



Exploring Differences between Charge and Discharge of LiMn₂O₄/Li Half-cell with Dynamic Electrochemical Impedance Spectroscopy



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ABSTRACT

The electrochemical impedance spectroscopy (EIS) of a lithium-ion battery is usually measured at open-circuit state under a constant state-of-charge (SOC). In this way, the differences between charge and discharge cannot be distinguished, because they both occur in one cycle of the alternating current. To explore the differences, in this study, we propose a new implementation method measuring the dynamic EIS (DEIS) of a LiMn₂O₄/Li half-cell (0.8 mAh) in the galvanostatic mode while the cell is under charging or discharging at a series of direct currents (DC). The results show the charge transfer resistance, R_{ct} , decreases with the increased DC. Also, R_{ct} during charging is usually smaller than that during discharging. The dependency of R_{ct} on the DC can be explained according to the Butler-Volmer equation. The difference in R_{ct} between charge and discharge, ΔR_{ct} , is ascribed to a significant surface concentration variation caused by the DC.

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1. Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful experimental method to gain deep insights into electrochemical systems [1,2]. In the last two decades, EIS is widely used in the study of lithium-ion batteries, including the investigation of intercalation process at the electrode/electrolyte interface [3], the determination of kinetic parameters [4], the evaluation of potential materials for lithium-ion battery [5], the exploration of the aging mechanism and thermal degradation [6], the study of low temperature properties [7], and the development of impedance-based models for battery management system (BMS) [8,9].

In most of the previous studies, the EIS was measured at stationary state, that is, batteries were first charged or discharged to a specific SOC. After a long period of rest when the batteries were stabilized at an equilibrium state, the EIS was measured. In this way, both the charge and discharge occurred in one cycle of the alternating current during the EIS measurement, thus, the differences between them cannot be distinguished.

Experimental evidences and practical applications indicate that it is important to distinguish between the charge and discharge: (1) the Hybrid Pulse Power Characterization (HPPC) method results in significantly different DC resistance for charge and discharge for use

in BMS [10]; (2) different overpotential resistance of charge and discharge were used to estimate the irreversible heat generation rate for the respective processes [11]; (3) it was common experience that charging a battery was more difficult than discharging it at low temperatures [7]. However, to the best knowledge of the authors, few works have been engaged in exploring the differences between charge and discharge and revealing its underlying causes.

Measuring the EIS while the cell is under charging or discharging is an effective approach to explore the differences between charge and discharge, and a number of groups have been engaged in developing this method. In 1989, Chenebault and Vallin [12] developed an impedance measurement method in a study of the anodic discharge of the Li metal electrode in LiAlCl₄/SOCl₂ electrolyte, for which the battery system was stimulated with a small sinusoidal signal while under charging. In 1990, Stoyanov et al. [13] applied a similar method, termed as “nonstationary impedance analysis”, to lead-acid battery. Osaka et al. [14] applied the method, now termed as “In-situ AC-impedance measurement method”, to lithium metal battery. The method was further applied to the manganese dioxide (EMD)/alkaline cell by Tachibana and Matsuki [15], and to lithium-ion battery by Itagaki et al. [16,17]. In Ref. [18], the impedance was measured at open-circuit-state but it was also called as “In-situ electrochemical impedance spectroscopy”. To avoid confusion, we termed the EIS measurement conducted at steady state as stationary EIS (SEIS), and that conducted while the cell is under DC charging or discharging as dynamic EIS (DEIS) throughout this paper.

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In ref. [16] and [17], Itagaki et al. applied the DEIS to study the formation mechanism of the solid electrolyte interphase (SEI) film on the graphite and LiCoO_2 electrode in lithium-ion batteries during the first cycle. They also revealed the differences between the charge transfer resistance, R_{ct} , obtained by the SEIS and that by the DEIS. Furthermore, they reported different R_{ct} for intercalation and de-intercalation reactions using the DEIS for the first time. However, the underlying causes for the difference between charge and discharge were not analyzed in details. Methodologically, Itagaki et al. measured the impedance during continuous charging and discharging at constant current, and then the DEIS at a specific SOC was linearly interpolated along the time-axis [16].

Moss et al. [8] and Dong et al. [9] applied the DEIS to consider the nonlinear dependency of R_{ct} on the DC in the equivalent electric circuit. In Ref. [8], a commercial Li-ion polymer battery with a nominal capacity of 800 mAh was used, and R_{ct} , measured by DEIS, exhibited an extraordinarily strong dependency on the applied DC. It was shown that when the amplitude of the DC was increased from 0 to 1 C (Hereafter, C or C-rate denotes the charge/discharge rate and 1 C signifies a charge/discharge rate that can fill/empty the total capacity of a battery in one hour), R_{ct} decreased sharply, and the R_{ct} of 1 C was only 30% of the value obtained using SEIS where no DC was applied. In addition, the maximum R_{ct} was obtained at a negative DC corresponding to the discharge regime, instead of at the zero DC.

