State of Charge Effects on the Parameters of Electrochemical Impedance Spectroscopy Equivalent Circuit Model for Lithium Ion Batteries

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Abstract. It is essential to know the behavior of the battery at all relevant internal and external conditions when the battery cell is in the new and the aging state. Electrochemical impedance spectroscopy (EIS) is a viable approach that can be used in lithium ion batteries (LIBs) to investigate the electrochemical behavior. In this paper, in order to investigate the state of charge effects on the LIBs, three types of commercial LIB cells were used, and the EIS measurements were performed under 100%, 80%, 50%, 20% and 0% SOC, respectively. An equivalent circuit model (ECM) including two constant phase angle elements in parallel with resistor elements is established to study the impedance characteristics for LIBs. The influence of the state of charge on the parameters of the ECM was analyzed. Based on the results we think EIS combined with ECM simulation tool can be used to derive useful information for improving battery design and state of health prediction.

1. Introduction

Lithium ion batteries (LIBs) are currently heavily used in consumer electronics such as laptops, mobile phones, medical devices, and also electric vehicles (EVs) due to high gravimetric and volumetric energy, high power density, long cycle life, and low self-discharge [1-2]. In order to operate the batteries in these systems, an understanding of the state of batteries, such as the state of charge (SOC) of batteries and state of health (SOH), is very important for effective and safe operation of the batteries. Therefore, a nondestructive analysis of the condition is in high demand for the premonitory diagnosis of the on-board batteries of electric vehicles, and of the installed batteries in load leveling systems [3].

A large amount of studies have been reported on the modeling and experimental investigation of lithium ion batteries [4]. Electrochemical impedance spectroscopy (EIS) is a viable approach that can be used in LIBs to investigate SEI statuses, insertion/de-insertion reactions, and diffusion behaviors [5]. To obtain the battery characteristics from the EIS, two ways have been summarized in published works. It can be implemented directly for precise analysis and parameter identification based on equivalent circuits. Most lithium-ion battery models today are based on equivalent circuit models (ECM). In the ECM approach, the associated equivalent circuit is used as a tool to predict battery characteristics. These models are composed of electrical components (resistances, inductances, capacitances, Warburg impedance, constant phase element, etc.) and their values are identified via EIS

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A previous work in details a schematic of an ECM that contains parameters that is important in the analysis of Li-ion batteries. With the knowledge of the internal workings of a battery, one can predict the discharge power performance, transient and dynamic behavior of Li-ion batteries thus suggesting the use of such models as control algorithms and energy storage designs [6-7]. It is essential to know the behavior of the battery at all relevant internal and external conditions when the battery cell is in the new and the aging state [8]. The previous studies reported the effects of temperature, SOC, the current and the previous history, etc. on the ECM parameters of LIBs [4-8]. However, each of these studies focused on only one type of battery. In this work, the effects of SOC on the ECM parameters of three types of LIBs were investigated.

2. Materials and methods

Electrochemical impedance spectroscopy (EIS) measurements were carried out at 25°C using Zahner Zennium machine with frequencies ranging from 1 kHz to 10 mHz, and the perturbation signal was 10 mV. Zahner Analysis software enabled the construction of the ECM using the graphical model. Various SOC values between 0% and 100% were obtained with the MACCOR SERIES 4200 Battery test system. Three types of lithium ion batteries were bought from Tianjin Lishen Battery Joint-Stock Co., Ltd. The Lithium Titanate Oxide Battery (LTO) (UPR3261TB) has a nominal capacity of 2 Ah. The cathode of the LTO cell is Lithium manganate, and the anode is Lithium titanate. The LTO cell was charged at a constant current of 2 A until the voltage reached 2.8 V. Following this, a constant voltage charge maintained the voltage at 2.8 V until the current decayed to 100 mA. Finally, a constant current discharge at 2 A led the battery to approach the desired SOC until fully discharged at 1.5 V. The Lithium iron phosphate (LFP) (IR18650EH) has a nominal capacity of 1.6 Ah. The cathode of the LFP cell is Lithium iron phosphate, and the anode is graphite. The LFP cell was charged at a constant current of 320 mA until the voltage reached 3.65 V. Following this, a constant voltage charge maintained the voltage at 3.65 V until the current decayed to 80 mA. Finally, a constant current discharge at 320 mA led the battery to approach the desired SOC until fully discharged at 2.5 V. The Lithium Nickel Manganese Cobalt Oxide (NMC) battery (IR18650SK) has a nominal capacity of 2.5 Ah. The cathode of the NMC cell is LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2 (NMC532), and the anode is graphite. The NMC cell was charged at a constant current of 500 mA until the voltage reached 4.2 V. Following this, a constant voltage charge maintained the voltage at 4.2 V until the current decayed to 125 mA. Finally, a constant current discharge at 500 mA led the battery to approach the desired SOC until fully discharged at 2.7 V. The EIS results of the batteries at 100%, 80%, 50%, 20% and 0% SOC were collected and analyzed, respectively.

