Revisiting the electrochemical impedance behaviour of the LiFePO_4/C cathode

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Abstract. In the present work, the electrochemical behaviour of LiFePO_4/C electrode has been reported. Specially, the electrochemical impedance spectroscopies (EIS) have been studied in detail. The discharge capacity is more than 120 mAh/g. There are two semicircles being found in the Nyquist plot for the cycled electrode and one semicircle for the as-prepared electrode. It is found that the interface capacitance is in an order of magnitude of $10\ \mu\text{F}/\text{cm}^2$ for the high-frequency semicircle, while for the second semicircle the interface capacitance is $5.3\sim 45.4 \times 10^3\ \mu\text{F}/\text{cm}^2$. It could be concluded that the high-frequency semicircle is to correspond to the charge transfer process. The function of the carbon layer is also briefly discussed.

Keywords. Lithium ion battery; impedance spectroscopy; electrochemistry; lithium iron phosphate.

1. Introduction

Recently, phosphates with olivine-type structure have attracted more attention, since Padhi *et al.*¹ demonstrated that LiFePO_4 can be used as cathode electrode materials in lithium ion rechargeable batteries. The electrochemical performance of pure phase phosphates is not satisfactory. The electrochemical activity can be improved via carbon-coating, element-doping, separator surface modification^{2–9}, etc. Most researchers accepted one of the basic facts that pure phosphor-olivine materials are almost electrochemically inactive while carbon-coating can obviously increase its discharge capacity, just because of the improved conductivity.

For carbon-coated LiFePO_4 electrode, its schematic model is showed in figure 1. Based on the majority of literatures, this carbon layer should be a solid, not a porous. The bulk is LiFePO_4 and the carbon thin film separates the bulk materials from the electrolyte. The charge exchange process should take place at the LiFePO_4 /electrolyte interface for pure phase LiFePO_4 electrode, and at carbon film/electrolyte interface for carbon-coated LiFePO_4 electrode. The carbon film/electrolyte interface may have a better electrocatalytic activity than the LiFePO_4 /electrolyte inter-

face. In other words, the improvement of the electrochemical activity could be one of the main reasons to improve the electrode capacity, at least the possibility can not be excluded at the moment. Pure phase LiFePO_4 electrode should have a satisfied electrochemical capacity at an enough small discharge-charge current density, if the low conductivity is the unique reason for its bad electrode capacity.

In this article, the electrode properties of LiFePO_4/C have been investigated. There are a series of electrochemical techniques to study the electrode process kinetics^{10–12}. The electrochemical impedance spectroscopy (EIS) was selected in this work because it is more sensitive to the multi electrode processes.

2. Experimental

Lithium iron phosphate was prepared via solid-state reaction method. The used chemicals were CH_3COOLi (AR), $\text{C}_6\text{H}_5\text{O}_7\text{Fe}\cdot 3\text{H}_2\text{O}$ (AR), $\text{NH}_4\text{H}_2\text{PO}_4$ (AR) and sucrose (AR). All chemicals were mixed in a stoichiometric ratio and the added amount of sucrose is 10 % of total mass. The precursor was wetly ball-milled using alcohol as the solvent. The ball-milling duration was set at 3 h and the rotating rate was set at 200 rpm. The ball-milled precursor firstly decomposed at the temperature of 300°C for 3 h in N_2 atmospheres. After decomposition, the precursor was then ball-milled for additional 1 h. Then, the precursor was pressed into

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Figure 1. The schematic diagram of the interface for as-prepared LiFePO_4 electrode.

a tablet form, and the tablet was heated at the temperature of 700°C for 20 h in N_2 -atmosphere and then naturally cooled to ambient temperature. Finally, black-colour powders have been obtained. The X-ray powder diffraction (XRD) with $\text{Cu K}\alpha$ radiation was used to identify the phase composition.

The mixture of active materials, PvDF binder and Super-P conductive (weight ratio is 8:1:1) was pressed onto Al mesh. The used electrolyte is 1M $\text{LiPF}_6/\text{EC}+\text{DMC}(\text{v/v}, 1:1)$, the reference electrode and the counter electrode are Li metal pressed onto nickel foam substrate. In addition, 2016-type coin cell was also assembled to measure its electrochemical capacity.

Galvanostatic discharge-charge, cyclic voltammograms and EIS were carried out at CHI-660C or PE Parc 2273 electrochemical stations. For EIS measurement the applied amplitude was 5 mV and the frequency ranged from 100 K to 0.001 Hz. The EQUIVCRT and ZsimpWin software were used to fit the impedance data.

