Graphical Abstract

Operando Odd Random Phase Electrochemical Impedance Spectroscopy as a Promising Tool for Monitoring Lithium-ion Batteries during Fast Charging

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Highlights

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- Implementation of operando EIS for lithium-ion batteries
- Using operando ORP-EIS to monitor SoC for fast-charging applications
Operando Odd Random Phase Electrochemical Impedance Spectroscopy as a Promising Tool for Monitoring Lithium-ion Batteries during Fast Charging

Xinhua Zhu*a, Noël Hallemansb, Benny Woutersa, Raf Claessensa, John Lataireb, Annick Hubina

aDepartment of Materials and Chemistry, Research Group Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2, Brussels, 1050, Belgium
bDepartment of Electrical Engineering, Research Group Fundamental electricity and Instrumentation, Vrije Universiteit Brussel, Pleinlaan 2, Brussels, 1050, Belgium

Abstract

Electrochemical impedance spectroscopy (EIS) is a powerful technique for characterization of lithium-ion batteries (LIBs). It has extensively been used in laboratory research, but seldom in industrial applications, e.g., electrical vehicles (EVs). This is because the latter needs EIS measurements during operation, but achieving valid EIS measurements in dynamic conditions has been a long-lasting challenge. In this work, LiNi0.6Mn0.2Co0.2O2 (NMC622)/graphite batteries are characterized by operando odd random phase EIS (ORP-EIS) under practical usage conditions. The validity of the EIS data is quantitatively assessed based on the robust theoretical framework of ORP-EIS. The measured impedance data reveals a continuous evolution of charge-transfer phenomena along changes of state-of-charge (SoC). The results are consistent with conventional stationary EIS data. Moreover, charge-transfer related parameters can be extracted through equivalent electric circuit models or graphical analysis methods from operando ORP-EIS. The parameters exhibit consistent behavior under various charging conditions including different temperatures, C-rates, and state-of-health (SoH). As a proof of concept, operando ORP-EIS provides unique physical insights on top of conventional current/voltage-based monitoring methods, and could be powerful technique to monitor the SoC of the batteries during fast charg-

*Corresponding author
Email address: Xinhua.Zhu@vub.be (Xinhua Zhu)
1. Introduction

Electrochemical impedance spectroscopy (EIS) is a non-invasive characterization and diagnosis technique for lithium-ion batteries (LIBs), providing comprehensive information related to multiple physical/chemical processes by resolving their characteristic frequency response [1]. Owing to its simple experimental setup and robust output, EIS has been extensively used in the battery research domain. Recently, due to the ongoing electrical vehicles (EVs) transition [2–6], many resources have been allocated to develop advanced EIS-based diagnostic tools to provide more reliable and safer online monitoring of battery systems.

Generally, EIS is measured at a steady state with a small amplitude excitation signal in order to satisfy the prerequisites of a valid EIS measurement, i.e., linearity, and stationarity. In theory, EIS can only resolve linear frequency responses. However, in batteries and other electrochemical systems, the current is an exponential function of the potential, often described by the Butler-Volmer equation. Therefore a small amplitude excitation is necessary so that the current-potential relationship is linear. On top of that, the electrochemical systems should also be stationary (time-invariant) during the EIS measurement [1, 7]. A valid measured system, with the constraints of linearity and stationarity, can be categorized as a linear time-invariant (LTI) system [8].

However, operando EIS approaches inevitably do not satisfy the constraints of LTI systems. In the literature, EIS measurements in non-stationary conditions are often called dynamic EIS (DEIS). Huang et.al. [2] conducted a continuous EIS measurement of a single frequency measurement during a full battery charge/discharge cycle in order to reduce the measurement time, and to minimize errors introduced by the time-varying system. A similar approach is adopted by Kuipers et al. [4]. They conducted a continuous EIS measurement with multiple high-frequencies to online monitor the electrical behavior of LIBs. Stoynov et al. [9] proposed a straightforward post-experimental method, i.e., ”4-dimensional analysis” to compensate for errors introduced by time-variation. This method is based on a time-interpolation
approach using spline functions, and has been further developed and applied to LIB studies by Itagaki et al. [10–12] and other researchers [13, 14]. Modeling approaches including dynamic equivalent electrical circuit modeling (EECM) [15, 16], and more sophisticated physics-based modeling have been applied [17–19] to analyze and interpret DEIS measurements. Particularly, the physics-based modeling is able to provide a reliable quantitative analysis on specific physicochemical processes occurring during DEIS. Most of the above-mentioned DEIS studies are based on a framework of linear time-varying (LTV) systems, in which the experimental conditions are often compromised and the linearity of EIS frequency response is presumably fulfilled.

Nevertheless, for batteries or some other electrochemical systems in dynamic conditions, the characteristics of the frequency response can deviate from the ideal linear framework due to the presence of non-linear distortions. Therefore, detection and quantification of this deviation is necessary to assess the validity of the EIS measurement and the data interpretation [20]. La Mantia et al. [21–23] introduced the dynamic multi-frequency analysis (DMFA), which is able to acquire time resolved impedance spectra and quantify non-linear distortions. DMFA was implemented by the superposition of a quasi-triangular voltage sweep and a multi-sine AC signal, which is a powerful tool to investigate surface/interface electrochemical reaction mechanisms, such as LiMn$_2$O$_4$ thin-film electrodes [24] and electrocatalytic reactions [25]. Carefully optimizing the superposition signal, in particular the potential sweep rate and the frequency distribution of the multisine signal for a given system, is crucial for DMFA to achieve optimal results.