3. Results and discussion

3.1. The equivalent circuit models for lithium ion batteries

A large amount of equivalent circuit models for LIBs were developed [4-13]. For a description of the physical and electrochemical effects that can be identified in the impedance spectrum, the impedance spectrum is divided into individual frequency ranges. In the very high frequency, an inductive behavior is measured in addition to the real part of the impedance. The behavior is mainly caused by the measurement setup such as the connecting lines and the type of cable wiring [11]. Barsoukov et al. [13] proposed common kinetic steps for the Lithium-ion batteries, which include electronic conduction through the particles and ionic conduction through the electrolyte in cavities between particles, charge transfer involves the resistance of an insulating layer and activated electron transfer resistance on the electronic/ionic conduction boundary, ions have to diffuse into the bulk of particles via solid-state diffusion. It was suggested by Yamada et al. [12] and Barsoukov et al. [13] that the two semicircles at the high frequency and the middle frequency were attributed to the lithium-ion transport in the SEI film and the charge-transfer resistance at amorphous particles, respectively. And the lithium diffusion in the particles gave the Warburg impedance, which was observed as a straight line at the low frequency. In this work, it was proved that the equivalent circuit model showed in Figure 1 could be used to
simulate the measured EIS of the batteries. The simulated results matched the measured EIS perfectly (Figure 2, 3 and 4). As it was noted in the literature \(^5\), L describes the high-frequency inductance, \(R_s\) denotes the sum ohmic resistance of the electrode, electrolyte, separator, and connection, \(R_1\) in parallel with CPE\(_1\) (constant phase element, CPE) simulates Li\(^+\) diffusion through the SEI layer. \(R_2\) in parallel with CPE\(_2\) simulates Li\(^+\) charge transfer reaction at the electrode/electrolyte interface; \(W\) simulates Li\(^+\) diffusion in the porous electrode under semi-infinite diffusion conditions, \(C_{\text{int}}\) describes the Li-ion accumulation effect in intercalation/de-intercalation electrodes for low-frequency perturbations.

Figure 1. The equivalent circuit model for LFP and NMC batteries.

Figure 2. The measured and simulated Nyquist spectra for LFP batteries.
3.2. The state of charge effects on the parameters of equivalent circuit models for lithium ion batteries

The EIS spectra of LFP, NMC and LTO battery in different SOC are illustrated in Figure 5, 6 and 7, respectively. The simulated parameters of the ECM for LFP, NMC and LTO battery in various SOC are showed in Table 1, 2 and 3, respectively. The results show that there is no obvious change in the horizontal intercepts of the Nyquist spectra of LFP battery in different SOC (Figure 5). The simulated
The results also show that there is no clear trend in the values of $R_s$ (Table 1). The difference between maximum and minimum of $R_s$ values is 1.7 mΩ, which is only around 5% of the minimum of $R_s$ value. The results indicate that the internal resistance of the LFP battery keeps nearly steady during discharging from 100% SOC to 0% SOC. There is no significant change of the semicircle radius at the high frequency in the EIS spectra showed in Figure 5. It can be deduced that the SEI keeps stable during the discharging. It is obvious that the radius of the semicircle at the medium frequency continuously became larger from 100% SOC to 0% SOC, and the radius significantly changed from 100% SOC to 80% SOC and from 20% SOC to 0% SOC. The simulated results (Table 1) also illustrate that the values of $R_2$ obviously increase from 100% SOC to 80% SOC and from 20% SOC to 0% SOC. It could be concluded that the charge-transfer resistance became higher and higher during discharging, especially from 100% SOC to 80% SOC and from 20% SOC to 0% SOC.

![Figure 5. The Nyquist spectra of LFP battery in different SOC.](image)

Table 1. The simulated parameters of the ECM for LFP battery in various SOC

| SOC   | L  | $R_s$ | CPE$_1$ | $R_1$ | CPE$_2$ | $R_2$ | W     | $C_{int}$ |
|-------|----|-------|---------|-------|---------|-------|-------|-----------|
|       | (nH) | (mΩ) | Y(mΩ$^{-1}$s$^n$) | n     | Y(mΩ$^{-1}$s$^n$) | n     | (mΩ) | (mΩ•s$^{-1/2}$) |
| 100%  | 832 | 32.6  | 1.87    | 0.0121| 2.04    | 1.06  | 0.644 | 22.1      | 16.4    | 0.130 |
| 80%   | 678 | 33.3  | 1.87    | 0.0152| 2.10    | 1.16  | 0.641 | 28.9      | 9.82    | 0.978 |
| 50%   | 750 | 34.2  | 1.80    | 0.0148| 2.16    | 1.12  | 0.656 | 28.6      | 11.2    | 2.33  |
| 20%   | 527 | 33.2  | 1.95    | 0.0161| 2.11    | 1.06  | 0.675 | 29.2      | 13.7    | 2.15  |
| 0%    | 602 | 34.3  | 1.82    | 0.0182| 2.19    | 1.31  | 0.660 | 36.7      | 16.5    | 0.413 |

