Electrochemical Impedance Spectroscopy Study of LiFePO₄/Li during Discharging Process

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Abstract. Electrochemical impedance spectroscopy (EIS) study has been applied to investigate the electrochemical properties of LiFePO₄/Li half-cell at initial state (before and after charge/discharge process), and a certain dept of discharge (DoD). The impedance spectra were collected over the frequency range from 42 Hz to 5 MHz. The EIS spectra of LiFePO₄/Li half-cell show the appearance of semicircles in which the diameter increased with DoD. An equivalent circuit was constructed to each spectrum in order to elucidate to electrochemical properties changes of LiFePO₄/Li half-cell battery as function of DoD. The information of bulk and interfacial resistances are obtained by modeling with the equivalent circuits according with the Nyquist plots of each spectrum. The experiment results show the increase in the resistance of LiFePO₄/Li half-cell with the DoD.

Keywords: Electrochemical impedance spectroscopy, Lithium ion batteries, Depth of discharge, LiFePO₄

1. Introduction
Lithium-ion batteries (LIB) are the most promising power system, since they exhibit higher operating voltage and energy density. Therefore, many intensive studies are being performed by many researchers, in order to develop a new battery system and to improve its performance [1].

Lithium iron phosphate (LiFePO₄) or LFP (lithium ferrophosphate), an olivine-type cathode material, has great potential application in lithium-ion batteries because of having high theoretical capacity (170 mAhg⁻¹), low manufacturing cost, good thermal stability, high reversibility Li-ion intercalation/de-intercalation, and high safety, as well as environmental friendly [2-4]. However, the LiFePO₄ has poor rate capability due to poor electronic conductivity (10⁻⁹ - 10⁻¹⁰ S cm⁻¹) and low Li⁺ diffusion rate (10⁻⁴ - 10⁻¹² cm² s⁻¹). Therefore, many studies have been conducted on the material preparation and characterization as well as the electrochemical performances of LiFePO₄ in order to improve their electronic and ionic transport properties [2,5-7].

The electrochemical properties of battery system can be studied by several techniques such as using cyclic voltammetry (CV), charge/discharge (CD), and electrochemical impedance spectroscopy (EIS). Recently, many researches used EIS technique, to study the electrode materials because it can explain the relationship between the micro-structure and the electrochemical properties [8]. For example, EIS had been used to study the reversibility of Li-ion intercalation/de-intercalation processes.
of LiFePO$_4$ [2,9,10]. However, most studies of electrochemical performance using EIS were conducted using full cell system. In other hands, a half-cell battery where metalic lithium foil is used as counter electrode (anode), the lithium foil is large enough, so that it can be considered almost does not affect the EIS behavior [8]. Thus, it can simplify the model when discussing the experimental data of EIS spectra.

In this study, EIS study of LiFePO$_4$/Li half-cell was conducted in order to understand the effect of charge/discharge process on the electrochemical performance of lithium ion batteries. The effect of charging was studied by measuring EIS of the battery cell before and after charging/discharging. While the effect of discharging was studied by taking the EIS spectra from battery cell with various depth of discharge (DoD). The DoD was defined as the percentage of battery capacity that has been discharged expressed as a percentage of maximum capacity. Equivalent circuit model was used to analyze the EIS spectra.

2. Experimental method

2.1. Cell battery preparation

In this study, a commercially available LiFePO$_4$ powder obtained from MTI was used as cathode active material. The powder was mixed with conductive carbon (acetylene black) and Polyvinylidene fluoride (PVDF) dissolved in N-Methyl-2-pyrrolidone (NMP) in the weight ratio of 91:4:5 to form slurry. The slurry was then coated on aluminum foil in a certain thickness using doctor blade. After solvent evaporation, the cathode sheet was pressed and dried at 120 °C under vacuum oven for 24 h. CR2032-type coin cells were assembled in a glove box (Vigor, China) with H$_2$O content was controlled below 1 ppm. Metallic lithium foil 1.0 cm$^2$ was used as anode. The electrolyte was commercially availabe 1.0 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1, v/v) and Celgard 2400 polyethylene was used as the separator.

2.2. Cell characterization

The performance of the prepared coin cell was examined using the charging and discharging activities (CD) and electrochemical impedance spectroscopy (EIS). A BST8-3 8 Channel Battery Analyzer used to examine the charge/discharge performance and to prepare the sample at a certain depth of discharge (0-100 % DoD). The measurement was conducted within cut-off voltages of 2.5-4.2V and charge/discharge rate of 0.1C. Here C is theoretical capacity, calculated based on cathode (LiFePO$_4$) active material weight. The DoD sample preparation was performed after 2$^{nd}$ cycle charge/discharge process. The impedance characteristic was studied by using a computer controlled impedance analyzer (HIOKI LCR Hi-Tester Model 3532, Japan) with an amplitude of the AC signal of 1V in the frequency range of 42 Hz to 5 MHz. Before collecting the EIS data, the sample was kept at least 1 hour after charging and discharging up to certain DoD for equilibration.