Another multisine EIS technique, odd random phase EIS (ORP-EIS) [26], is implemented in a different theoretical framework, where a specially designed broadband periodic random phase multisine excitation is used to identify the presence of non-linear distortions in LTI systems [27–30]. Since then, the theoretical framework of ORP-EIS has been further expanded for identification of LTV systems [31, 32], and the time-resolved instantaneous impedance can be extracted [33, 34]. Recently, Hallemans et al. [35–37] have implemented new expansions to the framework of ORP-EIS, which can be applied to the best linear time-varying approximation (BLTVA) of a general class of non-linear time-varying (NLTV) systems. Moreover, it compensates for drift signals in the system’s response, making it applicable to operando EIS. It has been demonstrated that the framework is valid to characterize LIBs in operation.
In this work, we introduce operando ORP-EIS for battery research by applying the method of \cite{35,37} on battery measurements, and also explore the possibilities of its practical applications. Comparing to existing dynamic EIS techniques, operando ORP-EIS shows merits on the experimental versatility, robust error analysis, and accessibility to a wide frequency range, particularly the low frequency range. The state-of-the-art LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2 (NMC622)/graphite batteries are investigated by operando ORP-EIS under practical charging (≥1C) conditions. The extracted charge-transfer resistance exhibits a consistent evolution as a function of state-of-charge (SoC), regardless of the charging conditions. We believe operando ORP-EIS might be a new path to achieve the ultimate fast-charging capability for battery systems without compromising the cycling life and safety.

2. Experimental

2.1. Operando ORP-EIS setup

The in-house designed galvanostatic ORP-EIS setup consists of a PCI-4461 DAQ-card (National Instruments) and a customized analog frontend to ensure optimal signal quality. During the measurement, an ORP multisine signal (galvanostatic) is superimposed to a DC charging current. The integrated excitation signal is generated by Python code and converted to an analog signal by the DAQ-card. The analog signal is further amplified by the analog frontend and fed to the batteries. The recorded frequency response goes through an inverse process to be stored in a computer as a digital signal. Next, the time-varying impedance data and its uncertainties are calculated through an in-house developed Matlab algorithm based on the algorithm presented by Hallemans et al \cite{35,37}.

2.2. NMC622/Graphite Cells

The used NMC622/graphite coin-type cells (EL-CELL) were assembled in an Ar-filled glovebox (Jacomex). 18 mm diameter NMC622 (Al substrate) and graphite disc electrodes (Cu substrate) were cut from single coated electrode sheets (Customcells). The area capacities of NMC622 electrodes and graphite electrodes are 2 mAh/cm$^2$ and 2.2 mAh/cm$^2$, respectively. The disc electrodes were dried in a vacuum oven (BUCHI) at 110 °C. The assembled cell contained 0.5 mL electrolyte of 1M LiPF$_6$ in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 v/v) with 2 wt% vinylene carbonate (VC)
additive, and glass fiber separator (1.55 mm thickness). The nominal capacity of the assembled NMC622/graphite cells was around 5 mAh operating between 3.0 V - 4.2 V. In practice, all cells were assumed to have an identical nominal capacity of 5 mAh, and 5 mA was the 1C rate. For the constant current charging, the SoC is linearly correlated to the total input charge $Q_{ch}$, for instance 100% SoC is equivalent to 5 mAh ($Q_{ch}$).

2.3. Operando ORP-EIS measurements

The used multisine AC signal has a frequency range of 0.05 Hz - 5 kHz with a root-mean-square (RMS) amplitude of 1 mA, which was chosen according to the total cell impedance. Each period of measurement takes 20 seconds, determined by the lowest measured frequency (0.05 Hz in this case). The amount of measured periods is chosen based on the total constant current charging time. However, each operando ORP-EIS measurement can only cover a partial SoC range due to hardware limitations as the measurable voltage window of the analog frontend is a trade-off between range and sensitivity. As such, four measurements were carried out to cover the full SoC window, with 1 hour relaxation time between the measurements. The time resolution of the derived time-varying impedance is adjustable. For this work, the time resolution is 10 seconds for all presented operando impedance data. In addition, the total number of periods also affects the accuracy of the impedance calculation. A rule of thumb is to use minimally 20 periods. In this work, we measured 45 and 30 periods for 1C and 1.5C charging experiments, respectively.

3. Results and discussion

3.1. Operando ORP-EIS for LIBs

This EIS study is carried out on the state-of-the-art NMC622/graphite LIB system. Commercial single-side coated electrodes were used for optimal consistency. The assembled cells were first preconditioned and then charged to 10% SoC. Due to drastic changes of cell voltage at < 10% SoC, the setup was not able to accurately define a reference voltage for the AC signal in 0 - 10% SoC. Therefore, all investigations in this work focus on SoC > 10%. Figure 1 shows the recorded time-domain input and output signal of the operando ORP-EIS measurement during 1C rate and 85 - 110% SoC. In Figure 1(a) the superimposed input AC + DC current signal lasts 900 seconds (i.e., 45 periods), which is equivalent to a change of 25% in SoC. It is worth
noting that here, the amplitude of the DC signal is 5 mA and the amplitude of the AC signal is 1 mA (RMS). The crest factor of the AC signal is minimized by randomizing the phases \[38\]. Figure 1(b) shows the output voltage signal. In addition to the AC response, a gradual increase of the cell voltage is also evident in the output. The time-domain data is further analyzed in the frequency-domain using the algorithm introduced by Hallemans et al. \[35\] to obtain the time-varying impedance of the measured system and to quantify the uncertainty introduced by the operando conditions and nonlinearities.

