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Electrochemical Properties of Olivine-Type LiFePO4/C Cathode Material for Lithium Ion Batteries

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Although olivine LiFePO₄ has been widely utilized as a cathode material for lithium ion batteries, there is still debate regarding the interpretation of the Nyquist plots of LiFePO₄ electrodes in the literature. In the present paper, the impedance spectra for lithium ion de-insertion and insertion in LiFePO₄ electrodes, with different percentages of graphite material serving as the conductive additive, were obtained at different potentials during the first charge-discharge cycle. The results reveal that the characteristic Nyquist plot of LiFePO₄ electrodes is strongly influenced by the content of the conductive additive. With increasing conductive content in the LiFePO₄ electrode, the characteristic Nyquist plot changes from a semicircle and an inclined line to two semicircles and an inclined line. The fundamental reason for this new phenomenon and the ascription of the time constants in the Nyquist plots of the LiFePO₄ electrodes are analyzed in detail based on simulated results of the experimental EIS data.

Keywords: lithium ion batteries, LiFePO₄, electrochemical impedance spectroscopy, conductive additive,

1. INTRODUCTION

For more than two decades, rechargeable lithium ion batteries (LIBs) have been widely utilized in many portable electronic devices due to their longer cycling life and higher energy density compared with other rechargeable batteries, and recently, LIBs have been implemented for electric and hybrid electric vehicle (EV/HEV) applications[1]. Olivine LiFePO₄ is at present a good candidate for the cathode material of lithium ion batteries because of its high theoretical capacity (170 mAh g⁻¹), low cost, acceptable environmental characteristics, cycling stability, and good thermal stability[2-7]. The major shortcoming of lithium iron phosphate lies in its poor conductivity (ionic and electronic), namely, sluggish mass and charge transport, which generally causes capacity losses at high charge-discharge currents[8]. Although several attempts have been made to improve the rate capability of LiFePO₄, such as coatings of conductive materials, doping of supervalent ions, minimizing the particle size, and developing new synthesis methods[9-14], the low intrinsic electronic conductivity is still a major challenge, the overcoming of which requires precise knowledge of the transport properties—the identification and comprehension of the kinetic mechanisms that are responsible for rapid charging and discharging in LiFePO₄ electrodes— that are not well-understood and need to be further explored.

Electrochemical impedance spectroscopy, EIS, is one of the most powerful electroanalytical techniques frequently used in the study of electrode kinetics[15-19], as it can provide unique information regarding the complex nature of electrode processes related to extensive time constants (demonstrated in terms of frequencies in EIS)[15-19], enabling the fundamental and systematic study of the electrode reactions and providing a deeper understanding of the underlying physical and chemical processes. In the past 30 years, numerous studies have been published on the application of EIS in the characterization of lithium ion batteries and their electrodes, as it allows for the prediction of the behavior of batteries and the determination of the factors limiting the performance of an electrode (such as its conductivity, charge-transfer properties, and properties of the passivation layer), which are of vital importance to improving the performance of lithium ion batteries and their electrodes [15-19].

An important problem with the application of EIS in electrochemical studies is that the interpretation of complex-plane impedance spectra related to complicated multistep electrode reactions, such as lithium intercalation into various intercalation compounds (e.g., graphite and transition metal oxides), may be highly ambiguous in practice due to the following facts. (i) The complex-plane impedance spectra commonly consist of only two types of elements, namely, semicircles and lines; thus, the many physically different procedures or separate stages of a complicated process give similar features in terms of impedance spectroscopy. (ii) The features related to different physical procedures or separate stages of a complicated process may overlap each other and become one element in Nyquist plots due to the subtle difference in their time constants[20].