3. Results and discussion

Figure 1 shows the 1$^{st}$ and 2$^{nd}$ charge and discharge of the assembled LiFePO$_4$ coin half-cell. It was observed that the discharged capacity at 1$^{st}$ cycle was 1.43 mAh. Considering weight of the active material (LiFePO$_4$) inside the coin (12.06 mg) the specific capacity of the coin cell battery was 116 mAh g$^{-1}$ or about 68% of the theoretical specific capacity of LiFePO$_4$ (170 mAh g$^{-1}$). In other hands, the 1$^{st}$ charging capacity was only 1.05 mAh. It means that the battery has charge efficiency 135% at the 1$^{st}$ cycle. The charge capacity or Coulombic efficiency (CE) as a battery parameter to monitor the magnitude of side reactions, has been of great interest in recent years [9]. The charge/discharge efficiency is the ratio of the energy can be taken out from a battery (discharging capacity) divided by the energy can be put in (charging capacity)[9]. Generally, efficiency is a dimensionless number between 0 and 1.0, or 0% to 100%. Efficiencies may not exceed 100%. However, in this study the charge efficiency at 1$^{st}$ cycle was exceed 100% as shown in Figure 2. This can occur because of the formation of solid electrolyte interphase (SEI), which forms in the first charge/discharge cycle, then decreases significantly in the second cycle, and decreases further in the third cycle and so on. Generally, SEI
formation is highest in the 1st charge/discharge cycle because pure anodes and cathodes previously did not form a passive layer which electronically isolated electrodes from electrolytes [11]. However, it is depending on negative-to-positive capacity ratio, surface area of particles, operation conditions, etc.[12]. In this study, the charge capacity at the 2nd cycle was 1.73 mAh and the discharge capacity was 1.38 mAh, thus the charge efficiency became 78%. After 2nd cycle and upto 10th cycle the charge efficiency was then stable at 98 – 100 % as shown in Figure 2. Therefore, we considered that after 1st cycle, the SEI at anode was relatively stable, so that further cycling, resulting in much lower SEI formation.

![Figure 1](image1.png)

**Figure 1.** The 1st and 2nd charge/discharge profile of LiFePO₄ coin cell.

![Figure 2](image2.png)

**Figure 2.** The charge efficiency of LiFePO₄ coin cell as function of cycle number.
During charge and discharge processes, chemical reactions occur at both sides of electrode. The reaction (1) occurs at the cathode or working electrode (iron phosphate) 
\[ \text{Li}^+ + e^- + \text{FePO}_4 \leftrightarrow \text{LiFePO}_4, \]  
and the reaction (2) occurs at the anode or counter electrode (lithium foil) 
\[ \text{Li}^+ + e^- \leftrightarrow \text{Li}. \] 
During discharge, lithium ions carry the current from the anode to the cathode and the delithiation happens at the anode and lithiation occurs at the cathode. During charging, the reverse happens when an overvoltage is applied. The lithiation and delithiation process may affect the impedance properties of the battery. Therefore we measured the impedance characteristic of LiFePO_4/Li half-cell before and after charge/discharge process as shown in Figure 3.

![Figure 3. Nyquist Plot of LiFePO_4/Li half-cell impedance experimental data and their equivalent circuits.](image)

Figure 3 displays the EIS spectra of LiFePO_4/Li half-cell before applied initial charging and after 2nd charging. The solid lines indicate the simulation curve when an equivalent circuit as shown in the figure is employed. The Nyquist plots show the appearance of semicircle for both before and after charging. However, the Nyquist plots at before charging are different from that at after 2nd cycle. The semicircle at the after charging is much smaller. This result shows the same tendency with previous report by Li Wang et al. [8]. The difference in radius between the before and after charging is revealing that the charge/discharge process changed the resistance of the battery. In order to investigate the changes in the EIS spectra of LiFePO_4/Li half-cell due to charging process, an equivalent circuits are employed as displayed in the Figure 3. The lithium foil as anode is large enough, so it can be considered almost does not affect the EIS behavior. Therefore, the total impedance could be regarded as the intrinsic resistance (Rs) which is related to the combined resistance of electrolyte and electrode material, charge transfer resistance (Rct) which is originated from the electronic and ionic resistances at the electrode-electrolyte interface, and the double-layer capacitance (Cdl) [8]. In the model of equivalent circuits as shown in Figure 3, R1 and R represent Rs and Rct, respectively. The phase element (CPE) has been introduced in the equivalent circuit instead of double-layer capacitance Cdl. Though the equivalent circuit simulated by the electrochemical impedance software is different from the previous research [8],
it can match the measurement results totally. The fitting results are shown by solid line in Figure 3 and the values of R1 and R2 are summarized in Table 1.