Figure 1: Time-domain data of an operando ORP-EIS measurement. (a) input current signal consisting of DC and AC (odd random phase multisine) signal; (b) output voltage signal. Experimental conditions: DC charge current is 5 mA (\(\sim\) 1C); amplitude of AC signal is 1 mA (RMS); frequency range is 0.05 Hz - 5 kHz; temperature 25 °C.

Figure 2 shows the operando impedance data measured at 1C charging rate with 10 - 110% SoC under 25 °C. Both Bode plot and Nyquist plot are presented. Figure 2(a) and (b) show the time-varying impedance measured from 10 - 60% SoC and 60 - 110% SoC, respectively. In the Bode modulus plots, besides impedance data, the standard deviation (\(\sigma\)) of the impedance data is also provided for justification of the measurement quality under operando experimental conditions. In most of the frequency range, more than three orders of magnitude difference between impedance data and the standard deviation can be observed, which ensures the validity of the measurement. However, the level of the standard deviation gradually increases at the low frequencies. Particularly, near the lowest frequency (< 0.5 Hz), the standard deviation becomes so high that the impedance data is no longer valid, and the Nyquist plots are also disrupted. Therefore, only impedance data acquired above 0.5 Hz will be further investigated in this work. For operando/dynamic EIS techniques, 0.5 Hz is one of the lowest resolved frequencies measured on a battery system \[2, 11, 6, 24\]. Yet, operando
ORP-EIS is capable to resolve even lower frequencies without any theoretical restrictions as demonstrated in the work of Collet et al. [39]. In this work, we could use a lower lowest-frequency bound to increase the frequency resolution and lowest resolved frequency, however the size of the data set will increase resulting in a longer computation time.

Figure 2: Impedance data achieved through operando ORP-EIS at various SoC. Both Bode plot and Nyquist plot are presented. (a) shows impedance data from 10% till 60% SoC; (b) shows impedance data from 60% till 110% SoC. The standard deviation (σ) of the impedance data introduced by operando experimental conditions is presented in the Bode modulus plot. Experimental conditions: DC charge current is 5 mA (∼1C); amplitude of AC signal is 1 mA (RMS); frequency range is 0.05 Hz - 5 kHz; temperature 25 °C. The impedance data under 0.5 Hz is indicated in the plots.

The Bode phase plots in Figure 2 indicate three characteristic time constants in frequency regions above $10^6$ Hz, between $10^2$ Hz and $10^3$ Hz, and from 0.5 Hz to $10^2$ Hz, which could be associated with three major physical phenomena. The high frequency time constant appearing in > 1 kHz region is often linked to the electrical contact between current collector and composite electrode [40, 41], however it is not always visible because of different battery systems or EIS setups. This time constant is most likely related to artifacts coming from the in-house setup, as measurements with a resistor also showed these artifacts at frequencies higher than 1 kHz (see supplementary material,
Nevertheless, the high frequency region neither has a major contribution to the total impedance, nor is it relevant to the focus of this work. The middle frequency region ($10^3 \text{ Hz}$ to $10^2 \text{ Hz}$) could be assigned to the behavior of the interfacial passivation layer, which exhibits low amplitude due to the use of high loading electrodes and their porous structure. The SoC induced impedance variations mostly happen in the low frequency region (0.5 Hz - $10^2 \text{ Hz}$), where charge transfer phenomena play the major role. It agrees with our previous EIS work [42], which investigated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) cathode materials at various SoC by a symmetrical cell approach.

To further (semi)quantitatively analyze the same set of impedance data, complex nonlinear least square (CNLS) fitting is carried out to an EECM. It is crucial to be aware of the ambiguity of EECM approaches which describe only macroscopically homogeneous systems. Due to the intrinsic porous structures and inhomogeneity of LIBs, EECM approaches cannot provide parameters that are physically well defined for batteries. Nevertheless the parameters extracted from a EECM can still be very relevant to the physical process if the chosen model is properly validated [41, 43]. Physics-based modeling approaches could help to achieve accurate physical parameters from EIS data [19, 44–47], but with the cost of computation time, and efforts of determining input parameters. Nevertheless, the EECM approach is sufficient for the purpose of a semi-quantitatively analysis in this work.

A widely used Vogit-type EECM is adopted as shown in Figure 3(a) [42, 48]. $R_s$ represents the electrolyte ohmic resistance. The high frequency time constant, which is related to hardware artifacts, is modeled by a parallel $R_f$ and $C_f$. The parallel $R_p$ and constant phase element 1 (CPE1) represent, respectively, resistive and capacitive behavior related to the passivation layer on the electrode-electrolyte interface. The dominating low frequency region, which is associated with the charge-transfer process, is modeled by a parallel $R_{ct}$ and CPE2. The mathematical description of the impedance of a CPE is given by:

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^{\alpha}}$$  \hspace{1cm} (1)

where $j$ is the imaginary unit, $j = \sqrt{-1}$, $\omega$ is the angular frequency, $Q$ is the parameter related to the double layer capacitance, and $\alpha$ is the constant phase exponent ($0 \leq \alpha \leq 1$). CPE are used in the EECM to sufficiently model the dispersed impedance response introduced by highly porous electrodes. Most of the fitted parameters and their uncertainties are presented in Figure S2.
Generally, the parameter errors are higher for the parameters modeling the high to middle frequency region, because the obtained impedance data does not provide sufficient information to identify the electrolyte resistance $R_s$, and the impedance in this region is also highly convoluted. On the other hand, the parameter errors are clearly lower in the parameters describing the middle to lower frequency region, which is associated with the charge-transfer process. Apart from the uncertainties of the fitting parameters, the goodness-of-fit is evaluated by the fitting residual as shown in the Bode modulus plot of Figure 3 (b) and (c). The average amplitude of the residual is at least two orders of magnitude lower than the impedance data, which ensures the fitting accuracy. In addition, the fitting residual is comparable to the experimental error ($\sigma$) introduced by the operando conditions and nonlinearities shown. As such, the quality of the time-varying impedance data is sufficient for EECM analysis. Furthermore, as seen in Figure 3, the impedance changes as function of the SoC mostly occur in the low frequency region, which is related to the charge-transfer process, which will be the main focus for SoC analysis. According to Figure S2 (a), the fitted $\alpha_2$ value in CPE2 is generally lower than 0.8, indicating a physical ambiguity of the CPE interpretation [1, 7]. Therefore, the only parameter that is eligible for a further semi-quantitative analysis is $R_{ct}$, which is directly associated with electrochemical kinetics by [19]:

$$R_{ct} = \frac{RT}{nFA_0j_0}$$

where $R$ is the gas constant, $T$ is the absolute temperature in Kelvin, $n$ is the number of electrons, $F$ is the Faraday constant, $A_0$ is the active surface area and $j_0$ is the exchange current density.

All $R_{ct}$ obtained from the EECM analysis are plotted against SoC in Figure 4(a). While charging, $R_{ct}$ decreases first in the low SoC region, and maintains at a constant level in the middle SoC region until at high SoC, $R_{ct}$ drastically increases. The parabolic-like trend agrees with previous EIS studies on similar Ni-rich cathode materials [42, 50], in which the changes of $R_{ct}$ reflect the changes of the kinetics (i.e., $j_0$ in Equation 2) as a result of the evolution of crystal lattice of the cathode material upon delithiation [50, 51]. Additionally, the $R_{ct}$ curves are divided into four segments due to four non-continuous operando ORP-EIS measurements. Each segment displays extra parabolic-like features, particularly in the first three segments, i.e., 10% - 35% SoC, 35% - 60% SoC, and 60% - 85% SoC. These features also lead to
Figure 3: Impedance data are fitted with an equivalent electric circuit model presented in (a). Bode plot and Nyquist plot of impedance data (b) for 10% till 60% SoC, and (c) for 60% till 110% SoC. The impedance data are displayed in dots; the fitted data are displayed in lines. The fitting residual and standard deviation ($\sigma$) of the impedance data are displayed in Bode modulus plots.

c onsiderable deviations on breaking points between any two segments. Yet, it is not clear what are the causes of the phenomena. One possible explanation could be attributed to the physicochemical changes of interfaces and kinetics upon charging. In this case, the deviations on breaking points reflect the distinctive physicochemical conditions between the end of the previous segment and the beginning of the following segment. Due to the uniqueness of operando ORP-EIS, this explanation needs a further dedicated study, preferably by combining physics-based modeling and other complementary experimental techniques. On the other hand, the observed phenomena might also be affected by the modeling ambiguity of the EECM approaches for porous systems such as LIBs [41]. The ambiguity is further amplified in the middle SoC region due to a convolution of the two time constants across the middle to low frequency region.
Apart from the operando measurements, a set of 11 stationary ORP-EIS measurements across 10% - 110% SoC are also conducted to verify and compare with the operando measurements. As shown in Figure 4(b), the set of stationary impedance presents a similar behavior, i.e., the SoC-induced changes appear mostly in the low frequency region (<100 Hz), and the impedance in this region decreases first and increases again in the high SoC region. Moreover, the stationary data are also fitted with the same EECM with comparable uncertainties. The best-fit parameters and their standard deviation are listed in Table 1, where the parameters related to the high to middle frequency, e.g., $C_f$, $R_f$, $R_p$ and CPE1 ($Q_1$, $\alpha_1$), show high uncertainties either due to the lack of complete information of the electrolyte resistance ($C_f$ and $R_f$), or the convoluted impedance ($R_p$ and CPE1). Nevertheless, the standard deviation for the parameters associated with charge-transfer process in the middle to low frequency region is much lower and thus more reliable for the analysis. $R_{ct}$ are plotted as well in Figure 4(a), showing a comparable parabolic-like trend and comparable values in the whole SoC range. Yet, the additional features exhibited in the individual operando segments are not visible in stationary tests, presumably because of the low SoC resolution. It is also worth noting that the stationary tests show overall comparable $R_{ct}$ values but generally higher than operando measurements. This phenomena has been reported in other dynamic impedance studies [2, 52]. It is also explicitly explained by Huang et al. [19] through a physics-based impedance modeling study that operando impedance requires a higher overpotential leading to lower $R_{ct}$ according to the Butler-Volmer equation. In general, operando ORP-EIS shows consistent results as achieved through stationary ORP-EIS.