For LiFePO₄, there is still debate regarding the interpretation of the AC-dispersions. It has been commonly reported in the literature[14,24-28] that the Nyquist plot of a LiFePO₄ electrode consists of two parts, namely, a semicircle in the high-frequency range, which is attributed to the charge transfer process (the charge transfer resistance coupled with the double-layer capacitance), and an inclined line in the low-frequency range reflecting the solid-state diffusion process. However, Jamnik attributed the semicircle in the high-frequency range of the Nyquist plot of a LiFePO₄ electrode to contact impedance between the electrode and current collector[21]. Moreover, Gaberscek reported that the Nyquist plot of a LiFePO₄ electrode consists of three parts, namely, a semicircle in the high-frequency range, and an inclined line in the low-frequency range, reflecting the solid-state diffusion process[22]. These researchers ascribed the semicircle in the high-frequency range to contact impedance (cathode/current collector); nevertheless, they could not be sure whether the semicircle in the mid-frequency range should be due to the interparticle resistance coupled with the double-layer capacitance or the charge transfer process. Thus, it can be reasonably concluded that the

interpretation of the Nyquist plot of $LiFePO_4$ electrodes in the literature is uncertain and confusing[14,21,22,24-28].

Practical battery electrodes are composite materials, in which the mass of active particles are bound to a current collector with a PVDF binder, and are usually prepared from a slurry of the particles and the binder in an organic solvent, which is spread on the current collector and followed by drying. Therefore, the preparation of composite intercalation electrode coatings, especially with manual preparation, may result in the nonhomogeneous distribution of the porous mass on the electrode—as is common with studies carried out in the laboratory, where the electrodes are mostly from manual production. The nonhomogeneous distribution of the porous mass may deteriorate the performance of the electrode and then have a significant influence on the Nyquist plot of the electrode, especially when the diameter of the active material particle is small, and the content of the conductive additive on the electrode is low.

Based on the above considerations, in this study, the processes of delithiation/lithiation in olivine LiFePO₄ electrodes with different weight percent (wt%) values of graphite as the conductive agent were investigated by cyclic voltammetry (CV) and EIS. It was found that the characteristic Nyquist plot is strongly influenced by the content of conductive additive, as was our presumption, and the ascription of the time constants in the Nyquist plots of the LiFePO₄ electrodes are discussed in detail according to simulated results for the experimental EIS data.

2. EXPERIMENTAL METHODS

The olivine LiFePO₄ electrode was prepared by spreading a mixture of olivine LiFePO₄ active material (provided by Shandong Bright Energy Material Limited Co., China), graphite (provided by Shanshan limited Co., Shanghai, China) and 10 weight percent (wt%) polyvinylidene fluoride binder (Kynar FLEX 910, Elf Atochem, Issaquah, WA, USA) dissolved in N-methyl-2-pyrrolidone solvent (Fluka Inc., St. Louis, MO, USA), followed by coating the slurry onto an aluminum foil current collector and drying at 60 °C. The weight percentages of the olivine LiFePO₄ active material were 80, 70, 60, and 40, and the respective weight percentages of graphite were 10, 20, 30, and 50 (termed LiFePO₄/G-10, LiFePO₄/G-20, LiFePO₄/G-30 and LiFePO₄/G-50). The average thickness of the electrode material coated on aluminum foil was 0.14 mm, and the loading of the active material coated on aluminum foil was 0.5 mg mm⁻².

Meanwhile, the graphite electrode used in this study consisted of 90 weight percent (wt%) graphite (Shanshan Limited Co., Shanghai, China) and 10% polyvinylidene fluoride binder. The electrolyte consisted of 1 mol L^{-1} LiPF₆ in a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1, volume ratio; Guotaihuarong Co., Zhangjiagang, China).

The phase identification was performed by powder XRD using Cu K α radiation on a Rigaku D/Max-3B diffractometer. Diffraction data were collected by step scanning over an angular range of 10-80° with a step width of 0.02° (35 KV, 30 mA). The particle morphologies of the samples were examined using a scanning electron microscope (SEM, USA, FEI QuantaTM 250).

