

流变相法制备倍率性能优异的 LiFePO_4/C 复合材料

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摘要: 以月桂酸为碳源和表面活性剂, 氢氧化锂、碳酸锂和醋酸锂为锂源, 采用流变相法制备 LiFePO_4/C 复合材料。运用 X 射线衍射(XRD)、扫描电子显微镜(SEM)、粒度分析、恒流充放电测试、循环伏安以及交流阻抗测试等方法对复合材料进行表征。结果表明, 不同的锂源对 LiFePO_4/C 复合材料的结构和电化学性能均有很大影响, 以氢氧化锂为锂源合成的 LiFePO_4/C 材料展示出最佳的循环性能和倍率性能。该材料在 0.1C 下放电比容量为 $153.4 \text{ mAh}\cdot\text{g}^{-1}$, 在大倍率 10 C 下, 容量保持率仍可达 76%, 甚至 10C 下循环 800 次后, 容量衰减率仅有 4%, SEM 结果显示该材料具有较小的粒径($\sim 200 \text{ nm}$), 且分布集中, 有效提高了电子迁移速率, 从而改进了 LiFePO_4/C 的倍率性能。

关键词: LiFePO_4/C ; 流变相法; 锂源; 高倍率

中图分类号: O646; TB33; TM912.9

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LiFePO_4/C Composite with Excellent Rate Capability Synthesized by Rheological Phase Method

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Abstract: LiFePO_4/C was synthesized by rheological phase method (a soft chemical method) using lauric acid as the carbon source and surfactant, lithium hydroxide, lithium carbonate and lithium acetate as the lithium source. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), particle size analysis, constant-current charge/discharge test, cyclic voltammetry (CV) and electrochemical impedance spectra (EIS). The results show that the effect of the lithium source on the morphology and the electrochemical performance of LiFePO_4/C composites is great. The LiFePO_4/C sample with lithium hydroxide as the lithium source exhibits the best cycling performance and rate capability. It shows a specific capacity of $153.4 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C, a capacity retention rate of 76% at high current density of 10 C, and a lossing rate of 4% at 10C after 800 cycles. The excellent performance of this LiFePO_4/C is attributed to the smaller size ($\sim 200 \text{ nm}$) and the narrower particle size distribution.

Key words: LiFePO_4/C ; rheological phase method; lithium sources; high rate

After the discovery of olivine-structured LiFePO_4 in 1997 by Goodenough and co-workers^[1], the material has always been one of the hottest cathode active

materials for Lithium-ion batteries. Recently, rapidly capacity fading of LiFePO_4 at high current density has been a bottleneck problem, which limits the

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application in large electric drives. Padhi et al^[1] showed that discharging would be ended when the discharging current increased and the lithium-ions of $\text{LiFePO}_4/\text{Li}_{1-x}\text{FePO}_4$ interface were not enough to preserve the current of discharge, so it is an useful way to improve the specific capacity at high rate by enhancing the diffusion rate of Li^+ . Some references^[2-5] reported that smaller particle size of LiFePO_4 could shorten the diffusion distance of Li^+ , which is beneficial to the enhancement of diffusion rate; uniformly distributed carbon layer on the surface of active powder can make sure the homogeneous insertion/deinsertion of Li^+ . So via reducing the particle size and improving the carbon coating, the bottleneck problem of LiFePO_4 can be achieved a breakthrough.

At present, various synthetic routes, such as solid state reaction^[6-8], sol-gel reaction^[9-10], co-precipitation reaction^[11-12], hydrothermal reaction^[13-14] and microwave heating reaction^[15-16] etc, have been applied to synthesize LiFePO_4 . For solid state reaction, simple preparative technology and devices make it to be beneficial to industrial production, but by this route, particles obtained are usually with irregular morphology, non-uniform particle size distribution, and the higher calcining temperature and longer calcining time would also cause tremendous energy consumption. Sol-gel reaction and co-precipitation reaction both belonging to liquid phase method are similar to some degree, such as the mixing of the raw materials in molecular scale, the narrower size distribution and the smaller particle size of the product. But the preparing condition of sol-gel reaction is harsh, moreover, particles are easy to agglomerate in stoving and calcination process, in view of these, it is difficult to scale up this method into industrial application. For co-precipitation reaction, different sedimentation rates and equilibrium solubility of components affect the stoichiometric ratio of the elements in the product, which is a significant impact factor on the products performance. The hydrothermal method is another kind of liquid phase reaction, owning some advantages mentioned above. But the hydrothermal reaction under high temperature and high pressure is more complex

and is hard to control in reactor, therefore a higher qualification is needed for equipment to meet the harsh reaction condition.

