The Electrochemical Impedance Spectroscopy Features of the Lithium Nickel Manganese Cobalt Oxide Based Lithium Ion Batteries During Cycling

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Abstract. 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, Lithium Nickel Manganese Cobalt Oxide (NMC) type lithium ion batteries were divided into four groups. They were charged and discharged under various currents. The results showed that the higher the charging or discharging currents were, the faster the NMC batteries capacities fading were. In order to investigate the electrochemical behavior of the NMC batteries during cycling, we established an equivalent circuit model including one capacitor element in parallel with resistor and one constant phase angle element in parallel with resistor elements to study the impedance characteristics of the NMC batteries. The simulated results indicate that when the capacities of the batteries are dropping, the sum ohmic resistance of them will go up, and the resistance of Li+ diffusion through the SEI layer keeps increasing during cycling. The charge transfer resistance of the NMC batteries decreased at first and then kept increasing after 100 cycles. Among the three parameters, the charge transfer resistance values are the most sensitive factors that are corresponding to the state of charge of the NMC batteries during one single discharging process. We think that the internal ohmic resistance values can be used to predict the state of health (SOH) of the batteries and the charge transfer resistance can be used to predict the state of charge of the NMC batteries.

1. Introduction
Lithium ion batteries (LIBs), with high gravimetric and volumetric energy density, high operating voltage platform, low self-discharge and long cycle life, have been widely used in the portable electronic devices, cellular phones and electric vehicles (EVs) etc. [1-2]. A certain number of studies have been reported on the modeling and experimental investigation of lithium ion batteries. Regarding the study of battery characteristics, the electrochemical impedance spectroscopy (EIS) method, as one of the most accurate methods, is applied to model its electrochemical system, predict battery life time, estimate the state of the charge of the battery and obtain thermal characterization [3]. For better understanding of the performance of lithium ion batteries, numerous authors have developed various models [4]. Most lithium ion battery models today are based on equivalent circuit models (ECM). These models are composed of electrical components (resistances, inductances, capacitances, Warburg impedance, constant phase element, etc.) and their values are identified via EIS [3]. Conventionally, equivalent circuits are used to interpret data obtained from EIS measurements. Conversely, the
associated equivalent circuit can be used as the tool to predict battery behavior [5]. 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 [6]. The previous studies reported the effects of temperature, SOC, the current and the previous history, etc. on the ECM parameters of LIBs [2-8]. Some research has been done on investigating the electrochemical impedance characteristic of ageing batteries. There is no discussion about the impact of the impedance and the available capacity on the estimating the SOH of the battery considering the characteristic demanded in practical applications, such as the rate of discharge ability [9]. The objective of this work is to apply the technique of ECM in the analysis of the ageing and SOC on the ECM parameters of Lithium Nickel Manganese Cobalt Oxide (NMC) type lithium ion batteries. The behavior of impedance elements in an ECM during ageing under variable cycling currents is considered.

2. Materials and methods
Batteries cycled by the MACCOR SERIES 4200 Battery test system. The Lithium Nickel Manganese Cobalt Oxide (NMC) type lithium ion batteries (IR18650SK) were bought from Tianjin Lishen Battery Joint-Stock Co., Ltd. They have a nominal capacity of 2.5 Ah. The cathode of the NMC cell is LiNi0.5Mn0.3Co0.2O2 (NMC532), and the anode is graphite. The NMC cells were divided into four groups. Their charging and discharging currents are listed in Table 1. The charge/discharge was carried out as the following steps. The NMC cell was charged at a constant current 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 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. The electrochemical impedance spectroscopy (EIS) measurements were carried out at 25℃ 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.

| Group | a | b | c | d |
|-------|---|---|---|---|
| Charging Current (A) | 0.5 | 1.25 | 1.25 | 2.5 |
| Discharging Current (A) | 0.5 | 1.25 | 2.5 | 2.5 |

3. Results and discussion
3.1. The capacities fade of the NMC batteries during cycling
The capacities decay trends of all the four groups of NMC batteries are illustrated in Figure 1. The results showed that both the charging and discharging currents could speed the NMC batteries fading. Both the charging and discharging currents of the batteries of group b were higher than those of the group a, and the fading speed of the batteries of group b was also faster than that of the group a. The retention capacities of the batteries of group a were higher than 86% after 600 cycles, while those of the group b were around 82%. The charging currents of the group b and c were the same, the discharging currents of the group c were higher than those of the group b. It was showed in Figure 1 that the retention capacities of the group c decreased much faster than that of the group b. The retention capacities of the group c were lower than 75% after 400 cycles, which were even lower than those of the batteries of group b after 600 cycles. Both the charging and discharging currents of the group d were the highest among the four groups. The decay speed of the batteries of the group d was also the fastest among the four groups. The retention capacities of the group d were lower than 80% after around 50 cycles and lower than 60% after around 100 cycles.
Figure 1. The retention capacity of the NMC batteries during cycling. All the retention capacities were normalized to the fresh cells, whose retention capacities were set as 100%. The a, b, c and d are corresponding to the groups of a, b, c and d listed in Table 1, respectively.