3. Results and discussion

The XRD pattern is showed in figure 2, from which it is clear that there is a olivine-type structure, and no other impurity is detected. Figure 3 shows the discharge-charge curves of the LiFePO_4 electrodes at two different current densities. It can be found that the rate dischargeability is not satisfactory, in comparison with the data reported.⁹ From figure 3, the total polarization resistance of the 2016 type cell is evaluated to be $13.8 \Omega \cdot \text{g}$ or $580 \Omega \cdot \text{cm}^2$. The measured cyclic voltammogram is showed in figure 4. The scanning rate is set at 1 mV/s . The oxidation and reduction peak potentials are 3.63 V and 2.94 V. Based on electrochemistry theory, the potential difference of oxidation and reduc-

Figure 2. The XRD pattern of the prepared sample.

tion peak potentials for a reversible reaction is 59 mV at 298 K. The peak potential difference is 690 mV for the used LiFePO_4/C electrode and much more than the peak potential difference of the reversible reaction, which may be due to the larger in-series resistance of electrolyte and binder.

The Nyquist plot in figure 5 is captured at the open circuit potential of 3.284 V on the as-prepared electrode. The basic characteristic is that it comprised of one semicircle and a straight line that is believed to be related with the diffusion process. After 5 discharge-charge cycles, the basic characteristics of impedance spectroscopy changed qualitatively, as shown in figure 6. There are two semicircles followed by a straight line. The manifestation of the second

Figure 3. The charge-discharge curves of LiFePO_4 electrode. The curve 1 was measured with 2032 cell and the curve 2 with three-electrode compartment.

Figure 4. The cyclic voltammogram for LiFePO_4/C electrode (scanning rate is 1 mV/s).

semicircle may provide some useful information on the Li intercalation–deintercalation mechanism. There are many literatures reporting the nature of two semicircles. Wu *et al.*¹³ reported the impedance measured on mesocarbon microbeads (MCMB) electrode and concluded that the high-frequency semicircle represents the resistance and capacitance of solid electrolyte interphase (SEI) and the second semicircle is related to the charge exchange process at the electrical double layer. In literature,¹⁴ there is only one semicircle at higher potential, but two semicircles when the electrode potential decreased below 1.0 V . The manifestation of the second semicircle was attributed to the formation of SEI layer at the electrode surface. Ogumi

Figure 5. The nyquist plot of as-prepared LiFePO_4/C electrode. The data was captured at open circuit potential of 3.284 V with amplitude of 5 mV .

*et al.*¹⁵ have also attributed the high-frequency semicircle to the formation of surface SEI layer at natural graphite electrode and Yoon *et al.*¹⁶ are of the same opinion. On the other hand, there is almost no report concerning the impedance data of pure-phase LiFePO_4 electrode, the authors guessed, which may be due to its too poor electrochemical activity. But there are literatures reporting the impedance measurement for carbon-coated LiFePO_4 electrode. Two semicircles were found in the Nyquist plots at LiFePO_4/C /polymer electrolyte interface,¹⁷ one is attributed to the charge exchange process and another is believed to be related to the polymer electrolyte film. Two semicircles manifest themselves at $\text{LiFe}_{0.9}\text{Mg}_{0.1}\text{PO}_4/\text{C}$ after cycled in $1\text{M LiPF}_6/\text{EC}+\text{DEC}+\text{DMC}+\text{EMC}$ electrolyte.¹⁸ The high frequency semicircle was attributed to the SEI formation and the second one is due to the charge exchange process. There exists only one semicircle in Nyquist plot for carbon-coated LiFePO_4 electrode in most public literatures.^{12,19–21} We have found that most of the authors preferred to accept such a conclusion: the semicircle is just the representation of the charge transfer process if there is only one semicircle; the high-frequency semicircle corresponds to the migration of Li-ion through the SEI layers while the intermediate frequency semicircle represents the charge transfer process when there are two semicircles. We proposed an opposite opinion based on our analysis. In this article the impedance data were analysed by EQUIV-CRT and ZsimpWin software with the equivalent circuit $R(RQ)(Q(RW))$ and the results are presented in table 1.