3.2. Operando ORP-EIS for monitoring of LIBs under various charging conditions

We have shown that operando ORP-EIS is able to track the characteristic changes of $R_{ct}$ while charging batteries, which could be a promising approach to monitor the SoC during fast-charging. Developing a health-aware fast-charging protocol without compromising the health of batteries is a crucial step to further accelerate the transition of EVs. The state-of-the-art monitoring approaches are mostly based on conventional parameters i.e., voltage, current and temperature, and assisted by the Coulomb counting method, however it becomes insufficient in more complex usage conditions [53]. Applying the fast-charging in a mismatched SoC region (i.e., low or high SoC region) leads to accelerated aging effects on batteries such
Table 1: Best-fit parameters and their standard deviation for the impedance data obtained from the set of 11 stationary ORP-EIS measurements across 10% - 110% SoC.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>10% SoC</th>
<th>20% SoC</th>
<th>30% SoC</th>
<th>40% SoC</th>
<th>50% SoC</th>
<th>60% SoC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_c/\Omega$</td>
<td>6.60±(±2.1%)</td>
<td>3.69±(±1.1%)</td>
<td>2.96±(±1.6%)</td>
<td>4.88±(±3.8%)</td>
<td>4.83±(±6.5%)</td>
<td>3.92±(±2.2%)</td>
</tr>
<tr>
<td>$C_1/F$</td>
<td>7.2e−6(±16.2%)</td>
<td>5.2e−6(±20.8%)</td>
<td>3.8e−6(±24.3%)</td>
<td>3.2e−6(±29.9%)</td>
<td>3.1e−6(±32.8%)</td>
<td>3.5e−6(±33.5%)</td>
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<tr>
<td>$R_f/\Omega$</td>
<td>1.53(±6.9%)</td>
<td>1.70(±9.0%)</td>
<td>1.88(±10.7%)</td>
<td>2.02(±11.3%)</td>
<td>2.04(±14.7%)</td>
<td>1.92(±15.0%)</td>
</tr>
<tr>
<td>$R_{ct}/\Omega$</td>
<td>0.64±(±4.2%)</td>
<td>0.50±(±7.4%)</td>
<td>0.39±(±10.6%)</td>
<td>0.30±(±16.3%)</td>
<td>0.25±(±19.9%)</td>
<td>0.25±(±18.9%)</td>
</tr>
<tr>
<td>$Q_1/\Omega$</td>
<td>2.3e−3(±12.5%)</td>
<td>2.3e−3(±19.1%)</td>
<td>2.5e−3(±21.6%)</td>
<td>2.4e−3(±24.6%)</td>
<td>2.3e−3(±38.4%)</td>
<td>1.9e−3(±38.8%)</td>
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<tr>
<td>$\alpha_1/\theta$</td>
<td>0.82±(±2.7%)</td>
<td>0.83±(±4.0%)</td>
<td>0.83±(±5.0%)</td>
<td>0.85±(±6.9%)</td>
<td>0.88±(±7.9%)</td>
<td>0.90±(±7.6%)</td>
</tr>
<tr>
<td>$R_{ct}/\Omega$</td>
<td>2.35±(±0.6%)</td>
<td>2.02±(±1.3%)</td>
<td>1.66±(±1.8%)</td>
<td>1.63±(±2.4%)</td>
<td>1.67±(±2.5%)</td>
<td>1.75±(±2.4%)</td>
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<tr>
<td>$Q_2/\Omega$</td>
<td>2.5e−2±(±0.6%)</td>
<td>3.0e−2±(±1.2%)</td>
<td>3.4e−2±(±1.7%)</td>
<td>3.7e−2±(±2.3%)</td>
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<td>70% SoC</td>
<td>9.49±(±4.5%)</td>
<td>4.98±(±4.2%)</td>
<td>9.04±(±8.0%)</td>
<td>5.12±(±5.1%)</td>
<td>5.22±(±2.6%)</td>
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<tr>
<td>80% SoC</td>
<td>3.7e−6(±25.6%)</td>
<td>3.6e−6(±24.2%)</td>
<td>2.0e−6(±21.2%)</td>
<td>5.0e−6(±20.4%)</td>
<td>5.0e−6(±19.0%)</td>
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<tr>
<td>90% SoC</td>
<td>1.85±(±11.4%)</td>
<td>2.1±(±10.8%)</td>
<td>1.73±(±10.4%)</td>
<td>1.62±(±9.1%)</td>
<td>1.51±(±6.5%)</td>
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<tr>
<td>100% SoC</td>
<td>0.35±(±10%)</td>
<td>0.40±(±8.0%)</td>
<td>0.43±(±6.7%)</td>
<td>0.48±(±4.7%)</td>
<td>0.52±(±3.4%)</td>
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<tr>
<td>110% SoC</td>
<td>2.3e−3(±22.9%)</td>
<td>2.5e−3(±19.7%)</td>
<td>2.5e−3(±17.7%)</td>
<td>2.5e−3(±13.8%)</td>
<td>2.5e−3(±10.8%)</td>
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<tr>
<td>$\alpha_1/\theta$</td>
<td>0.85±(±4.7%)</td>
<td>0.83±(±4.1%)</td>
<td>0.84±(±3.6%)</td>
<td>0.83±(±2.8%)</td>
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</tr>
<tr>
<td>$R_{ct}/\Omega$</td>
<td>1.60±(±1.7%)</td>
<td>1.61±(±1.4%)</td>
<td>1.72±(±1.2%)</td>
<td>1.99±(±0.7%)</td>
<td>2.96±(±0.4%)</td>
<td></td>
</tr>
<tr>
<td>$Q_2/\Omega$</td>
<td>4.3e−2±(±1.6%)</td>
<td>4.0e−2±(±1.3%)</td>
<td>3.5e−2±(±1.1%)</td>
<td>2.8e−2±(±0.8%)</td>
<td>2.6e−2±(±0.5%)</td>
<td></td>
</tr>
<tr>
<td>$\alpha_2/\theta$</td>
<td>0.61±(±1.0%)</td>
<td>0.65±(±0.9%)</td>
<td>0.69±(±0.7%)</td>
<td>0.76±(±0.5%)</td>
<td>0.84±(±0.3%)</td>
<td></td>
</tr>
</tbody>
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Figure 4: (a) Charge transfer resistance $R_{ct}$ as a function of state-of-charge (SoC); the error bars indicate the fitting errors. (b) Bode plot and Nyquist plot of stationary ORP-EIS measurements at different SoC; experimental conditions: 0.05 Hz - 5 kHz, 1 mA (RMS) amplitude; temperature 25 °C.

as the destabilization of the lattice structure, the release of lattice oxygen, side (electro)chemical reactions and excessive heat generation etc, leading to a rapid degradation of the batteries and safety hazards [54–57]. Many researchers thus are shifting their focus to more physics-oriented strategies
providing direct insights towards the battery materials [58].