3.2. The equivalent circuit models for lithium ion batteries

A large amount of equivalent circuit models for LIBs were developed [4-14]. It was proved in our previous work that an equivalent circuit model including two constant phase angle elements in parallel with resistor elements can be used to analyse the electrochemical behavior of NMC batteries [15]. Due to the long duration of parameterization when using CPE elements, the simulation speed will be greatly reduced with CPE models for a battery cell simulation [12]. In order to speed up the simulation processes, a simplified model showed in Figure 2 was used to simulate the measured EIS of the batteries. The simulated results also could match the measured EIS perfectly (Figure 3). As it was noted in the literature [4], L describes the high-frequency inductance. Rs denotes the sum ohmic resistance of the electrode, electrolyte, separator, and connection. R1 in parallel with C1 simulates Li+ diffusion through the SEI layer. R2 in parallel with CPE simulates Li+ charge transfer reaction at the electrode/electrolyte interface. W simulates Li+ diffusion in the porous electrode under semi-infinite diffusion conditions. Cint describes the Li-ion accumulation effect in intercalation/de-intercalation electrodes for low-frequency perturbations.

Figure 2. The equivalent circuit model for NMC batteries.
Figure 3. The measured and simulated Nyquist spectra for NMC batteries. The cycling current of the NMC cells was 1.25 A.

3.3. The influence of cycling on the parameters of equivalent circuit models for NMC batteries

Figure 4. The $R_s$ values of the NMC batteries during cycling. The a, b, c and d are corresponding to the groups of a, b, c and d listed in Table 1, respectively.

The simulated parameters $R_s$, $R_1$ and $R_2$ values of the NMC batteries are showed in Figure 4, 5 and 6, respectively. The results in Figure 4 showed that the $R_s$ values of all the four groups of batteries at various state of charge kept increasing during cycling. The increasing trend of the group d could be divided to three stages. The $R_s$ values of the group d increased slowly during the first 100 cycles. Then, the $R_s$ values of them increased dramatically from 100 cycles to 200 cycles. At last, they kept increasing slowly again from 200 cycles. As it was showed in Figure 1, the retention capacities of the group d dropped significantly from 100 cycles to 200 cycles, which was much faster than those of the other stages. These results indicate that the $R_s$ values are closely related to the batteries decay. It can
be concluded that when the capacities of the batteries are dropping, the $R_s$ values of them will go up. As it is described in section 3.2, the $R_s$ denotes the sum ohmic resistance of the battery. Thus, the internal ohmic resistance values can be used to predict the state of health (SOH) of the batteries.

The $R_1$ values of the four groups of batteries also kept increasing during cycling. It indicates that the resistance of Li$^+$ diffusion through the SEI layer keeps increasing during cycling. However, it is hard to find regular patterns of the increasing trends. The $R_2$ values of the four groups decreased at first and then kept increasing during cycling. The increasing speeds of the batteries under 20% and 0% SOC are significantly faster than those of the other state of charge. We can conclude that the charge transfer resistance of the batteries is increasing after 100 cycles.

Figure 5. The $R_1$ values of the NMC batteries during cycling. The a, b, c and d are corresponding to the groups of a, b, c and d listed in Table 1, respectively.

Figure 6. The $R_2$ values of the NMC batteries during cycling. The a, b, c and d are corresponding to the groups of a, b, c and d listed in Table 1, respectively.
3.4. The state of charge effects on the parameters of equivalent circuit models for NMC batteries

It is illustrated in Figure 7 that the $R_s$, $R_1$ and $R_2$ values keep going up during discharging from 100% SOC to 0% SOC. It indicates that the sum internal ohmic resistance, the Li$^+$ diffusion through the SEI layer resistance and the charge transfer resistance keep increasing during the NMC batteries discharging. There is difference between the increasing trends of the three parameters. The $R_s$ values increased very slowly during discharging. There is little difference between the highest and the lowest $R_s$ value during one single discharging process. The $R_1$ values increased slowly when the batteries were discharged from 100% SOC to 50% SOC and then they went up much faster when the batteries were discharged from 50% SOC to 0% SOC in the first 100 cycles. However, the $R_1$ values dropped when the batteries were discharged from 100% SOC to 80% SOC and then went up significantly when the batteries were discharged from 80% SOC to 0% SOC after 100 cycles. During cycling, the $R_2$ values increased steadily when the batteries were discharged from 100% SOC to 50% SOC and then went up dramatically when the batteries were discharged from 50% SOC to 0% SOC. Among the three parameters, the $R_2$ values were the most sensitive parameters corresponding to the state of charge of the batteries, especially when the state of charge was lower than 50% SOC. The results indicate that the parameter $R_2$ can be used to predict the state of charge of the LIBs.

4. Conclusion

The NMC batteries were divided into four groups. They were charged and discharged under various currents. The results showed that the higher the charging or discharging currents were, the faster the NMC batteries capacities fading were. The behavior of the EIS has been shown to be related to the fundamental electrochemical properties of the LIBs. In order to investigate the electrochemical behavior of the NMC batteries during cycling, we established an equivalent circuit model including one capacitor element in parallel with resistor and one constant phase angle element in parallel with resistor elements to study the impedance characteristics of the NMC batteries. The simulated results indicate that the $R_s$ values were closely related to the batteries decay. It can be concluded that when the capacities of the batteries are dropping, the $R_s$ values of them will go up. It indicates that the resistance of Li$^+$ diffusion through the SEI layer keeps increasing during cycling. The $R_2$ values of the NMC batteries decreased at first and then kept increasing after 100 cycles. Among the three parameters, the $R_2$ values are the most sensitive factors that are corresponding to the state of charge of the NMC batteries during one single discharging process. We think that the internal ohmic resistance values can be used to predict the state of health (SOH) of the batteries and the charge transfer resistance can be used to predict the state of charge of the NMC batteries.

Acknowledgment

This research is funded by Chinese Academy of Inspection and Quarantine (2019JK009) and National key R & D program of China (2017YFF0210703).

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