Two findings of the work in [8,9] need to be further discussed: (1) in the linear regime of the Butler-Volmer equation, the R_{ct} should be almost constant. However, no plateau of R_{ct} with respect to the DC was detected in the Ref. [8]. One possible reason is that battery temperature may rise significantly during the DC charge/discharge in the DEIS measurement. The increased temperature causes the R_{ct} to further decrease beside the overpotential effect; (2) Based on the Butler-Volmer equation, the maximum R_{ct} is expected to occur at the zero DC instead of at a negative DC as reported in Ref. [8]. One possible reason may be that when the absolute value of the DC discharge current was small, the reversible heat was endothermic and dominated the total heat generation of the cell. Therefore, the endothermic reversible heat generation resulted in a temperature decrease. As a result, R_{ct} increased as compared to the zero DC case.

Analysis of the previous studies leads to the following observations:

- (1) The DEIS is capable of examining the current dependency of R_{ct} and distinguishing the R_{ct} between charge and discharge. This will help in improving the accuracy of the heat generation estimation as well as the state of charge (SOC) estimation to be used in the BMS.
- (2) It's preferable to use a battery with small capacity to investigate the DC dependency of R_{ct} . In this way, the battery can dissipate the heat generated inside the battery quickly, thereby maintaining a nearly constant temperature during the test so as to decouple the effect of temperature from other factors like SOC, DC.
- (3) There are few studies on the effect of various factors, including the temperature and the magnitude of the DC, etc., on the difference in R_{ct} between charge and discharge. In addition, the underlying causes for the differences needs to be further explored.

In this study, a $\text{Li}_x\text{Mn}_2\text{O}_4/\text{Li}$ half-cell with a capacity of 0.8 mAh is used. Unlike the method proposed by Itagaki et al. [16], the cell is first adjusted to a specific SOC, and then applied for a short period charging or discharging current, followed by superimposing a sinusoidal signal on the DC to measure the DEIS. Using this method, we measure the differences in R_{ct} between the charge and discharge

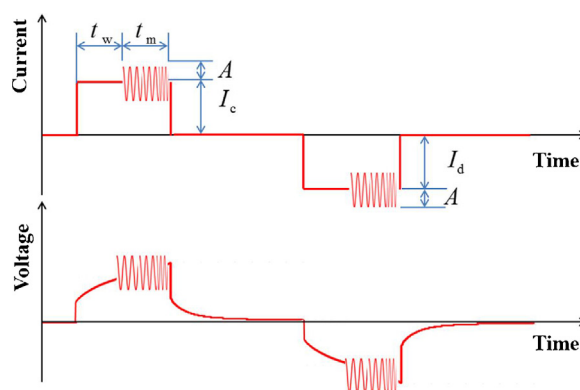


Fig. 1. A schematic plot of the DEIS measurement. I_c and I_d represent the DC, charging and discharging, correspondingly. t_w and t_m are the wait time and the impedance measurement duration, respectively. A is the amplitude of the stimulation signal.

and examine the effects of different factors on the differences, ΔR_{ct} . An explanation for the ΔR_{ct} based on a single particle model is proposed.

2. Experimental

A coin-cell (type: 2032) with a LiMn_2O_4 working electrode and a Li metal counter electrode was used in this study. After the stabilizing operation, the capacity of the coin-cell at 10°C was 0.8 mAh. The DEIS was measured with an Autolab PGSTAT302 N impedance analyzer (Eco Chemie, Netherland) in an environment chamber GDJW-225.

As shown in Fig. 1, The DEIS measurement method developed in this study differs from the one proposed by Itagaki et al. [16]. The cell was first adjusted to a specific SOC, then settled at open circuit, afterwards, the EIS was measured after applying a short DC (charging or discharging). Note that during the DEIS measurement, the DC was not interrupted. A wait time was introduced here to avoid the initial transient state. The SOC variation was controlled carefully during the measurement, therefore, the DEIS were measured at an approximately same SOC for charging and discharging, respectively. In addition, the method proposed in this study allow us to evaluate the parameters effect on the ΔR_{ct} , since we can keep the cell at the specified SOC when varying the other measurement parameters, such as the DC or temperature.

The parameters of the DEIS measurement are listed in Table 1. As pointed out in Ref. [20], errors may appear as a result of the voltage drift since the battery is in a nonstationary state during the DEIS measurement. In addition, the errors depend on the measurement period and the variation rate of the battery system, which are decided by the lowest analyzed frequency and the DC, respectively. Therefore, special attention was paid to these two parameters.

Regarding the lowest analyzed frequency, trade-off have to be made. Obviously, a higher lowest analyzed frequency will reduce the measurement period, but it may not cover the charge transfer semicircle adequately. Based on the results in preparatory experiments, we set 10 Hz as the lowest analyzed frequency. In terms of the DC, there are two considerations: first, it shouldn't be too large otherwise the SOC variation during the DEIS measurement may exceed the preset threshold value, ΔSOC , such as 1% proposed in Ref. [9]; Second, it should be greater than the amplitude of the stimulation signal, A , in order to separate the charge and discharge process. The above two constraints can be expressed as follows:

$$A \leq I_c, I_d \leq \frac{C \cdot \Delta\text{SOC}}{(t_w + t_m)} \quad (1)$$

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