In this work, the characteristic behavior of the NMC622/graphite batteries, where $R_{ct}$ decreases in the low SoC region, reaches a low-valued plateau in the middle SoC region, and rapidly increases in the high SoC region, works as the fundamental principle of designing the fast-charging protocol: the fast-charging sequence is applied solely in the middle SoC region where $R_{ct}$ is low (i.e., fast kinetics) and deactivated in the low SoC and high SoC regions that show high $R_{ct}$. Monitoring the $R_{ct}$ provides directly physicochemical information, which can be applied to robustly identify the safe operating area (SOA) for the fast-charging protocol. Moreover, to further verify the capability of operando ORP-EIS in complex usage scenarios, we measured NMC622/graphite batteries under different temperatures, charging current, and different state-of-health (SoH).

Figure 5 presents results from the same NMC622/Graphite LIBs. $R_{ct}$ is derived from the identical operando ORP-EIS protocol and EECM analysis as shown earlier. Figure 5(a) and (b) investigate the temperature influence during 1C charging. $R_{ct}$ under 15 °C shows distinctive higher values in the whole SoC range due to the overall decreased kinetics under low temperature (see Equation 2). The plateau at the middle SoC region, which is suitable for a fast-charging sequence, spans a narrower SoC window than the other two higher temperatures. This phenomenon indicates a reduced overall charging capacity under the low temperature condition. Similar observation has been extensively reported and associated with a multi-facet physico-chemical mechanism in literature [59]. On the other hand, as shown in Figure S3 (a zoomed plot), $R_{ct}$ under 45 °C shows lower values than under 25 °C, but the difference is less significant and mainly observed in the middle SoC region. Additionally, $R_{ct}$ under 45 °C exhibits smoother transitions in the middle SoC region, and particularly at the breaking points of the segments. It could be associated with enhanced Li$^+$ transport properties minimizing the difference of interfacial conditions between the end of a measuring segment and the beginning of the next segment. This explanation agrees with the literature reporting that elevating temperature while conducting a fast-charging is an effective approach to mitigate the aging impact introduced from a fast-charging [60, 61]. In addition, Figure 5(b) shows voltage profiles during 1C charging (without ORP-EIS) under the same temperatures. The profile of 15 °C displays the highest polarization, the profile of 45 °C displays the lowest polarization, and the profile of 25 °C is in the middle. This trend could be partially attributed to variations of kinetics because of different
temperature as discussed in Figure 5(a), and partially attributed to thermodynamics since the electrode potential is temperature dependent [49, 54]. In general, monitoring the cell voltage could be sufficient for elementary battery charge/discharge management, but it is not able to provide further insights of the running batteries, especially when more complex conditions are considered instead of temperature only.

Figure 5: (a) Charge transfer resistance $R_{ct}$ vs. state-of-charge (SoC) and (b) cell voltage vs. SoC at different experimental temperatures. (c) $R_{ct}$ vs. SoC and (d) cell voltage vs. SoC under different charging rates. (e) $R_{ct}$ vs. SoC and (f) cell voltage vs. SoC at different state-of-health conditions. $R_{ct}$ is obtained from operando ORP-EIS and equivalent electric circuit model analysis, and the cell voltage profiles are measured through conventional galvanostatic cycling.
Batteries under different charging currents are investigated and presented in Figure 5 (c) and (d), i.e., the plot of $R_{ct}$ and the voltage profiles respectively. In Figure 5 (c), the plateau in the middle SoC region, which is suitable for fast-charging, spans a slightly smaller SoC window because of the reduced charging capacity under a higher current than the 1C measurement. In Figure 5 (d), the voltage profile of 1.5C shows a higher polarization than 1C profile, which is mostly ascribed to the difference of ohmic drop rather than the difference of kinetics shown in the $R_{ct}$ plot. In both figures, the difference between 1C and 1.5C is trivial and consistent. Owing to the hardware limitation of the present setup, we are not able to acquire quality data at a higher C-rate than 1.5C. However, in theory, operando ORP-EIS is surely capable of handling a higher C-rate test with properly optimized analog frontends. It will be further explored in future work.

Next, the influence of SoH is further investigated as shown in Figure 5 (e) and (f). The aged cell was cycled 310 times under 1C rate, 100% depth of charge/discharge, and room temperature before the operando ORP-EIS measurement. The cell capacity dropped only a few percent during the cycling aging as shown in the capacity retention plot (Figure S4). However, Figure 5 (e) shows that the aged cell demonstrates significant higher $R_{ct}$ over the whole SoC region, and the fast-charging window around the middle SoC is also considerably reduced comparing to the fresh cell. Previous work [42] has demonstrated that $R_{ct}$ could work as a robust indicator for SoH of LIBs since it reflects both the loss of capacity and interfacial conditions, i.e., $A_0$ and $j_0$ in Equation 2 receptively. The voltage profile, Figure 5 (f), presents a consistent behavior that the aged cell exhibits greater polarization owing to the larger $R_{ct}$.

According to Figure 5, the voltage profiles provide limited information of LIBs, and mostly concerning apparent parameters such as the polarization. If a complex condition is considered, it could be difficult to accurately define or predict battery systems based on only voltage profiles. On the contrary, operando ORP-EIS provides an unique access to physics-based parameters of LIBs, particularly $R_{ct}$, which is directly associated with the electrochemical reactions regardless of cycling conditions.