In this work, we resolved the problem that the capacity of LiFePO_4 faded rapidly at high rate through controlling the particle size of LiFePO_4 . The rheological phase method combines the advantages of solid state reaction and liquid state reaction, such as decreasing energy consumption, reducing the particle size of the product and being suitable for industrial production. LiFePO_4/C synthesized by the rheological phase method has excellent rate capability because of its smaller particle size. We also studied the effect of different lithium sources on the performance of samples.

1 Experimental

1.1 Synthesis of LiFePO_4/C

The LiFePO_4/C composites were prepared by rheological phase method. Iron phosphate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, AR), lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$, AR), lithium carbonate (Li_2CO_3 , AR), lithium acetate ($\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, AR) and lauric acid ($\text{C}_{12}\text{H}_{24}\text{O}_2$, AR) were used as raw materials. $\text{LiOH} \cdot \text{H}_2\text{O}$, Li_2CO_3 and $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ were separately mixed with stoichiometric amount of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and grounded for 2 h to get a solid reactant mixture, which was then mixed with lauric acid dissolved in ethanol and grounded for 1 h to get a solid-liquid rheological body, it looked like a kind of mushy slurry. Then, the different rheological bodies were calcined at 650 °C in a tube furnace for 6 h under nitrogen flow, then naturally cooled to room temperature to obtain the LiFePO_4/C composites. The products prepared with lithium hydroxide, lithium carbonate, lithium acetate as lithium sources are marked with A, B, C, respectively.

1.2 Materials characterization

The crystalline structure of each product was characterized by X-ray diffraction (XRD, Philips X'Pert PW1730) with $\text{Cu K}\alpha$ radiation ($\lambda=0.15418\text{ nm}$) at scanning angle of 10°~80° and scanning rate of 8°·min⁻¹. The particle morphology and particle size of samples were observed by scanning electron microscopy (SEM, SPA400 Seiko Instruments). The

particle size distribution was tested by JL-1155 laser particle size distribution tester. The carbon content was tested by CS-902 analytical instrument.

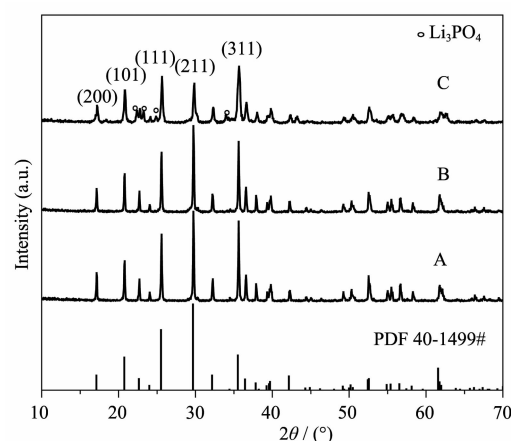
1.3 Electrochemical characterization

To make electrode, 80wt% LiFePO_4/C composite, 13wt% acetylene black and 7wt% of polyvinylidene fluoride (PVDF) were mixed in N-methylpyrrolidone (NMP) as solvent. The obtained slurry was then deposited uniformly onto a thin Al foil, and dried in vacuum at 80 °C for 10 h. The dried filmed Al foil was cut into disks as cathode electrode. The electrolyte was 1 mol·L⁻¹ LiPF_6 dissolved in ethylene carbonate (EC), diethylene carbonate (DEC) and dimethylene carbonate (DMC) with a molar ratio of 1:1:1. The Li foil was used as anode and the Celgard 2400 as the separator. The coin-type cells were assembled in a glove box filling with argon. The cells were measured by galvanostatic constant current charging/discharging tests with the potential range of 2.5~4.3 V using a battery test system (Neware BTS-610) at room temperature (25 °C). The cyclic voltammetry (CV) and electrochemical impedance(EIS) of the cell were conducted by a CHI660B electrochemical work station, CV tests were carried out in the potential range of 2.5~4.3 V at a scanning rate of 0.10 mV·s⁻¹.