The Nyquist spectra patterns and the simulated parameters of the ECM for the NMC battery showed a similar trend to the LFP battery (Figure 5 and 6, Table 1 and 2). Both the $R_s$ and $R_1$ values of the NMC battery have no significant changes during discharging process, and the values of $R_2$ also obviously increase from 100% SOC to 80% SOC and from 20% SOC to 0% SOC (Table 2). The difference between the $R_2$ values of the NMC battery at 0% SOC and 20% SOC is 33.8 mΩ which is
much higher than that between 80% SOC and 100% SOC. This phenomenon indicates that the charge-transfer resistance of the NMC battery dramatically increased during discharging from 20% SOC to 0% SOC, which is somehow different from the LFP battery.

![Figure 6. The Nyquist spectra of NMC battery in different SOC.](image)

| SOC  | L    | R_s  | CPE_1 | R_1  | CPE_2 | R_2  | W    | C_int |
|------|------|------|-------|------|-------|------|------|-------|
| 100% | 508  | 42.5 | 83.8  | 0.496| 72.0  | 0.991| 0.620| 19.8  | 2.75 | 3.43 |
| 80%  | 423  | 42.5 | 111   | 0.701| 71.5  | 1.47 | 0.558| 25.6  | 4.17 | 5.03 |
| 50%  | 579  | 44.1 | 80.0  | 0.897| 72.5  | 1.19 | 0.620| 24.0  | 2.27 | 4.89 |
| 20%  | 693  | 43.6 | 11.9  | 0.825| 70.3  | 1.61 | 0.578| 27.7  | 2.04 | 1.88 |
| 0%   | 691  | 44.3 | 9.72  | 0.680| 70.0  | 3.83 | 0.431| 61.5  | 5.98 | 0.42 |

The Nyquist spectra and the simulated parameters of the ECM for the LTO battery have some different patterns comparing with the LFP and NMC batteries. The R_s values of the LTO batteries are ranging from 1.24 to 1.51 mΩ, which are much lower than that of the LFP and NMC batteries. In addition, the values of R_s in 100% SOC and 0% SOC are nearly the same and lower than that of the other SOCs. The R_2 value of the LTO battery in 100% SOC is also significantly lower than that of the other SOCs. As the LTO battery is discharged from 100% to 80% SOC, the R_2 value decreases, and then it keeps as a platform when discharging the LTO battery from 80% SOC to 20% SOC. At last, it dramatically increases when discharging the LTO battery from 20% SOC to 0% SOC. The Nyquist spectra also shows that the radius of the semicircle at the medium frequency obviously becomes longer during the LTO battery discharging form 20% SOC to 0% SOC.
Figure 7. The Nyquist spectra of LTO battery in different SOC.

Table 3. The simulated parameters of the ECM for LTO battery in various SOC

| SOC  | L (μH) | R₀ (mΩ) | CPE₁ | R₁ (μΩ) | CPE₂ | R₂ (mΩ) | W (mΩ•S⁻¹/²) | Cₑₓₜ (KF) |
|------|--------|---------|------|---------|------|---------|-------------|------------|
| 100% | 1.30   | 1.24    | 8.72 | 0.571   | 12.9 | 128     | 0.426       | 1.03       | 2.52       | 13.7       |
| 80%  | 1.30   | 1.51    | 48.5 | 0.634   | 23.2 | 6.34    | 0.907       | 0.650      | 1.08       | 31.4       |
| 50%  | 1.44   | 1.44    | 120  | 0.899   | 22.2 | 4.10    | 0.937       | 0.728      | 1.05       | 14.7       |
| 20%  | 1.21   | 1.46    | 10.1 | 0.761   | 22.3 | 3.71    | 0.954       | 0.706      | 0.932      | 8.90       |
| 0%   | 1.28   | 1.25    | 2.78 | 0.207   | 19.0 | 78.9    | 0.473       | 6.64       | 3.67       | 0.184      |

Westerhoff et al. [11] reported that all of the influencing variables (temperature, state of charge, aging) result in the expansion of the second semicircle and thus lead to an increase in charge-transfer resistance. To be able to state which of the three factors is responsible for the increase, the other parameters have to be included as well. In our study, when the environmental temperature is fixed, the expansion of the second semicircle is still observed during one single discharging process, which indicates that the SOC could independently lead to an increase in charge-transfer resistance. These findings can help us derive more useful information of the LIBs electrochemical behavior using EIS combination ECM simulation tools.

