Li/SOCl$_2$ shows a high value due to the passivation phenomena which is the result of using SOCl$_2$ as electrolyte and the cathode active material [40].

6. Non-linear harmonic analysis of Li primary battery chemistries

To help us distinguish the type of distortion in the data, Non-linear Harmonic response is first analyzed by comparing excitations with different DC levels. Each excitation results in different harmonic response depending on the presence of non-linearity or non-stationarity. The first is achieved at the open circuit potential of the battery, which will result in applying both positive (charge) and negative (discharge) currents. Primary batteries have well-defined discharge reactions that is irreversible, and any positive excitation will result in undefined reactions. The second is with applying a DC-offset along with the AC excitation. This excitation will ensure not to apply charging current to the battery but will cause a continuous discharge and hence a change in the DC voltage.

Fig. 5 shows the obtained non-linear harmonic spectra for both cases applied to Li/SOCl$_2$ battery. As can be seen, there are significant variations and trends in the harmonic levels for each type of excitation. In the first case, we can see the odd harmonics, 3rd and 5th, show higher amplitudes than the even ones, 2nd and 4th, with an increase in the amplitude as the frequency decreases. In the second case, the amplitude of the harmonics decreases as the order of the harmonic increases, with the second harmonic to be the highest. It can be also noticed that all harmonics increase their amplitude until around 10 Hz and stay at a constant level. These observed variations are resulting from the type of distortion dominating the response. In the first type, more non-linear distortions are observed caused by the asymmetric voltage response signals obtained from the irreversible discharge reaction of the cell. Mathematically, any asymmetry in the time domain signal will result in an increase in the odd harmonics instead of even ones [41,42]. On the other hand, for the second type of excitation, the DC-offset is causing more non-stationary response by discharging the battery as the experiment proceeds. The harmonic response, in this case, shows the increase in all harmonic levels irrespective of them being odd or even. The higher order appears to have a higher amplitude. For the rest of the experimental data presented, we obtained the harmonic spectra at open circuit potential since applying any DC-offset results in mainly non-stationary response.

6.1. Simulation results

We first performed harmonic analysis for simulated G-EIS measurements for the obtained RC equivalent circuits under two excitations

![Fig. 7. Simulated Non-linear Harmonic Spectra for (a) Lithium Thionyl Chloride (Li/SOCl$_2$) (b) Lithium Manganese Dioxide (Li/MnO$_2$) (c) Lithium PolyCarbon Monofluoride (Li/PolyC) (d) Lithium Iron Sulfide (Li/FeS$_2$) different Li primary battery chemistries with DC offset between 1 kHz and 50mHz.](image-url)
mentioned above. The first, is with relatively large AC excitations which shows distortions as form of initial transient, see Fig. 6. The spectra show variation in the harmonics level in the form of a peak-like structure that peaks at the time-constant of the RC circuit. For each battery, the simulation shows three distinct regions corresponding to each time constant in our RC circuit model. As discussed previously for the Fe\(^{2+}\)/Fe\(^{3+}\) electrochemical system, the presence of capacitive behavior results in the initial transient of the response and the appearance of such harmonic behavior. Though, this type of behavior should be expected for the batteries and don’t emerge from non-linearities in the electrochemical processes.

The second is by simulating the harmonic response for the G-EIS measurement under constant DC-offset. The obtained results are shown in Fig. 7. The harmonics show an increase in the level of the harmonics and the flattening in the peaks which shows how non-stationarity caused by drift increase the harmonic levels at least by two times and results in harder recognition of the processes in the harmonic spectra.

These simulations provide valuable information for the nature of harmonic response expected from the G-EIS measurement under constant DC-offset. The obtained results are shown in Fig. 7. The harmonics show an increase in the level of the harmonics and the flattening in the peaks which shows how non-stationarity caused by drift increase the harmonic levels at least by two times and results in harder recognition of the processes in the harmonic spectra.

Increasing the AC amplitudes increases the odd-numbered harmonics in all the batteries, see Fig. 9. This increase is related to the non-linearity caused by the asymmetric structure of the voltage response signals. The asymmetry is observed because of the undefined charging reaction of the primary batteries. Primary batteries are irreversible.

6.2. Experimental measurements

The harmonic spectra obtained for the four Li primary batteries from 1 kHz to 50mHz at moderate and high AC amplitudes are shown in Figs. 8 and 9 respectively. These amplitudes were assigned according to the capacity of the battery and recommended maximum discharged currents. In every spectrum, we observe a jump around 2.5 Hz which is as mentioned previously from the change in the filter of the instrument.

Fig. 8. Measured Non-linear Harmonic Spectra for (a) Lithium Thionyl Chloride (Li/SOCl\(_2\)) (b) Lithium Manganese Dioxide (Li/MnO\(_2\)) (c) Lithium PolyCarbon Monofluoride (Li/PolyC) (d) Lithium Iron Sulfide (Li/FeS\(_2\)) primary battery chemistries at ≥ 99% State of Charge with increased AC amplitude excitation between 1 kHz and 50mHz.
systems, which have well-defined discharge reactions. The positive current excitation gives unknown electrochemical response, which results in an asymmetric voltage response.

7. Comparison between the experimental measurements and simulations

The simulations demonstrated non-stationarity behavior originated from the initial transient of the voltage response. Similar behavior was observed in some parts of the experimental measurements. Depending on the battery, initial transient harmonics is observed between $10^{-6}$ and $10^{-3}$ V. The overlay of second and third harmonics for both simulated and experimentally measured are shown in Fig. 10. Distinctive similar behavior is clearly seen for Li/MnO$_2$ battery Fig. 10 (c and d) which shows high harmonic contribution from initial transient. Though the harmonics for Li/SC$_2$ show higher amplitudes indicating the existence of other form of non-linear/non-stationary response, see Fig. 10(a and b).