Figure 6 (a) provides an overview of all the $R_{ct}$ plots presented in Figure 5. It is obvious that low temperature or reduced SoH exhibit more significant impact on $R_{ct}$ than other conditions, but the parabolic-like feature is preserved regardless. A robust fast-charging protocol can be proposed solely based on this feature of $R_{ct}$: a high charging current is applied in the middle
SoC with low $R_{ct}$, and cut-off in the high SoC or low SoC region with increased $R_{ct}$. In practice, to more accurately identify start/end points of the fast-charging sequence, the derivative of $R_{ct}$ with respect to SoC is calculated. The derivatives are estimated through a Legendre polynomial fitting method. Their uncertainties are also estimated by taking into account the uncertainty of the EECM analysis as well as the uncertainty of the derivative estimation. In Figure 6 (b) and its zoomed figure (c), the derivatives are negative in the low SoC region, and then reach near zero at around 20% - 30% SoC, which can be characterized as the starting point of the fast-charging sequence. The end point of the fast-charging sequence can be identified where the derivative is significantly higher than zero. In addition, despite of different charging conditions, the start point is located around 20% - 30% SoC. But the end point is considerably varying according to the conditions. Under the harsh conditions, i.e., low temperature or reduced SoH, the end point is located at 70% SoC, in contrast to > 90% SoC for the other favorable conditions.

Another merit of using the derivative, i.e., the rate of change of $R_{ct}$ instead of $R_{ct}$ itself, is that it allows to characterize batteries with different nominal capacities resulting in different magnitude of $R_{ct}$. Nevertheless, as shown in Figure 6 (c), errors presented in the derivative analysis are not negligible, especially the errors around the breaking points of the experimental segments. The magnitude of the errors undermine the robustness of the method. Fortunately, this issue could be mitigated through an improved analog frontend that covers the entire SoC range in a single measurement.

![Figure 6: (a) Charge transfer resistance $R_{ct}$ vs. state-of-charge (SoC). (b) Derivative of $R_{ct}$ with respect to state-of-charge (SoC) as function of SoC. (c) Zoomed figure (b).](image)

**Graphical methods for Operando ORP-EIS**

EECM analysis is one of the major approaches to interpret EIS data. Choosing a physically accurate EECM is an essential but not a straightforward task, because there is more than one model that is mathematically
equivalent to describe the same impedance data. Apart from the ambiguity of EECM, CNLS fitting EIS data to EECM requires additional computation cost and introduces extra uncertainties, which are discouraged in industrial applications. Alternatively, graphical methods [62, 63], providing a fundamental step to understand and evaluate impedance data, are proposed to analyze the operando ORP-EIS data in a simple manner. Several commonly used graphical methods based on phase angles - frequency plot, real impedance - frequency plot and imaginary impedance - frequency plot, could be applied to analyze the ORP-EIS data, particularly the charge-transfer related time constant in the low frequency region (<100 Hz). In the constructed EECM (Figure 3 (a)), this part of the impedance is mostly associated with (CPE2//Rct) part of the circuit. The real (Zr) and imaginary (Zj) impedance of this part of the circuit can be expressed as [7],

\[
Z_r = R_{\text{sum}} + \frac{R_{\text{ct}}(1 + \omega^\alpha R_{\text{ct}}Q \cos(\frac{\alpha\pi}{2}))}{1 + 2\omega^\alpha R_{\text{ct}}Q \cos(\frac{\alpha\pi}{2}) + \omega^{2\alpha} R_{\text{ct}}^2 Q^2} \tag{3}
\]

\[
Z_j = -\frac{\omega^\alpha R_{\text{ct}}^2 Q \sin(\frac{\alpha\pi}{2})}{1 + 2\omega^\alpha R_{\text{ct}}Q \cos(\frac{\alpha\pi}{2}) + \omega^{2\alpha} R_{\text{ct}}^2 Q^2} \tag{4}
\]

where \(R_{\text{sum}}\) is the sum of resistance \(R_s\), \(R_f\) and \(R_p\), \(\omega\) is the angular frequency, \(Q\) and \(\alpha\) are the parameters of CPE2 (Eq. 1). As indicated in Equation 3 and Equation 4, only the imaginary impedance is independent from the ohmic resistance (\(R_s\)) and other resistive contributions (\(R_r\) and \(R_p\)) prior to the time constant of (CPE2//Rct). Therefore, the use of the imaginary impedance - frequency plot is preferred in order to avoid the difficulties of determining other resistive contributions [63].

Moreover, the absolute imaginary impedance \(|Z_j|\) is used for the convenience of analysis and presentation. Figure 7 (a) and (b) show the absolute values of the imaginary impedance \(|Z_j|\) as a function of frequency at different SoCs. The spectra display a characteristic evolution while charging the batteries. To achieve a quantitative analysis, the peak values of \(|Z_j|\) are identified and plotted against the SoC (Figure 7 (c)), exhibiting a comparable parabolic-like behavior as shown in the \(R_{\text{ct}}\) vs. SoC plots, for instance Figure 4. For (CPE2//Rct), the imaginary impedance \(Z_j\) reaches the highest magnitude at the characteristic frequency \(\omega_c\), formulated as [63, 64]

\[
\omega_c = (R_{\text{ct}}Q)^{-\frac{1}{\alpha}} \tag{5}
\]
According to Eq. 4 and Eq. 5, we can derive

\[ |Z_j|_{\text{max}} = \frac{R_{ct} \sin\left(\frac{\alpha \pi}{2}\right)}{2 + 2 \cos\left(\frac{\alpha \pi}{2}\right)} \]  

(6)

in which the direct correlation between \( |Z_j|_{\text{max}} \) and \( R_{ct} \) is revealed. In addition, the CPE exponent \( \alpha \) is another variable in Eq. 6 and \( |Z_j|_{\text{max}} \) monotonically increases with \( \alpha \). At the same time, \( \alpha \) is often interdependent to \( R_{ct} \) \[65, 66\], which has been observed in this work as well. In the EECM fitting results (Figure S2), the \( \alpha \) increases with the increase of \( R_{ct} \), showing a comparable parabolic-like trend as a function of SoC. In this case, the positive correlation between \( R_{ct} \) and \( \alpha \) assures that \( |Z_j|_{\text{max}} \propto R_{ct} \).