4. Conclusion

In this paper, an equivalent circuit model including two constant phase angle elements in parallel with resistor elements is established to study the impedance characteristics for lithium ion batteries. In order to investigate the state of charge effects on the ECM parameters, three types of commercial LIB cells were used, and the EIS measurements were performed under 100%, 80%, 50%, 20% and 0% SOC, respectively. The influence of the state of charge on the parameters of the ECM was analyzed. The parameters CPE₁, CPE₂, W and C for the three types of LIBs have been found to vary with
discharging and the parameters $R_s$ and $R_1$ have been found to keep nearly stable during discharging. The parameter $R_2$ for LFP and NMC in parallel with CPE$_2$, which is closely related to the charge-transfer resistance, has shown increasing trend during discharging, and the most obvious increase is observed when the batteries are discharged from 100% SOC to 80% SOC and from 20% SOC to 0% SOC. The parameter $R_2$ for LTO in parallel with CPE$_2$ decreases when the battery discharging from 100% SOC to 80% SOC and keeps stable during discharging from 80% SOC to 20% SOC, and a dramatic increase is observed when the LTO is discharged from 20% SOC to 0% SOC. The behavior of the EIS has been shown to be related to the fundamental electrochemical properties of the LIBs and this paper provides that SOC play a critical role on the specific EIS patterns. Based on these results we expect to use impedance parameter model to obtain useful information to improve battery design and the health predictions.

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References
[1] Armand, M.; Tarascon, J.-M.; (2008) Building Better Batteries, Nature, 451: 652–657.
[2] Hassoun, J.; Panero, S.; Reale, P.; Scrosati, B.; (2009) A New, Safe, High-Rate, and High-Energy Polymer Lithium-Ion Battery, Adv. Mater. 21: 4807–4810.
[3] Osaka, T.; Nara, H.; Mukoyama, D.; Yokoshima, T.; (2013) New analysis of electrochemical impedance spectroscopy for lithium-ion batteries, J Electrochem. Sci. Te., 4(4): 157-162.
[4] Zhu, J. G.; Sun, Z. C.; Wei, X. Z.; and Dai, H. F.; (2014) A new electrochemical impedance spectroscopy model of a high-power lithium-ion battery, RSC Adv., 29988-29998.
[5] Huang, Q. A.; Shen, Y.; Huang, Y. H.; Zhang, L.; Zhang, J. J.; (2016) Impedance Characteristics and Diagnoses of Automotive Lithium-Ion Batteries at 7.5% to 93.0% State of Charge, Electrochimica Acta, 219: 751-765.
[6] Moss, P. L.; Au, G.; Plichta, E. J.; and Zheng, J. P.; (2008) An Electrical Circuit for Modeling the Dynamic Response of Li-Ion Polymer Batteries, J. Electrochem. Soc., 155(12), A986–A994.
[7] Gomez, J.; Nelson, R.; Kalu, E. E.; Weatherspoon, M. H.; Zheng, J. P.; (2011) Equivalent circuit model parameters of a high-power Li-ion battery: Thermal and state of charge effects, J. Power Sources, 196: 4826-4831.
[8] Waag, W.; Käbitz, S.; Sauer, D. U.; (2013) Experimental investigation of the lithium-ion battery impedance characteristic at various conditions and aging states and its influence on the application, Applied Energy, 102: 885-897.
[9] Dai, H. F.; Wei, X. ZH.; Sun Z. CH.; (2009) A new SOH prediction concept for the power Lithium-ion battery used on HEVs, 2009 IEEE Vehicle Power and Propulsion Conference, 1649-1653
[10] Stroe, D. I.; Swierczynski, M.; Stan, A. I.; Knap, V.; Teodorescu, R.; Andreasen, S. J.; (2014) Diagnosis of Lithium-Ion Batteries State-of-Health based on Electrochemical Impedance Spectroscopy Technique, 2014 IEEE, 4576-4582.
[11] Westerhoff, U.; Kurbach, K.; Lienesch, F.; Kurrat, M.; (2016) Analysis of Lithium-Ion Battery Models Based on Electrochemical Impedance Spectroscopy, Energy Technol., 4, 1620-1630.
[12] Yamada, Y.; Iriyama, Y.; Abe, T.; and Ogumi, Z.; (2010) Kinetics of Electrochemical Insertion and Extraction of Lithium Ion at SiO, J. Electrochem. Soc., 157 (1): A26-A30.
[13] Barsoukov, E.; Macdonald, J. R.; (2005) Impedance Spectroscopy Theory, Experiment, and Applications. Second Edition. John Wiley & Sons, Inc., Hoboken, New Jersey, PP. 444-445