

Article

State-of-Charge-Dependent Impedance Modeling of a Commercial LiFePO₄ Cell: EIS Measurements and Parameter Identification

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Abstract

This study presents the results of electrochemical impedance spectroscopy (EIS) conducted on a commercial 38120S cylindrical LiFePO₄ cell with a nominal capacity of 10 Ah. Measurements were performed at various states of charge, and the parameters of an equivalent circuit model were subsequently identified. The model consists of an inductance, ohmic resistance, two resistor–constant phase element (R-CPE) pairs, and a CPE representing diffusion effects. To ensure high measurement repeatability and minimize data dispersion, a surrogate model was used for equipment calibration, and a custom fixture was designed to maintain consistent cell positioning. Each measurement session was preceded by an open-circuit voltage reading and a relaxation period of approximately 24 h to ensure steady-state conditions. Furthermore, impedance spectra were analyzed over a range of frequencies by simulating model responses using various CPE constants. These simulations were visualized in LTspice and discussed, providing practical insights into the initialization of equivalent circuit model identification algorithms.

Keywords: LFP; LiFePO₄; EIS; SOC; CPE; dynamic model; ECM; LTspice

1. Introduction

In the face of increasing energy demand, the need to reduce greenhouse gas emissions, and the reduction in coal extraction, battery energy storage systems (BESS) play a crucial role in integrating renewable energy sources into the power grid [1–3]. BESS are typically made from a single type of electrical cell or supercapacitors [4,5]. Among the various cell production technologies, lithium iron phosphate (LiFePO₄) cells are gaining popularity due to their unique properties [6].

First and foremost, LiFePO₄ cells are significantly safer than other lithium cells, with higher thermal stability, greatly reducing the risk of ignition [7,8]. LiFePO₄ cells can withstand up to 5000 charge and discharge cycles, which, with daily cycles, equates to about 13 years of operation [3]. The output power of the energy storage system is also high due to the ability to charge and discharge the cell with a large current of around 3C, which, with a 200 Ah cell, results in a current of 600 A. This allows for up to 2 kW of power from a single cell [9].

Due to the flat discharge characteristic of LiFePO₄ cells, it is not easy to accurately assess the state of charge (SOC) based solely on the measurement of the open-circuit voltage (OCV) in steady-state conditions [10,11]. In many practical cases, achieving a true steady state is challenging, as the battery energy storage system is often in continuous operation.



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Even when the BESS operates in a quasi-steady-state condition—maintaining a constant SOC level—the individual cells are still undergoing relaxation processes [12,13]. To enable SOC and state of health (SOH) estimation, as well as to predict output voltage behavior under dynamic load variations, dedicated cell models have been developed [4,14–18].

Dynamic models of LiFePO_4 cells were characterized by the ability to predict the behavior of the cell under varying operating conditions, taking into account parameters such as voltage, temperature, current, SOC, and SOH [19,20]. These models aim to accurately simulate the cell's response to dynamic load changes, which is critical for applications such as battery management systems (BMS) in electric vehicles or energy storage systems [18,21].

Currently, several types of models were used [15,17,22,23], with the two main categories being equivalent circuit models (ECM)—which represent the cell's behavior using electrical components such as resistors, inductors, capacitors, and voltage sources—and physical and electrochemical models—which describe the actual mechanisms occurring in the cells, such as ion transport, double-layer properties, and the formation of the solid electrolyte interface (SEI) layer [14,24]. The SEI layer forms on the surface of the anode during the first charge cycles, as a result of a reaction between the electrolyte and the anode's active material. It consists of the products of these reactions, creating a thin, insulating layer that has both electrical and chemical properties [19].

The equivalent circuit model can be identified using the EIS method. This technique involves measuring the system's response to applied voltage or current signals over a range of frequencies. By varying the frequency, it is possible to investigate how the system responds to dynamic load conditions. The measured response enables the calculation of impedance as a function of frequency, which can be decomposed into resistive and reactive components (inductive and capacitive). This, in turn, facilitates the identification of the cell's electrical ECM and allows for the analysis of changes in the Nyquist plot in relation to specific model parameters.

In recent years, the EIS method has attracted significant interest due to its ability to directly reflect the internal electrochemical properties of cells, and even entire battery packs, in a non-invasive manner [14,25–27]. EIS can represent internal electrochemical reaction processes in lithium-ion batteries, such as polarization and diffusion processes [14,28–30]. Because of its non-destructive nature and detailed insight into electrochemical processes, there are many studies on battery state estimation, aging pattern analysis, and the monitoring of internal faults using EIS [31–33].

The main challenge was the selection of an appropriate ECM model that would be universal across the entire SOC range while simultaneously enabling the identification of parameters associated with SOC. It was essential to distinguish parameters that are strongly independent of SOC from those that are weakly dependent on SOC, as this separation allows subsequent studies to focus on the variability of these parameters with respect to temperature or pressure. After numerous attempts at model selection, a model incorporating two R–CPE pairs were ultimately adopted, as it best satisfied the stated objectives.