For the as-prepared electrode (figure 5), there is no SEI layer formed at the surface. As a result, there is no contribution from the SEI layer to the measured impedance and only one semicircle manifests itself in the Nyquist plot. In such a condition, the unique semicircle must represent the charge transfer process. Fitting the data showed that the corresponding resistance element is 5.334Ω and the Q element is 8.06×10^{-5} ; after 5 cycles, there are two semicircles and the corresponding Q elements are $\sim 10^{-5}$ and ~ 20 , respectively, depending on the state of charge. Note that the (RQ) part of the equivalent circuit $R(RQ)(Q(RW))$ represents the semicircle in the high-frequency domain while it is just the equivalent circuit $(Q(RW))$ to relate with the intermediate frequency semicircle and the sloping line. It is reasonable only if it is considered that, the high-frequency semicircle for the cycled electrodes and the unique one for the as-prepared electrode represent one same electrode reaction step. Attributing high-frequency semicircle to the migration through SEI layer will lead to the impedance spectroscopy for the as-prepared electrode can not be reasonably explained.

Figure 6. The Nyquist plots of LiFePO₄/C electrode after 5 charge–discharge cycles. (a) 100 % state of charge, 303 K, (b) 0 % state of charge, 303 K, (c) 0 % state of charge, 283 K, (d) 50 % state of charge, 280 K, (e) 50 % state of charge, 303 K.

Table 1. The simulated parameters by using an equivalent circuit R(RQ)(Q(RW)).

	As-prepared	100 %SOC, 303 K	0 %SOC, 303 K	0 %SOC, 283 K	50 %SOC, 303 K	50 %SOC, 283 K
R1	2.145	5.64	2.14	2.55	2.23	2.93
R2	5.334	21.2	5.07	6.82	3.933	6.903
Q3	8.06E-5	2.77E-5	5.22E-5	4.8E-5	2.99E-5	3.52E-5
N3	0.81	0.73	0.85	0.834	0.9	0.86
CC*	16.7	2.13	15.9	12.4	14.5	11.8
Q4	-	0.024	0.027	0.0234	0.0212	0.0208
N4	-	0.66	0.62	0.686	0.52	0.54
R5	-	9.16	53.16	128.1	9.415	38.15
CC**	-	12.6	37.2	45.4	5.3	17.1
W6	0.037	0.325	0.136	0.0467	0.219	0.0749

*: the calculated capacitance value, $\mu\text{F}/\text{cm}^2$;

**: the calculated capacitance value, $\times 103 \mu\text{F}/\text{cm}^2$.

Based on the above mentioned analysis, we considered that the high frequency semicircle should represent the charge transfer step. Such a conclusion is controversial with the traditional viewpoint.

Based on the dependence of the EIS vs. the temperature, some parameters can be calculated. The calculated exchange current density has a magnitude of 0.2 A/g. If the Arrhenius equation is assumed to be available, then the corresponding activation energy is about 13.6 kJ/mol and 59.0 kJ/mol for the states of charge with 0 % and 50 %, respectively. Larger activation energy is believed to be the main factor decreasing its discharge capacity at lower temperature.

For the as-prepared LiFePO_4/C electrode, there is no SEI formed at the surface, as a result, there is no contribution from SEI layer to the impedance, but the charge exchange step does contribute to the impedance. In such case the surface model is showed in figure 1 and the impedance spectroscopy figure 5 does just correspond figure 1. After cycling for 5 times, the SEI is formed. In this case the interface model is proposed, as showed in figure 6, in which a SEI layer is clear to see. The migration process of lithium ion through SEI layer leads to the manifestation of the additional semicircle in Nyquist plots, as showed in figure 7.

After analysing the data reported in literature²² (the carbon density is assumed to be 2.2 g/cm³ and the LiFePO_4 2.5 g/cm³, carbon content is 1.9 wt.% and the particle size is 5 μm), it is assumed that the carbon film covers the particle homogeneously, then the carbon thin film at the particle surface should be more than 25 nm. If the diffusion coefficient of lithium ion in carbon material was assumed to be 10⁻¹⁰ cm²/s,^{14,23,24} the utmost current density is about 0.06 A/cm² or 720 A/g. As the particle size decreases, the possible

maximum current density increases, because the carbon layer becomes thinner. From the above analysis it can be seen that the diffusion of lithium ion through the thin carbon film does not limit the electrode performance in principle and the thin carbon film should have no contribution to the manifestation of two semicircles in Nyquist plot.