All electrochemical impedance experiments were conducted in a three-electrode glass cell, with

Li foil serving as both auxiliary and reference electrodes, using an electrochemical work station (CHI660D; Chenhua Co., Ltd., Shanghai, China). The amplitude of the ac perturbation signal was 5 mV, and the frequency range was from 10^5 to 10^{-2} Hz. The electrode was equilibrated for 1 h before EIS measurements. The impedance data were analyzed using Zview software. Cyclic voltammetry (CV) measurements were carried out in a three-electrode glass cell, with Li foil as both auxiliary and reference electrodes, using an electrochemical work station (CHI660D; Chenhua Ltd., Co., Shanghai, China) between 2.5 V and 4.2 V with a scan rate of 0.05 mV s⁻¹. The charge/discharge cycles were carried out in a potential range of 2.5 V to 4.2 V at 0.2 C in a 2025 coin cell, and lithium metal was used as the anode.

3. RESULTS AND DISCUSSION

The joint committee for powder diffraction studies (JCPDS) of olivine LiFePO₄ and the XRD pattern of the LiFePO₄ are shown in Figure 1. All of the patterns are in good agreement with the JCPDS standard and can be indexed to the olivine structure with the space group *Pnma*.



Figure 1. JCPDS standard of olivine LiFePO₄ and the XRD pattern of commercial LiFePO₄.

Figure 2 shows typical SEM micrographs of the commercial LiFePO₄. It can be seen that the active material of the electrodes mainly consists of two types of particles that are agglomerated together, i.e., particles that have a diameter of 0.2 to 0.5 μ m, and particles that have a diameter of 1 to 1.2 μ m.

Figure 3 displays the first charge-discharge curves of LiFePO₄/G-10, LiFePO₄/G-20, LiFePO₄/G-30 and LiFePO₄/G-50, and the variations in the discharge capacity of olivine LiFePO₄ with cycle number. It can be seen that the charge/discharge curves of the cell have only one voltage plateau at approximately 3.4 V, which is a typical feature of olivine LiFePO₄, and can be attributed to the extraction and insertion of lithium ions. The initial specific discharge capacities of LiFePO₄/G-10, LiFePO₄/G-20, LiFePO₄/G-30 and LiFePO₄/G-50 are 146.9 mAh g⁻¹, 150.0 mAh g⁻¹, 149.5 mAh g⁻¹, 162.1 mAh g⁻¹, respectively. The disparity in voltage plateaus between the charge and discharge processes decreases with the increase in the content of the conductive additive in the electrode,

indicating that the polarization of the electrode improves with the increase of the content of the conductive additive. After 50 cycles, the capacity retentions are 51%, 98%, 99%, and 99%. Clearly, the conductive agent content of the Li/LiFePO₄ cell has a great influence on the performance of the cell.



Figure 2.SEM images of commercial olivine LiFePO₄ (a), graphite (b), LiFePO₄/G-10 (c), LiFePO₄/G-20 (d), LiFePO₄/G-30 (e) and LiFePO₄/G-50 (f).



Figure 3. (a) Charge-discharge curves of LiFePO₄/G-10, LiFePO₄/G-20, LiFePO₄/G-30 and LiFePO₄/G-50. (b) Variations in the discharge capacity with cycle number.

The CV profiles of the LiFePO₄ at a scan rate of 0.05 mV s⁻¹ are shown in Figure 4. Only one pair of redox peaks is observed in these CV profiles, and it characterizes the insertion and extraction of lithium ions in LiFePO₄[23]. It should be noted that the CV profiles of the LiFePO₄ electrodes with increasing weight percent of conductive agent show a more symmetrical and spiculate peak profile.



Figure 4. CV profiles with a scan rate of 0.05 mV s⁻¹ of LiFePO₄/G-10 (a), LiFePO₄/G-20 (b), LiFePO₄/G-30 (c) and LiFePO₄/G-50 (d).

This phenomenon should be attributed to the polarization of the electrode being improved with the increase in content of the conductive additive, in accordance with the charge-discharge test results.