1.1. ECM-Type Dynamic Model

An equivalent circuit model is proposed, consisting of an inductance (L), ohmic resistance (R_0), two R–CPE pairs, and a CPE_D representing the diffusion process. The CPE_D was used instead of the traditional Warburg element to avoid fixing the fractional exponent. The R–CPE pairs are responsible for accurately modeling the high- and mid-frequency responses and can be associated with charge transport and double-layer effects at the electrode–electrolyte interfaces. Although the model is somewhat more complex than those commonly used, it enables highly accurate representation of the real behavior of the cell.

The model (Figure 1) contains the minimum number of elements necessary to accurately reflect the dynamics of a LiFePO_4 cell in various SOC. The effects of the double-layer and charge transport related to the electrodes are represented by a dual R-CPE pair. In cases where there are no significant differences in the double-layer capacitances of the electrodes, two R-CPE pairs connected in a series of overlays in the EIS spectrum, so, in that case, a singular R-CPE pair can represent both capacitances. It is always advisable to use a CPE instead of a pure capacitor C , since a CPE can replicate a capacitor when α equals 1.

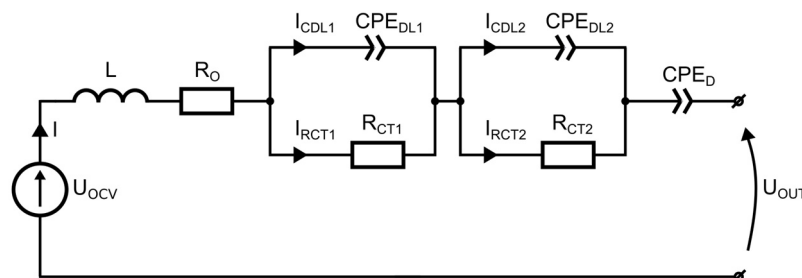


Figure 1. Dynamic model (ECM).

The impedance of CPE is shown below (Equation (1)):

$$Z_{CPE}(s) = \frac{1}{CPE \cdot s^\alpha} \quad (1)$$

The CPE_D element reflects the phenomenon of diffusion within the cell. It dominates at the lowest frequency range, usually below 10 Hz (depending on the capacity of the cell). On a Nyquist plot, it appears as a straight line. It often states that the diffusion element is well represented by Warburg resistance [34,35], but after performing numerous EIS measurements, it is clear that for LiFePO_4 -type cells, the CPE exponent α is certainly not 0.5, but varies between 0.3 and 0.8 depending on the specific cell and the SOC level.

The application of a CPE_D in the diffusive branch of the ECM model arises from the fact that the actual mass transport processes in LiFePO_4 electrodes deviate from the assumptions of ideal Warburg diffusion. The heterogeneous electrode structure, the distribution of active particle sizes, and the two-phase lithium intercalation mechanism lead to the dispersion of diffusion time constants [11,36]. The CPE_D enables these effects to be accounted for through the phase exponent, which describes the degree of non-ideality of the diffusion process [18]. The improved fitting of impedance spectra in the low-frequency range confirms the validity of this approach [36–38].

The two parallel R_{CT} and CPE_{DL} components correspond to the high- and mid-frequency ranges in EIS analysis. When they appear independently, they are represented as characteristic semi-ellipses on the Nyquist plot, but they are often at least partially overlapped.

The R_O element is simply the ohmic resistance related to current flow through the internal conductors of the cell as well as the external terminals. R_O manifests as a rightward shift in the entire Nyquist plot by the value of R_O . The L component is related to inductance, which begins to dominate at the high end of the frequency spectrum during EIS—typically at frequencies of about 1 kHz. The influence of L may cause the cell's behavior to become inductive at these high frequencies.

The voltage U_{OCV} represents the open-circuit voltage of the cell after relaxation has occurred. Naturally, U_{OCV} is not constant and varies with the cell's state of charge. There are various methods of parameterizing U_{OCV} , which have been described in the

literature [21,39–41]. The output of the model is the terminal voltage U_{OUT} , which changes due to the charging or discharging current “ I ” applied to the cell (Equation (2)).

$$U_{OUT} = U_{OCV} - U_L - U_{RO} - U_{DL1} - U_{DL2} - U_D \quad (2)$$

The output voltage at the cell terminals is equal to the open-circuit voltage after the relaxation process, reduced by the voltage drops across the individual elements of the model.