Table 1. Nyquist Analysis of LiFePO4/Li half-cell before and after charging.

|                | Before charging | After 2nd charging |
|----------------|-----------------|--------------------|
| R1 (Ohm)       | 4.6             | 6.1                |
| R2 (Ohm)       | 265.9           | 59.1               |

Table 1 displays the variation of R1 (Rs) and R2 (Rct) with charging process, respectively. It can be found that Rct decreases after charging process, revealing that the charge/discharge process enhance the transference performance of lithium-ion in the electrolyte. There is no obvious differences of Rs at before and after charging since it come from the intrinsic resistance of the electrolyte and electrode.

Figure 4. The discharging process (solid line) and the discharging stop position (circle mark) to obtain a certain DoD (a) (0%) (b) 25% (c) 50% (d) 75% and (e) 100% of LiFePO4/Li half-cell.

In order to study the EIS spectra of LiFePO4/Li half-cell during charging process, we measured the EIS of the battery cell with various DoD as shown in Figure 4. As mentioned before, DoD indicates the percentage of the battery that has been discharged relative to the overall capacity of the battery. Practically the samples were prepared by discharging the battery at a certain time with considering the time used to discharge until lower voltage cut off. For example, when the total discharging time is 10 hours, to obtain 25% DoD the battery is discharged for 2.5 hours at the same condition. After keeping for at least 1 h at room temperature, and measuring the EIS, the sample then fully charged and used for other DoD sample with similar manner. The EIS spectra of LiFePO4/Li half-cell at each DoD are shown in Figure 5.

Figure 5 shows the Nyquist plots of EIS spectra of LiFePO4/Li half-cell at various DoD. The solid lines indicate the simulation curve when equivalent circuits are employed. The Nyquist plots show the appearance of semicircle for all DoD. However, the semicircles are different one and others in the radius. The radius of the semicircle increased with the DoD. In order to investigate the changes in the EIS spectra of LiFePO4/Li half-cell due to discharging process, equivalent circuits are employed to fit the experimental data. The circuits used same with that for Figure 3, consisted of the intrinsic resistance (R1), charge transfer resistance (R2) and the double-layer capacitance which represented by CPE. It is clear that the equivalent circuit simulated by the electrochemical impedance model (solid line) are perfectly matched with the measurement results. The values of R1 and R2 are summarized in Table 2.
Figure 5. Nyquist Plot of LiFePO₄/Li half-cell impedance experimental data and their equivalent circuits.

Table 2 demonstrated the variation of R1, and R2 with various DoD. It is clear that there are no significant differences of R1 at entire DoD. R1 is the intrinsic resistance (Rs) which is related to the combined electrolyte and electrode material resistances, thus it may not be affected by charge/discharge process. While the R2 increased with the DoD. The higher the DoD the higher the R2. Here R2 is charge transfer resistance (Rct) which is originated from the electronic and ionic resistances at the electrode/electrolyte interface. The increase in Rct, revealing that the discharge process decreased the transference performance of lithium-ion in the electrolyte. In general, internal resistance of battery cell includes (a) ohmic resistance, (b) charge transfer resistance or active resistance, and (c) diffusion resistance known as concentration resistance [13,14]. Hence the increase in charge transfer resistance, enhance the battery internal resistance. In other word, internal resistance of battery growth along with the discharging process.

Table 2. Nyquist Analysis of LiFePO₄/Li half-cell with various DoD.

| DoD  | 0   | 25  | 50  | 75  | 100 |
|------|-----|-----|-----|-----|-----|
| R1 (Ohm) | 6.1 | 4.5 | 4.2 | 4.3 | 4.5 |
| R2 (Ohm)  | 59.1| 295.2| 391.0| 498.9| 616.0|

4. Conclusion

EIS measurements of assembled LiFePO₄/Li half-cell have been conducted at initial state (before and after charge/discharge process), and a certain depth of discharge (0-100%, DoD). Entire EIS spectra of LiFePO₄/Li half-cell show the appearance of semicircles. The radius of semicircle decreased with charging and increased with discharging processes. The EIS spectra can be fitted totally with an equivalent circuit, composed of the intrinsic resistance, charge transfer resistance and the double-layer capacitance which is represented by CPE. The charge/discharge did not affect the the intrinsic resistance significantly but affected the charge transfer resistance. It was found that the charge transfer resistance decrease with charging and increased with discharging. Since charge transfer resistance is a part of internal resistance, it was clear that the discharging or capacity loss increased the internal resistance of the LiFePO₄/Li half-cell.
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