The Nyquist plots of LiFePO₄/G-10, LiFePO₄/G-20 and LiFePO₄/G-30 at various potentials from 3.3 to 4.2 V during the first delithiation process are shown in Figure 5, and Figure 6 gives the following converse pathway. For the sake of clarity, each plot is shifted by 10 Ω along the real axis. It can be seen that the Nyquist plots at open circuit potential (OCP), namely, 3.3 V, all consist of two well-separated parts, namely, one semicircle in the high-frequency (HF) range and an inclined line in the low-frequency (LF) range, similar to the results reported in the literature[14,24-29], and the Nyquist plots do not change significantly during the whole charge-discharge process. As discussed in the introduction, the semicircle in the high-frequency region is commonly attributed to the charge transfer process (charge transfer resistance coupled with double-layer capacitance)[14,24-28]; however, Jamnik[21] attributed the semicircle in the high-frequency region to contact impedance between the

electrode and current collector.



Figure 5. Nyquist plots of LiFePO₄/G-10 (squares), LiFePO₄/G-20 (dots) and LiFePO₄/G-30

(triangles) at various potentials from 3.3 to 4.2 V during the first delithiation.

Moreover, it can be seen that the semicircle in the high-frequency region decreases with the increase of the content of the conductive additive in the LiFePO₄ electrode at the same potential, indicating the conductive agent content has a great influence on the interface resistance of cells, which corresponds to the CV and charge-discharge test results (namely, the semicircle in the high-frequency region should be attributed to contact impedance, as suggested by Jamnik[21]).



Figure 6. Nyquist plots of LiFePO₄/G-10 (squares), LiFePO₄/G-20 (dots) and LiFePO₄/G-30 (triangles) at various potentials from 4.1 to 3.0 V during the first lithiation.

If the semicircle in the high-frequency region is attributed to contact impedance, this puts forward a new question, namely, why there is no semicircle related to the charge transfer process in the Nyquist plot?





Figure 7. Nyquist plots of LiFePO₄/G-50 at various potentials from 3.3 to 4.2 V during the first delithiation.

Figure 8. Nyquist plots of LiFePO₄/G-50 at various potentials from 4.1 to 3.0 V during the first lithiation.

We suppose that this may be due to the semicircle related to contact impedance being too large, which makes the semicircle related to the charge transfer process move to a lower-frequency range. If the hypothesis is true, it can be reasonably deduced that there will be two semicircles in the Nyquist plot when the LiFePO₄ electrode contains sufficient content of the conductive additive, namely, the nonhomogeneous distribution of the porous mass on the electrodes improves.

Therefore, the Nyquist plots of the LiFePO₄ electrode with 50 wt% conductive additive (LiFePO₄/G-50) at various potentials from 3.3 to 4.2 V during the delithiation process are presented in Figure 7, and Figure 8 gives the following converse pathway. As we expected, it can be seen that the Nyquist plot at OCP (3.3 V) is comprised of three well-separated parts, that is, a semicircle in the highfrequency range (HFS), a quarter circle in the mid-frequency range (MFS) and an inclined line in the low-frequency range (LFIL). This property is different from those of LiFePO₄ electrodes with contents of the conductive additive below 30 wt%. With the increase in the electrode potential, the HFS does not change significantly during the whole charge-discharge process. The quarter circle in the midfrequency region, which is strongly potential dependent, shows an increasing tendency to move toward the real axis with the increase in the electrode potential, and at last, turns into a semicircle at 3.47 V; this is similar to the results of LiMn₂O₄[20], LiCoO₂[17] and graphite electrodes[19,30] as previously reported by our group, indicating the quarter circle in the mid-frequency region may be related to the charge transfer process. On further charging from 3.6 to 4.2 V, namely, the delithiation process is finished, the semicircle in the mid-frequency region converts into an arc, further demonstrating that the MFS is related to the charge transfer process. According to Gaberscek [22], the semicircle in the highfrequency range is ascribed to the contact impedance (cathode/current collector), and the inclined line in the low-frequency range reflects the solid-state diffusion process. However, they could not be sure whether the semicircle in the mid-frequency range should be due to interparticle resistance coupled with the double-layer capacitance or the charge transfer process. However, the results obtained in this study clearly show that the semicircle in the mid-frequency range should be attributed to the charge transfer process, and this will be further demonstrated below.