The Laplace transform of U_{OUT} was calculated from Ohm’s law (Equation (3)).

$$U_{OUT}(s) = U_{OCV} - \left(sL + R_0 + \frac{R_{CT1}}{1 + R_{CT1} \cdot CPE_{DL1}s^{\alpha_1}} + \frac{R_{CT2}}{1 + R_{CT2} \cdot CPE_{DL2}s^{\alpha_2}} + \frac{1}{CPE_Ds^{\alpha_D}} \right) \cdot I(s) \quad (3)$$

The voltage source U_{OCV} can be identified using the GITT method [42–44]. The remaining parameters— R , L and CPE elements—were identified using electrochemical impedance spectroscopy. All of these parameters are influenced by SOC in different ways.

1.2. Simulation and Analysis of the Dual R-CPE Model in LTspice

The simulations were carried out using LTspice, a program that enables the simulation of electronic circuits and, through the use of controlled sources, the analysis of elements described by the Laplace transform.

The above model (Figure 2) accurately represents the ECM shown in Figure 1. The controlled sources E1, E2 and E3 implement the Laplace equations containing CPE elements. In this case, E1 and E2 represent the parallel combination of R_{CT1} and CPE_{DL1} as well as the parallel combination of R_{CT2} and CPE_{DL2} , while E3 corresponds to CPE_D .

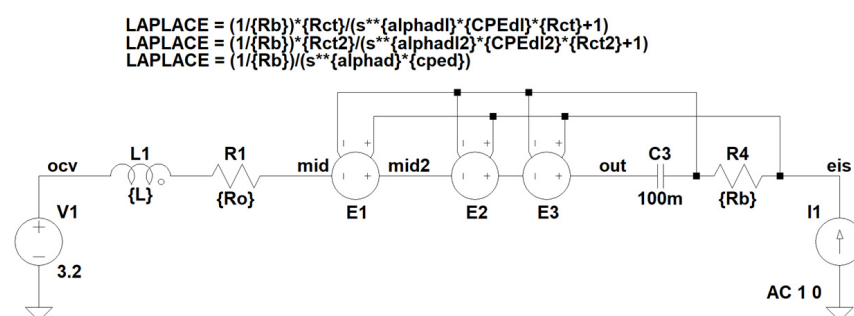


Figure 2. The schematic of the model simulated in LTspice.

It is assumed that the individual parts of the model correspond to distinct effects that can be distinguished in the Nyquist plot. However, these effects will overlap if the constants of the CPEs have similar values. The constants that differ significantly, for example by one or two orders of magnitude, will cause the effects originating from the individual elements to be clearly separated.

Moreover, inductance can affect the high-frequency region by lowering the overall reactance. In some cases, inductance can introduce uncertainty when reading R_O directly from the Nyquist plot. When the reactance of CPE_{DL1} cancels out the reactance of the inductance L , the resulting impedance is purely resistive—not only the ohmic resistance, but also the resistive component of CPE_{DL1} , in parallel with R_{CT1} . This can lead to an overestimation of R_O .

A significant inductance value will strongly influence the characteristics related to the double-layer and charge transport.

Resistances, on the other hand, determine the size and shift in the characteristic. Resistances connected in parallel with CPEs correspond to the size of the semi-ellipses.

When α equals 1, which corresponds to a regular capacitance, R_{CT} is equal to the diameter of the semicircle; when α is less than 1, R_{CT} represents the chord of an ellipse.

The CPE_D representing the diffusion phenomenon forms a straight line—essentially a half-line starting at the real axis at the point $R_0 + R_{CT1} + R_{CT2}$, inclined at an angle $\gamma_D = \alpha_D \cdot 90^\circ$ to the real axis.

Figure 3 shows six Nyquist plots corresponding to the dual R-CPE model presented in Figure 1. The model parameters are mostly identical, with R_{CT1} being equal to R_{CT2} . The only differences are found in the values of CPE_{DL2} and CPE_D , which were varied to illustrate how different CPE constants affect the Nyquist plot. The plots that exhibit two distinct peaks correspond to cases with a large difference between the CPE constants.

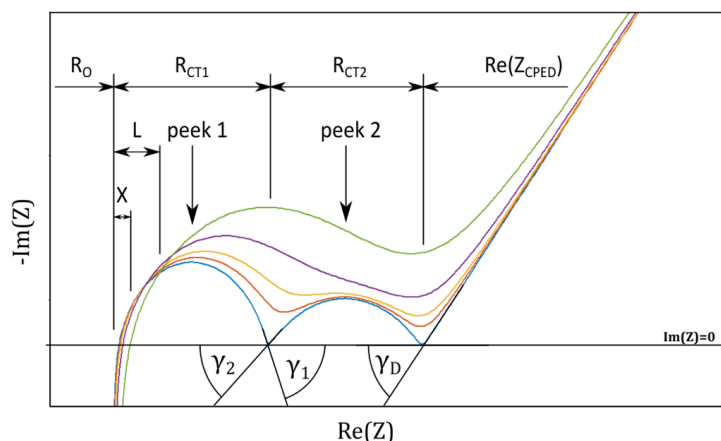


Figure 3. Nyquist plot based on the presented model (Figures 1 and 2). R_0 , R_{CT1} , R_{CT2} were constant, but the constants of CPEs varied.