Constant-phase elements $Z_{CPE} = Q(j\omega)^n$ have been used for fitting the impedance data. According to the literature,¹⁰ the following equation can be used to calculate the interface capacitance,

$$(Y_0 R_{ct})^{1/n} \sin \frac{n}{2} \pi = C_{dl} R_{ct}.$$

The true reaction electrode area can be calculated with the equation

$$S_{true} = \frac{3m}{2r\rho}.$$

Here the m is the mass of active materials, r is the radius of the particle, ρ is density. In this equation it is assumed that the half of active particle is embedded in the binder. Using the above-mentioned equations, the interface capacitance can be calculated, as shown in table 1. It can be evaluated that the interface capacitance for as-prepared electrode is 16.7 $\mu\text{F}/\text{cm}^2$. After cycled for several times, the interface capacitance that corresponds to the high-frequency semicircle is in the range of 2~16 $\mu\text{F}/\text{cm}^2$ while the one that corresponds to the second semicircle has an order of magnitude of ten thousands $\mu\text{F}/\text{cm}^2$. These data have indirectly confirmed the correctness and reliability of our analysis. According to literature,²⁵ the double layer capacitance for metallic electrode is about 20 $\mu\text{F}/\text{cm}^2$. The calculation of the interface capacitance has also supported our conclusion that the high-frequency semicircle is to correspond to the charge exchange process.

In the above discussion, an assumption is not mentioned but is understandable that the LiFePO_4 particle is entirely coated by carbon film (left diagram in figure 8). It is impossible if the preparation process is able to give

Figure 7. The schematic diagram of the impedance for cycled LiFePO_4 electrode.

Figure 8. The model for carbon-coated LiFePO_4 particles.

LiFePO₄ particles covered partly by carbon and that a free surface can survive (right diagram in figure 8). During cycling, the carbon thin film will be separated from LiFePO₄ bulk, if the particle surface is assumed to be partly covered by carbon film and there exists free surface. But until now, there is still no report available concerning delamination phenomenon of carbon film from bulk particle.

The improvement in the conductivity of carbon-coated LiFePO₄ is accepted by most of researcher as the main reason why its electrode capacity is increased obviously. Such a conclusion is not entirely reasonable. If it is right, then the pure phase LiFePO₄ should exhibit a satisfied discharge capacity when the current density is small enough. But indeed, the capacity is still very small at low discharge current. The main factor that causes the capacity of LiFePO₄ to be low is the poor electro-catalytic activity of pure-phase LiFePO₄ at which the total electrochemical process is controlled by the charge transfer step. At least the possibility can not be absolutely excluded at the moment. It is believed that, the SEI formed at pure-phase LiFePO₄ is instable or of low electro-catalytic. When the interface of LiFePO₄/electrolyte is replaced by LiFePO₄/C film/SEI/electrolyte interface, the charge exchange rate is increased obviously, because the SEI formed at carbon materials is high electro-catalytic. It should be pointed out that the SEI mentioned in the article maybe different from that formed at anode carbon materials. However, it is already evidenced that the SEI layer formed at anode carbon surface is suitable for reversible Li-ion migration.

At last let us evaluate the diffusion coefficient in LiFePO₄ particle. The equation in the literature²⁶

$$\sigma = \frac{RT}{n^2 F^2 A^{0.5} \sqrt{2DC}}$$

is used to evaluate the diffusion coefficient. The diffusion coefficients in carbon film and bulk particle was assumed to be D_1 and D_2 , respectively and the corresponding length is l_1 and l_2 , then the apparent diffusion coefficient D has the following form

$$D = \frac{l_1 + l_2}{D_1 l_2 + D_2 l_1} D_1 D_2.$$

For carbon coated LiFePO₄, we can directly say, $D \approx D_2$ because the carbon thin film has a smaller thickness and the diffusion in carbon film is far faster than that in LiFePO₄ phase. When the average particle size is assumed to be 1 μm , based on the true reaction area, the diffusion coefficient is about 2.2 and $1.9 \times 10^{-19} \text{ m}^2/\text{s}$, at 303 and 283 K, respectively, which is in agreement with the data.^{27,28}

4. Conclusions

In this article, the carbon coated LiFePO₄ electrode was investigated. The discharge capacity is more than 120 mAh/g. The CV measurement has shown a larger peak potential difference. It is found that the two semicircles manifest themselves in the Nyquist plot for the electrode cycled for 5 times while only one semicircle can be found for the as-prepared electrode. After analysing the simulated parameters, it could be concluded that the high frequency semicircle should represent the charge-transfer step. The increased electrode capacity of carbon-coated LiFePO₄ is not only due to the improved conductivity, but also to the increased electro-catalytic activity for charge exchange process. Replacing the LiFePO₄/electrolyte interface by the LiFePO₄/carbon thin film/electrolyte is the uppermost reason, in other words, the carbon film functions as an excellent electro-catalyst. The calculation gives a diffusion coefficient of 1.9 and $2.2 \times 10^{-19} \text{ m}^2/\text{s}$ for the electrode of 50% state of charge at 283 and 303 K, respectively.

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