Fig. 9. Non-linear Harmonic Spectra for (a) Lithium Thionyl Chloride (Li/SC$_2$) (b) Lithium Manganese Dioxide (Li/MnO$_2$) (c) Lithium PolyCarbon Monofluoride (Li/PolyC) (d) Lithium Iron Sulfide (Li/FeS$_2$) different Li primary battery chemistries at $\geq$ 99% State of Charge at high AC amplitude excitation between 1 kHz and 50mHz.

8. Conclusion

Investigation of non-stationarity and non-linearity in the Harmonic Distortions of Galvanostatic-EIS measurements of Li primary batteries was performed by mathematical simulations and experimental measurements. The analysis was first performed experimentally on a dummy cell and a simple one electron redox system. Second, the harmonic responses were simulated based on RC equivalent circuits representing the processes in the batteries. In both, the non-stationarity behaviors of initial transient and voltage drift were identified to originate from the capacitive nature of the processes. It was concluded that such harmonic response is expected to appear for high AC excitation for any capacitive system. The harmonic analysis for different Li primary battery chemistries showed the existence of both non-linear and non-stationary behavior in the voltage response. The non-stationarity was identified to be from what is observed in the simulations as, either from the initial transient of the response signal or from the voltage drift. The other harmonic response was concluded to be from non-linear processes during the measurement.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Data availability

Data will be made available on request.

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Appendix

**FFT Mathematics:** To analyze the response signal in the frequency domain, Fourier Transform is used which is a mathematical tool for transforming periodic functions of time into a function of frequency. It resolves the periodic function of time into an equivalent infinite summation of sine and cosine waves. The resulting infinite series is the Fourier Series which can be expressed in exponential form as:

\[
x(t) = \sum_{n=-\infty}^{\infty} c_n e^{j\omega_n t}
\]

where, \( n = \) sample number, \( \omega = \) angular frequency = \( 2\pi f \), \( c_n \) are the Fourier series coefficients.

Fourier Transform is used to solve for the coefficients \( c_n \). The result is a group of coefficients which are function of frequency and can be obtained by the following sum:

\[
c_f = \sum_{n=0}^{N-1} x_n e^{-j2\pi n/N}
\]

where, \( N = \) number of samples, \( n = \) sample number, \( x_n = \) value of the input signal at \( n \), \( f = \) frequency = \( 0,1,2,3,\ldots,N-1 \) and \( c_f = \) coefficient value.

The Fourier transform calculations were performed within SciPy v0.15.1 fft module with Spyder v3.3.3 as the developing environment [43].

The harmonics are obtained by analyzing the time domain AC perpetuation in the frequency domain by means of the FFT mathematics explained above. For the G-EIS measurement the potential response can be written as:

\[
E(t) = A \sin(\omega t) + \varnothing
\]

where, \( A = \) amplitude of the wave, \( \omega = \) angular frequency = \( 2\pi f \), \( t = \) time and \( \varnothing = \) phase. This voltage response can be written as Fourier Series in the exponential form as:

\[
E(t) = \sum_{k=0}^{\infty} E_n e^{j\omega nt}
\]

where, \( n = \) sample number, \( \omega = \) angular frequency = \( 2\pi f \) and \( E_n \) the Fourier series coefficients. The harmonics were obtained by computing for these coefficients and drawing the magnitudes versus corresponding frequencies.

For a Linear Time-Invariant signal, the value of the coefficients will have power only at the corresponding frequency of the analyzed current or voltage signal called the fundamental signal, see the current response in Fig. A1. The rest of the coefficients will have minimal power, which represents the noise level of the signal. For a signal that contains non-linearity, besides the fundamental signal, there are other signals with different amplitudes at the \( n \) multiple frequencies of the fundamental signal which are called harmonics. This can be seen in the voltage response in Fig. A1.

- **Simulation mathematics:** The simulations were performed on an equivalent circuit model of three RC elements connected in series. In a previous publication, we employed the same fundamentals for NHA of simplified Randles’ cells [14].

To begin with, the voltage across the whole system can be calculated as the individual voltages of the resistance and three R-C elements. The overall voltage for one RC can be expressed as:

\[
i_k \times R_p = \frac{\int_0^t i_k dt}{C}
\]

In this formula, \( i_k \) is the current that passes through the parallel resistance, and \( i_c \) is the current that passes through the capacitor. As the summation of these currents gives the total current of the whole system as follows:

\[
i_k + i_c = i
\]

When above equations are reorganized as a function that represents \( i_c \) in terms of \( C, R_p \) and \( i \), following statement can be written for a three R-C system:

\[
i_c = i - \frac{1}{C_1 \times R_{p1}} \times \int_0^t i_c dt - \frac{1}{C_2 \times R_{p2}} \times \int_0^t i_c dt - \frac{1}{C_3 \times R_{p3}} \times \int_0^t i_c dt
\]

This equation shows the current of the overall system, however, it can be used to calculate the currents pass through the capacitors. In addition, the magnitude of the current is not limited or defined in these equations. Only the input is stated in the equations.

After calculating the current through capacitor and resistor, the voltage response can be expressed as following:

\[
E = i[j] \times R_p + \sum_{n=1}^{total \ RC} \sum_{k=0}^{index} \frac{\int_0^t i_c[k] \times t}{C}
\]
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