The peak frequency can be calculated from Equation (4):

$$f_{peak} = \frac{1}{2\pi} \cdot \left(\frac{1}{R_{CT} \cdot CPE_{DL}} \right)^{1/\alpha} \quad (4)$$

As the shape of the plots becomes smoother, the spacing between the constants decreases. In Figure 3, the letter “L” indicates the influence of inductance on the shape of the R-CPE model, shifting the Nyquist plot to the right. Inductance has a non-negligible impact on the reading of R_0 from the plot. Therefore, the difference between R_0 and the additional part of $Re(Z)$ that is not attributed to R_0 is marked with the letter “X”. This additional real part arises directly from the CPE, which does not behave as an ideal capacitor. While the inductance is compensated by the capacitive response, the CPE still contributes a residual real component, even after reactance compensation.

2. Materials and Methods

Parameter identification of the model was conducted through laboratory experiments using the electrochemical impedance spectroscopy method. A dedicated test setup was prepared for the experiments: an electronic load (ITECH IT8511, Itech Electronic Co., Ltd., New Taipei City, Taiwan), a frequency response analyzer (PSM3750, Newtons4th Ltd., Leicester, UK) working together with a high-precision power amplifier (AE Techron 7224, Elkhart, IN, USA), and a measurement shunt (N4L BATT470m-200, Newtons4th Ltd., Leicester, UK) designed for voltage excitation spectroscopy in the frequency range 0.01 Hz–1 MHz.

The EIS technique was employed to determine the complex impedance of the $LiFePO_4$ cell and its variation with frequency at different SOC. Data analysis and model parameter identification were conducted using a MATLAB R2016a script developed specifically for

this study, in addition to widely used EIS analysis software, including FitMyEIS and LinKK (version 1.3). The FitMyEIS was used to fit model frequency response to measured data. The LinKK program was used for checking the Kramers–Kronig relations, for which the modulus weighting method was used and a sequential type of fitting. The weights are equal for the imaginary and real parts of each point of the impedance. They are represented as Equation (5):

$$w_j = \frac{1}{Z_{j,\Re}^2 + Z_{j,\Im}^2}, \quad (5)$$

This makes the weights proportional to the inverse of the modulus of the impedance. For each fitted model parameter, a fitting quality was assessed as the Weighted Residual Sum of Squares (WRSS) (Equation (6)):

$$WRSS = \sum \frac{|Z_{j,exp}| - |Z_{j,fit}|}{w_j}, \quad (6)$$

Parameter identifiability and robustness were ensured by constraining the range of parameter variability during the identification process. The ranges were selected to be as wide as possible so as not to restrict the algorithm's ability to search for the correct value of the identified component, while also ensuring that none of the identified parameters reached the boundaries of the admissible range.

The experimental procedure included setup calibration using surrogate aluminum model EN AW-2017, EIS measurements at constant temperature, and subsequent ECM identification. The surrogate model resistance was measured using the four-wire method, applying a 100 A DC current for a very short duration and measuring the resulting voltage drop. The measured resistance was below $R = 7 \mu\Omega$, consistent with the model's geometry and the material's known resistivity.

System calibration was performed using a surrogate cell through a short-circuit procedure (Figure 4). This calibration was conducted at the same 60 frequencies used for the actual cell measurements, ensuring frequency-consistent correction of the measurement system. A sinusoidal excitation signal with a logarithmic frequency sweep was applied, maintaining identical frequency points across all measurement series. The amplitude and phase of both voltage and current were recorded directly, from which the real and imaginary components of the cell impedance—resistance and reactance—were derived.



Figure 4. Surrogate model. Aluminum EN AW-2017 cylinder. $R = 7 \mu\Omega$.

EIS measurements were conducted at various states of charge. The SOC was determined by coulomb-counting during cell discharge at a constant current rate of 0.1C. The SOC 0% was equal to 2.0 V OCV.

The tested cell was a LiFePO_4 HW 38120S with a capacity of 10 Ah and a nominal voltage of 3.2 V (Table 1, Figure 5).

Table 1. Parameters of the tested cell.

Parameter	Value
Type	LiFePO ₄ cylindrical
Nominal capacity	10 Ah
Internal resistance nom.	≤6 mΩ
Nominal voltage	3.2 V
Bottom cut-off voltage	2.0 V
Up cut-off voltage	3.65 V
Dimensions	Φ38 × 146

**Figure 5.** Tested LiFePO₄ cell HW 38120S.

The measurement frequency range spanned from 0.1 Hz to 1 kHz. The current forcing voltage changes at the cell terminals was approximately 1.5 A at the peak, while the measured voltage varied from 600 μ V (0.1 Hz) to 7.5 mV (1.5 Hz). The measurement range was divided into three subranges: 0.1–4 Hz (24 points), 4–64 Hz (18 points), and 64 Hz–1 kHz (18 points). This division was necessary to adjust the gain of the power amplifier, which was carried out manually. The temperature was measured using a contact thermometer placed on the external surface of the cell. Throughout all measurements, the ambient temperature was controlled and kept at 23 °C $\pm$ 0.8 °C.