It is worth noting that the physical interpretation of CPE in battery systems is ambiguous. In fact, the origin of the CPE behavior in impedance measurements remains matter of controversy \[66\], and it should be carefully studied case by case. To the best of our knowledge, there are limited studies \[67\], focusing on the physical interpretation of the CPE behavior in LIB system, presumably due to the complex nature of battery electrodes including a porous structure and different functional components. In this work, we have shown the characteristic interdependence between the fitted \( R_{ct} \) and the CPE parameters (\( Q \) and \( \alpha \)) in Figure S2. The SoC-induced changes of these parameters are mainly associated with the changes of the active material (NMC622) with very little contributions from the porous structures or non-active components (binder and conductive agents etc.). It is worth a in-depth investigation on this phenomena in future, which might be a unique path to understand the CPE behavior in battery systems.

Besides the physical ambiguity of the CPE, another potential limitation of this approach is that the diffusion impedance in the low frequency region could be convolved with the charge-transfer time constant resulting in the difficulty of identifying \( |Z_j|_{\text{max}} \). However, based on the results from this work and literature, most battery systems show well-separated time constants between the charge-transfer impedance and the diffusion impedance.

Through the same treatment, all \( |Z_j|_{\text{max}} \) under different charging conditions are extracted and plotted against SoC, and shown in Figure 8(a). All the plots with the different conditions exhibit an identical behavior as the plots of \( R_{ct} \) (Figure 6 (a)), suggesting that the proposed SoC monitoring method by using \( R_{ct} \) is also viable through monitoring \( |Z_j|_{\text{max}} \). Additionally, derivatives of \( |Z_j|_{\text{max}} \) with respect to SoC are also presented in Figure 8 (b).
Figure 7: Absolute imaginary impedance vs. frequency: (a) 10 - 60% SoC, (b) 60 - 110% SoC; the maxima of the imaginary impedance for each SoC are marked. (c) peak amplitude vs. SoC. Experimental conditions: DC charge current is 5 mA (∼1C); amplitude of AC signal is 1 mA (RMS); frequency range is 0.05 Hz - 5 kHz; temperature is 25 °C.

and the zoomed figure (c), showing identical behavior as the derivatives of $R_{ct}$, but with lower error levels. Here the errors are estimated by taking into account the uncertainties of the imaginary impedance, and uncertainties of the derivative estimations. Owing to the lower errors in the $|Z_j|_{max}$ plots, the transient behavior between the end of a measuring segment and the beginning of the next segment is more visible compared to the $R_{ct}$ plots (Figure 6). In Figure 8 (c), the transient feature is much stronger under unfavorable cycling conditions, i.e., the low temperature or the low SoH. This could be a reflection of the changes of Li$^+$ transport properties under different conditions. We plan to further investigate this transient phenomena in our future work.

Figure 8: a) Absolute peak values $|Z_j|_{max}$ vs. state-of-charge (SoC). (b) Derivative of $|Z_j|_{max}$ with respect to state-of-charge (SoC) as function of SoC. (c) Zoomed figure (b).

In summary, the graphical analysis method, based on the imaginary impedance, is able to achieve identical or even better results than EECMS method for the purpose of SoC monitoring. The avoidance of parametric regression significantly reduces the complexity of the analysis and also benefits from the error estimation. Additionally, it will be more integrable for machine learning approaches in future expansions of this technique.
4. Conclusion

In this study, we have firstly provided a brief overview on the existing dynamic EIS techniques for LIB studies. Comparing to the literature, operando ORP-EIS has shown advantages on the versatility, robust error analysis and wide measurable frequency range, particularly the capability of low frequencies accessibility. Next, we carried out galvanostatic operando ORP-EIS experiments for investigating NMC622/graphite batteries under practical ($\geq 1$C) charging conditions. Time-varying impedance spectra and the data uncertainties were derived under the theoretical framework of ORP-EIS. Through the EECM analysis, the charge-transfer resistance $R_{ct}$ shows a characteristic parabolic-like behavior as a function of SoC, i.e., decreases first in the low SoC region, reaches a low-value plateau in the middle SoC region, and rapidly increases in the high SoC region. Moreover, variations of the characteristic feature under different charging conditions were investigated, in which the SoC region with the low $R_{ct}$ is significantly reduced under unfavorable conditions, such as the low temperature or the reduced SoH. As such, directly monitoring the changes of $R_{ct}$ through operando ORP-EIS could be a robust approach to identify SoC of batteries during fast-charging. Lastly, the graphical analysis that is based on the imaginary impedance, has been discussed and proved to be a good alternative method to track the changes of charge-transfer impedance in operando ORP-EIS measurements. Comparing to the EECM analysis, the graphical analysis is free of parametric regression, which makes it easier to be implemented in practical applications.

To further improve the operando ORP-EIS technique in battery applications, for the hardware perspective, we will optimize the analog frontend to achieve a larger measurable potential window without compromising too much its sensitivity; for the software perspective, we will develop an algorithm, which is able to calculate the time-varying impedance instantaneously during the measurements with a reasonable computation cost.

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