According to the experimental results obtained in this work, a simplified equivalent circuit model is used to fit the impedance spectra of the electrode during the first charge/discharge cycle, as shown in Figure 9. In the equivalent circuit, R_s is the ohmic resistance, and R_1 and R_2 are the resistances related to the HFS and MFS, respectively. The constant phase elements (CPEs) Q_1 and Q_2 are the capacitances related to the HFS and MFS, respectively. The low-frequency region, however, cannot be modeled properly by a finite Warburg element. We chose to replace the finite diffusion by a CPE, i.e., Q_D , which has been used to characterize graphite electrodes, allowing us to obtain a good superposition with the experimental data[31].



Figure 9. Equivalent circuit proposed for the analysis of the LiFePO₄ electrode in the charge-discharge

process.

The equivalent circuit parameters of the LiFePO₄ electrode obtained from simulation of the EIS experimental data at 3.3 V and 3.48 V are shown in Table 1. It can be seen that R_1 of the LiFePO₄ electrode decreases with increasing content of the conductive additive in the LiFePO₄ electrode at the same potential. The variations in the corresponding resistance of the semicircle in the high-frequency region (R_1) obtained from fitting the experimental impedance spectra of LiFePO₄/G-10, LiFePO₄/G-20, LiFePO₄/G-30 and LiFePO₄/G-50 as a function of the electrode potential in the first delithiation-lithiation process are shown in Figure 10. The variations in R_1 during the charge/discharge cycle are similar, although the content of the conductive additive in each LiFePO₄ electrode is different.

conductive agent	3.3 V		3.48 V	
	$R_{l}\left(\Omega ight)$	$R_{2}\left(\Omega ight)$	$R_{l}\left(\Omega ight)$	$R_{2}\left(\Omega ight)$
10	130.9	-	113.4	-
20	64.26	-	56.08	-
30	22.3	-	18.78	-
50	9.827	35.94	9,194	11.7

Table 1. Equivalent circuit parameters of LiFePO4/G-10 (a), LiFePO4/G-20 (b), LiFePO4/G-30 (c) andLiFePO4/G-50 (d) obtained from simulation of the EIS experimental data at 3.3 V and 3.48 V



Figure 10. Variation in R_1 as a function of the electrode potential, which is calculated by fitting the

experimental impedance spectra of LiFePO₄/G-10 (a), LiFePO₄/G-20 (b), LiFePO₄/G-30 (c) and LiFePO₄/G-50 (d) for the first charge/discharge cycle.

According to the theories of electrochemistry [17,19,32,33], the charge transfer resistance (R_{ct}) is given by the following:

$$R_{ct} = \frac{1}{fFAk_s x^{0.5} (1-x)^{0.5}}$$
(1)

where x is the insertion level, f denotes the usual electrochemical constant (equal to F/RT, with F and R being the Faraday and gas constants, respectively, and T being the absolute temperature), k_s is the heterogeneous rate constant, and A denotes the total electroactive surface area. Equation 1 points out that R_{ct} has nothing to do with the content of the conductive additive in the electrode. Meanwhile, equation 1 clearly predicts a rapid increase in R_{ct} with decreasing x when x < 0.5, a rapid decrease in R_{ct} with decreasing x when x > 0.5, and the minimum R_{ct} can be obtained when x = 0.5. It can be seen that R_1 for LiFePO₄ electrodes with different percentages of the conductive additive decreases with the increase in the electrode potential of the charge process and increases with the decrease in the electrode potential of the discharge process. This behavior does not behave according to equation 1, and it can be concluded that the ascription in the literature of the semicircle in the high-frequency range to the charge transfer process [14,24-28] may be a mistake. Therefore, the semicircle in the high-frequency range is ascribed to the contact impedance between the electrode and current collector, as suggested by Jamnik [21]. To further demonstrate the above assumption, impedance spectra of the blank electrode without LiFePO₄, namely, the graphite electrode comprised of 90 wt% graphite and 10 wt% polyvinylidene fluoride binder and commonly used as an anode, are recorded at various potentials from 3.0 to 4.2 V. Figure 11 displays a sequence of characteristic Nyquist plots recorded at various potentials from 3.3 to 4.2 V. It can be seen that the Nyquist plot of the graphite electrode at OCP (3.3 V) consists of two well-separated parts, namely, one semicircle in the high-frequency range and an inclined line in the low-frequency range, which are similar to those of LiFePO₄ electrodes with the percent of graphite material as the conductive additive below 50 wt%. It has undoubtedly been demonstrated that the semicircle in the high-frequency region corresponds to contact impedance, and the inclined line in the low-frequency region represents the blocking character of the delithiated electrode at equilibrium potential [19,34,35]. With the increase in the electrode potential from a potential of 3.3 to 4.2 V, the characteristic Nyquist plots of the graphite electrode remain nearly invariable. The variations in the corresponding resistance of the semicircle in the high-frequency range (R_1) obtained from fitting the experimental impedance spectra of the graphite electrode as a function of the electrode potential from 3.3 to 4.2 V are shown in Figure 12.