Within each range, the generator voltage was automatically adjusted according to the load current to ensure that the current through the shunt did not exceed its maximum rated value of 1.5 A_{rms} while maintaining a sufficiently high voltage across the shunt. The cell itself was capable of higher operating currents, permitting discharge currents up to 30 A and charge currents up to 20 A.

3. Results

The experimental results comprise 12 Nyquist plots corresponding to evenly spaced states of charge (SOC) between 0% and 100%. Each plot consists of 60 measurement points.

The data are presented in the form of Nyquist plots.

Figure 6 presents twelve Nyquist plots. The data points represent the experimental measurements, while the continuous lines correspond to the fitted equivalent circuit model. The differences between the experimental data and the fitted curves are minimal, indicating that the equivalent electrical circuit was appropriately selected for the investigated cell and that a high quality of fit was achieved.

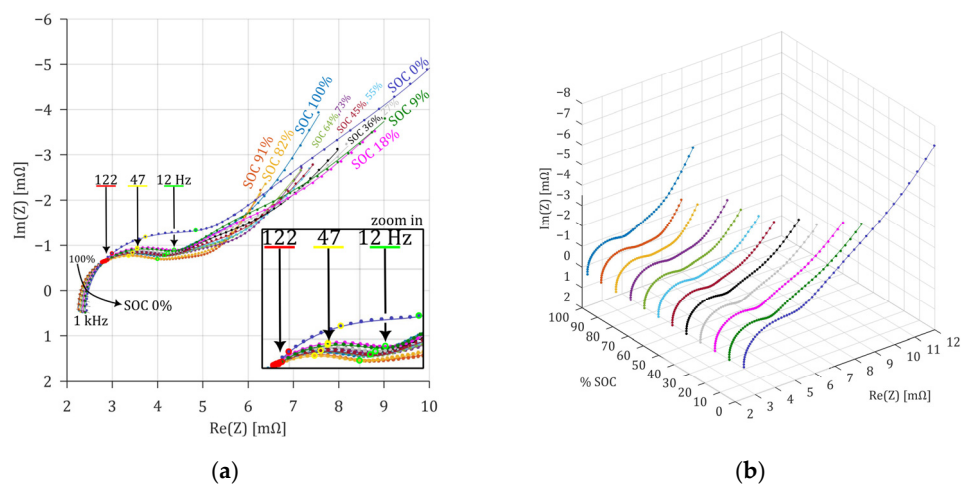


Figure 6. Nyquist plot based on measurement data for the frequency range 0.1 Hz–1 kHz: (a) shows characteristic points frequency; (b) shows the fitting quality for each dataset.

The most significant changes between different SOC levels occurred at low frequencies below 12 Hz. In this range, the frequency responses of the double-layer, represented in the model by the elements CPE_{DL2} and R_{CT2} , overlapped with the diffusion-related processes, modeled as CPE_D . Initially, at high SOC values near full charge, the magnitude of CPE_D was approximately five times greater than that of CPE_{DL2} , which was sufficient for the second double-layer branch of the model to be clearly distinguishable and identifiable. As the cell was discharged, this second branch was gradually absorbed into the diffusion branch. At full discharge, the high-frequency branch showed increased resistance, while the resistance of the second branch also increased significantly, ultimately leading to the diminishing and blurring of the second branch effect ($R_{CT2} \parallel CPE_{DL2}$).

In the Bode plot (Figure 7), the data is shown by marked points and fitting by lines that represent the changes over different frequencies. The impedance curves for most SOC levels are closely clustered, indicating similar electrochemical behavior across this range. A noticeable deviation is observed for the 0% SOC curve, which shifts toward higher impedance values. The 100% SOC curve lies between the others, with slight undulations suggesting minor measurement variability or dynamic changes at full charge.

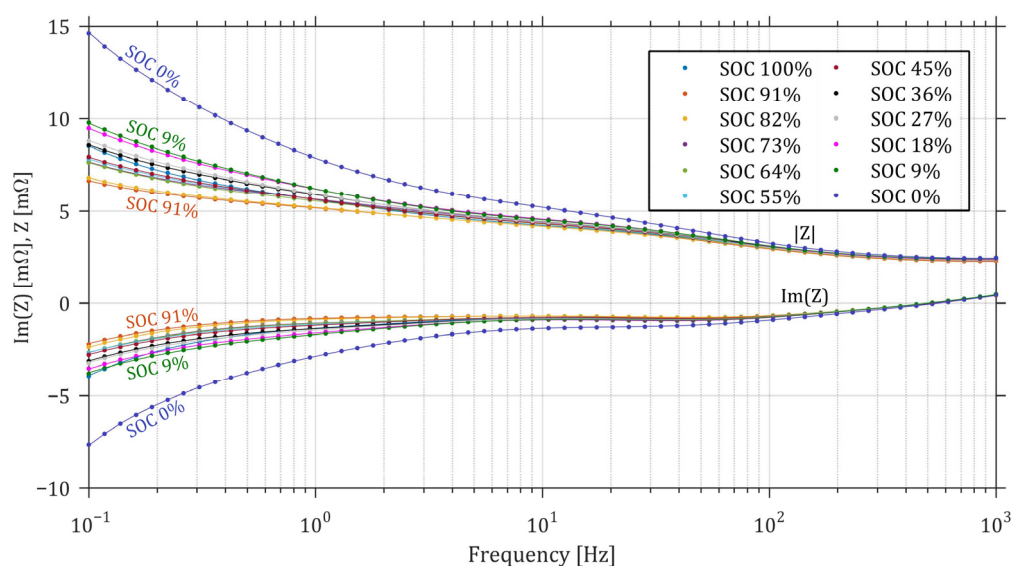


Figure 7. Bode plot based on experimental data in the frequency range 0.1 Hz to 1 kHz. Measurement points are indicated by markers, and the fitted model is represented by lines.

Changes in the individual model parameters as a function of SOC were observed, as confirmed by the Table 2. For certain parameters, such as R_O and α_1 , deviations from the median remained below 4% (Figure 8a), indicating a very minor impact of SOC on these parameters. For inductance L , deviations from the median were less than 7%, although a slight trend was noted: as SOC increased, inductance diminished. Changes in CPE_{DL1} relative to the median reached up to 14%; however, it should be noted that the largest variations occurred at SOC <10%, with values for other SOC levels not exceeding 7%. The exponents of the remaining CPEs, namely α_2 and α_D , varied by no more than 18% and 25%, respectively (Figure 8d). For α_D , the trend was increasing as SOC grew. The resistance R_{CT1} remained relatively stable at approximately 1.9 m Ω , with deviations not exceeding 7%, except for two cases: at SOC 82%, the deviation reached 12.4%, possibly due to model underfitting (higher WRSS factor; see Table 2), and for a discharged cell, this value increased by 34% compared to the median. The largest changes were observed for CPE_{DL2} , R_{CT2} , and CPE_D ; among these, CPE_D exhibited a distinctly increasing tendency with rising SOC, while CPE_{DL2} generally decreased (Figure 8c). R_{CT2} showed the greatest change among all parameters at complete discharge, with resistance increasing 3.5 $\times$ bigger compared to the median. For other SOC levels, R_{CT2} fluctuations did not exceed 26% peak-to-peak.