Figure 11. Nyquist plots of the graphite electrode at 3.30 V, 3.47 V and 4.2 V.

It can be seen that R_1 of the graphite electrode decreases with increasing electrode potential during the charge process and increases with the decreasing electrode potential during the discharge process. This behavior is also similar to those of the LiFePO₄ electrodes with different percentages of the conductive additive, further demonstrating that the semicircle in the high-frequency range of the Nyquist plots of the LiFePO₄ electrodes with different percentages of the conductive additive should be mainly related to the contact impedance.



Figure 12. Variation in R_1 as a function of the electrode potential, which is calculated by fitting the experimental impedance spectra of the graphite electrode during the first charge/discharge cycle.

The variations in R_2 obtained from fitting the experimental impedance spectra of LiFePO₄/G-50 as a function of the electrode potential in the charge-discharge process are shown in Figure 13. As can be seen for the lithium ion desertion process, namely, in the potential range of 3.3-3.7 V, R_2 first decreases and then increases with the increase in the electrode potential; a similar variation trend is shown for the discharge process, in accordance with the prediction of equation 1, demonstrating that the semicircle in the mid-frequency range of the Nyquist plots measured for the LiFePO₄ electrode is related to the charge-transfer process. Furthermore, with increasing electrode potential, R_2 remains nearly invariable below 3.3 V and above 3.7 V during the charge process, corresponding to an interparticle resistance that does not change significantly during the delithiation-lithiation process. Thus, it can be concluded that the semicircle in the mid-frequency region may be related to not only the charge-transfer step but also the interparticle impedance.



Figure 13. The variation in R_2 as a function of the electrode potential, which is calculated by fitting the experimental impedance spectra of LiFePO₄/G-50 during the charge/discharge cycle.

Considering that the interparticle resistance should not change substantially during the delithiation-lithiation process, variations of the semicircle in the mid-frequency region can be mainly attributed to the charge transfer process.

4. CONCLUSIONS

The electrochemical impedance spectra of LiFePO₄ electrodes, with different percentages of graphite material serving as the conductive additive, were collected as a function of potential in the delithiation-lithiation process. The results revealed that the characteristic Nyquist plot of the LiFePO₄ electrode is strongly influenced by the content of the conductive additive, namely, with increasing content in the LiFePO₄ electrode, the characteristic Nyquist plot changes from a semicircle and an inclined line to two semicircles and an inclined line. When the content of the conductive additive in the LiFePO₄ electrode is below 30 wt%, the Nyquist plot provides a semicircle in the high-frequency (HF) region and an inclined line in the low-frequency region; thus, the semicircle in the high-frequency range cannot be ascribed to the charge transfer process but to the contact impedance between the electrode and current collector. When the content of the conductive additive in the LiFePO₄ electrode is 50 wt%, the Nyquist plot consists of three well-separated parts, namely, two semicircles and an inclined line. It was found that the depressed semicircle in the high-frequency range can be ascribed to the interparticle resistance and charge transfer process; however, its variation as a function of the electrode potential is primarily due to the charge transfer resistance.

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