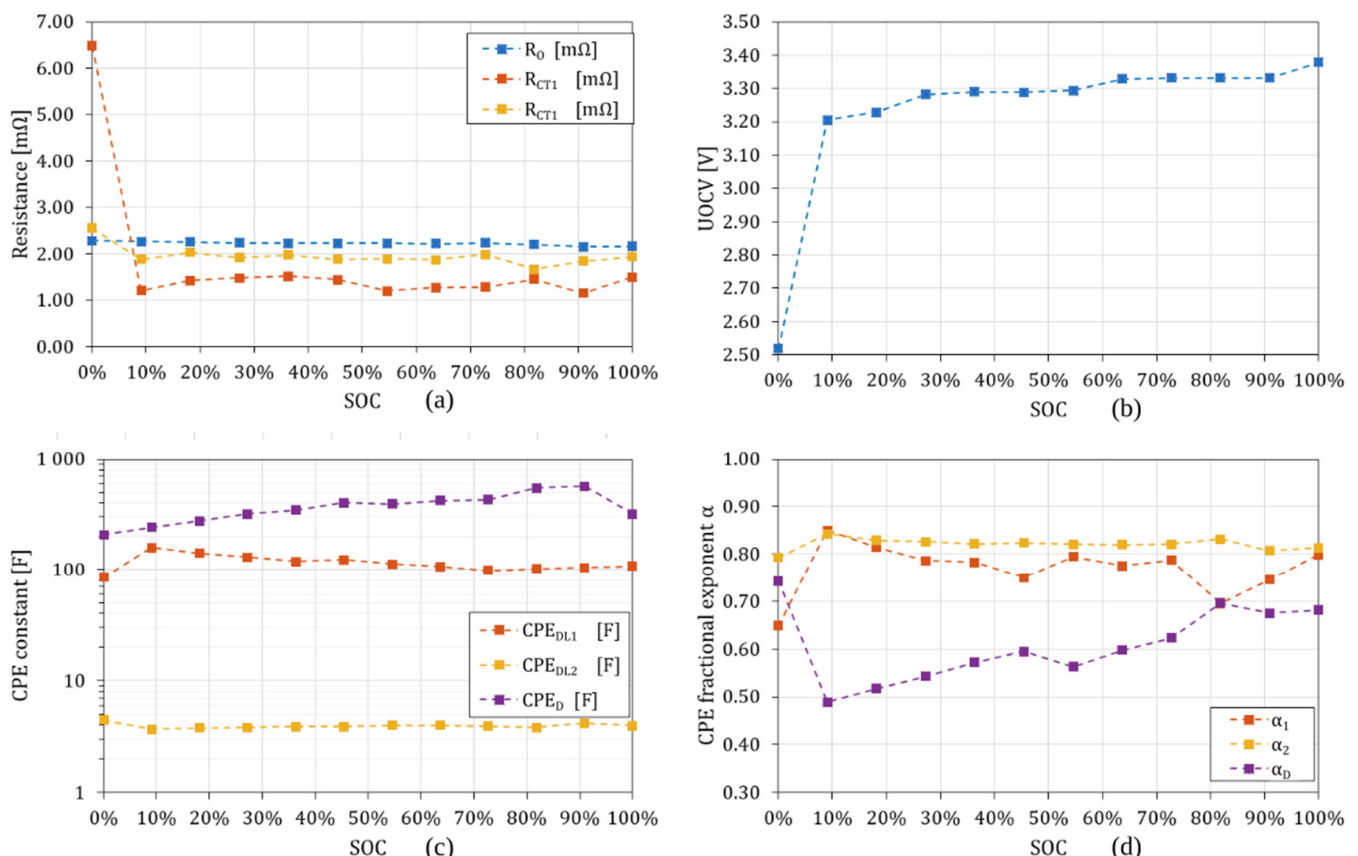


Figure 8. Changes in ECM parameters over the SOC level: (a) ohmic resistance and current transfer resistances changes over the SOC; (b) open-circuit voltage changes; (c) constant-phase element value changes; (d) changes in the fractional exponents of the CPEs over the SOC.

For 45% SOC, the WRSS value was slightly higher compared to the remaining results. This increase originated from a somewhat poorer model fitting at this operating point, which in turn was related to instrumentation- and methodology-related factors. Specifically, during the transition of the frequency range from 0.1–4 Hz to 4–64 Hz—required due to an adjustment of the power amplifier gain—a minor shift in the measured data occurred, thereby increasing the uncertainty of the obtained results. Such a change in the frequency

range requires a settling period to allow for transient, non-stationary processes associated with the interruption of the EIS measurement and the change in signal amplification to decay. Although the impact on the measured data was small, it was noticeable and resulted in an increased WRSS value.

Table 2. Identified model parameters.

%SOC	L [nH]	R ₀ [mΩ]	CPE _{DL1} [F]	α ₁	R _{CT1} [mΩ]	CPE _{DL2} [F]	α ₂	R _{CT2} [mΩ]	CPE _D [F]	α _D	WRSS ¹
0	104.4	2.29	4.44	0.79	2.55	85.1	0.65	6.48	207.1	0.74	8.50×10^{-4}
9	104.9	2.27	3.70	0.84	1.88	159.3	0.85	1.20	243.3	0.49	9.61×10^{-4}
18	102.9	2.25	3.78	0.83	2.03	141.7	0.81	1.43	276.5	0.52	6.54×10^{-4}
27	100.6	2.23	3.84	0.83	1.92	130.2	0.79	1.48	319.5	0.54	6.64×10^{-4}
36	102.0	2.23	3.87	0.82	1.97	118.8	0.78	1.52	346.2	0.57	6.01×10^{-4}
45	100.5	2.23	3.88	0.82	1.88	123.5	0.75	1.44	403.2	0.59	1.34×10^{-3}
55	102.7	2.22	4.01	0.82	1.89	113.1	0.79	1.20	394.1	0.56	6.70×10^{-4}
64	101.7	2.22	3.98	0.82	1.87	106.7	0.77	1.28	421.6	0.60	6.11×10^{-4}
73	103.1	2.23	3.92	0.82	1.99	98.3	0.79	1.28	432.4	0.62	7.03×10^{-4}
82	100.6	2.20	3.82	0.83	1.67	102.0	0.69	1.45	549.7	0.70	7.43×10^{-4}
91	95.1	2.15	4.17	0.81	1.85	105.0	0.75	1.15	570.3	0.67	4.77×10^{-4}
100	97.8	2.16	3.97	0.81	1.93	108.1	0.80	1.49	320.8	0.68	6.93×10^{-4}

¹ WRSS—Weighted Residual Sum of Squares, calculated using FitMyEIS (Equation (6)).

Figure 8 presents the majority of the model parameters as a function of the state of charge. Some parameters remained invariant with respect to SOC or exhibited no clear trend. However, several parameters showed systematic changes across the SOC range from 10% to 80%, maintaining consistent tendencies. The most pronounced variations were observed at the fully discharged state of the cell. The open-circuit voltage increased with SOC, following a characteristic and well-documented profile typical for LiFePO₄ cells (Figure 8b).

4. Discussion

The selection of the ECM model aimed to achieve the most accurate possible representation of the Nyquist impedance characteristics. In some cases, a model with a single R–CPE pair proves sufficient for a given state of charge. However, in order to correctly represent the cell behavior over the entire SOC range, it is necessary to include a second R–CPE pair. Many authors employ simpler models [4,45]. Other studies indicate that models containing capacitors in RC pairs are sufficient for accurate cell modeling [46]. Still others use a Warburg resistance connected in series with a capacitor and placed in parallel with a resistor in the second pair [47,48]. Nevertheless, none of these models accurately reproduces the behavior of the investigated cell across all SOC values.

Models that include capacitors instead of CPE elements tend to produce semicircular shapes after parameter identification, since an RC element corresponds to a semicircle in the Nyquist plot, whereas an R–CPE element forms a segment of an ellipse, which better reflects real electrochemical behavior. Although the Warburg impedance is a natural choice for representing diffusion phenomena, it has a fixed fractional order of $\alpha = 0.5$. This may explain why some authors incorporate the Warburg impedance into an RC pair (the Randles model), allowing the linear tail of the Nyquist characteristic to be distorted and thus creating an approximation that is slightly closer to reality. This topic is discussed in detail in [35].

For the investigated cell, the low-frequency tail of the impedance characteristic is nearly perfectly linear. However, at the transition between the diffusion-dominated region

and the mid-frequency range, a double-layer effect becomes evident and shows a strong dependence on SOC, which necessitates the inclusion of this phenomenon in the ECM.

5. Conclusions

Measuring the impedance of lithium cells, in this case LiFePO₄ cells, is difficult due to a number of limitations and the many factors affecting the measurement setup. A significant challenge is measuring impedance where the resistive part is on the order of single milliohms, and the reactive part is in the hundreds of microohms, as was the case for the tested 10 Ah cell. When testing a 100 Ah cell, one can expect impedance values to be an order of magnitude lower, which is directly supported by the cell manufacturer's documentation, where the internal resistance is <6 mΩ for 10 Ah cells versus <0.6 mΩ for 100 Ah cells. For larger cells or parallel battery packs, it may be necessary to supply a very high current to measure the voltage, whose value can be at least five (or possibly six) orders of magnitude lower than the current amplitude. This requires very precise measurement, with a significant contribution from the measurement equipment used. Increasing the current can lead to a rise in cell temperature, causing measurement errors. Maintaining a constant current amplitude requires fine-tuning the generator settings, since the sinusoidal signal has a much higher output impedance than the measured object, and the variable impedance of the object as a function of measurement frequency forces the amplitude.

Despite the numerous challenges associated with EIS measurements and model identification, it is worth pursuing highly accurate EIS measurements in order to observe and correctly interpret changes in the characteristics arising from factors that influence the cell properties.

The results indicate the variability of the exponent α_D in the CPE_D diffusion element. For the investigated cell, this value ranged from 0.49 to 0.74, reaching extreme values at a very low SOC, specifically 9% and 0%. For SOC values equal to or greater than 9%, α_D generally shows an increasing trend with SOC. This behavior stems from the non-ideal nature of the mass transport processes in LiFePO₄ electrodes, which deviate from the theoretical Warburg diffusion model due to the heterogeneous electrode structure, particle size distribution of the active material, and the two-phase lithium intercalation mechanism, leading to the significant dispersion of diffusion time constants. Moreover, intercalation processes and the associated dynamics of the SEI layer at different SOC levels induce mechanical stresses that alter effective diffusion pathways and the availability of an active surface area. The application of the CPE_D element with a variable exponent α_D thus allows for a significantly more accurate fitting of the model to the real impedance spectrum of the LFP cell, accounting for these physicochemical non-idealities.

EIS allows for an understanding of the internal properties of cells and the factors affecting them through repeated measurements at given parameters, such as temperature, humidity, applied pressure, relaxation time, state of charge, and state of health.

EIS enables identification the cell and allows for it to be represented as a model, which can be used, for example, to build an energy storage simulator or to further model the processes of energy storage and release—this is crucial in research work on the development or diagnostics of energy storage systems.

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Abbreviations

The following abbreviations are used in this manuscript:

BESS	Battery Energy Storage Systems
CPE	Constant Phase Element
EIS	Electroimpedance Spectroscopy
ECM	Equivalent Circuit Models
LFP	Lithium Ferrophosphate
OCV	Open-Circuit Voltage
SEI	Solid Electrolyte Interface
SOC	State of Charge
SOH	State of Health
WRSS	Weighted Residual Sum of Squares

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