2 Results and discussion

2.1 Structure and morphology analysis

Fig.1 shows the X-ray diffraction patterns of the LiFePO_4/C synthesized with different lithium sources. Compared with the normal pattern of LiFePO_4 (PDF

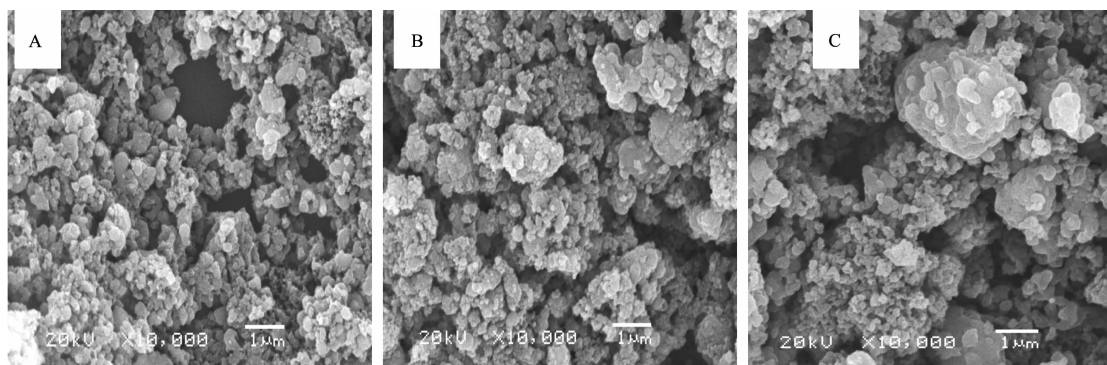


(a) $\text{LiOH} \cdot \text{H}_2\text{O}$; (b) Li_2CO_3 ; (c) $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$

Fig.1 XRD patterns of LiFePO_4/C synthesized with different lithium sources

No.40-1499), the crucial diffraction peaks of three samples are well matched with the standard of an orthorhombic olivine-type structure with a space group of $Pnma$. All the peaks of sample A and B are sharp without any peaks of impurities, which proves that the product is well-crystallized. However, the pattern of sample C appears an obvious impurity Li_3PO_4 , analyzed by Jade 5.0, which indicates that reaction of the raw materials are incomplete, in addition, the wide and weak peaks suggest the poor crystallinity. No residual carbon-related diffraction peak is detected here, which indicates that the residual carbon is amorphous and the carbon can not affect the crystalline structure of LiFePO_4 .

Fig.2 shows the SEM images of LiFePO_4/C synthesized with different lithium sources. All the samples used lauric acid as carbon source and the carbon content is about 2.3%. Sample A has the



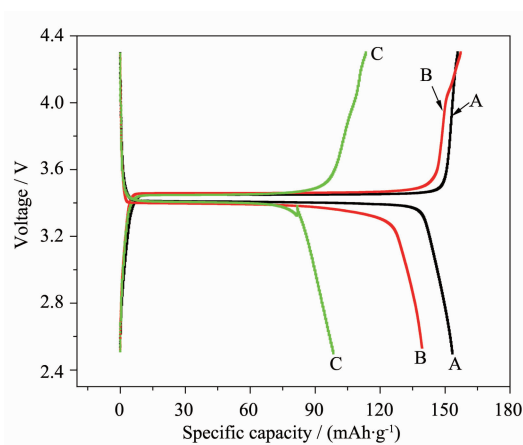
(a) $\text{LiOH} \cdot \text{H}_2\text{O}$; (b) Li_2CO_3 ; (c) $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$

Fig.2 SEM images of LiFePO_4/C synthesized with different lithium sources

smallest particle size of about 200 nm and uniform size distribution; the particle size of sample B is also small but the distribution is non-uniform and some primary particles seem a little agglomerated; the particle size of sample C is big and agglomerate even more seriously. Smaller particles have large specific surface area, which contribute not only to the effective contact of electrolyte and the surface of LiFePO_4 , but also to the diffusion of Li^+ , so we anticipate that the sample synthesized by lithium hydroxide based rheological phase method will have the optimal performance. It indicates that the various systems of raw materials has great effect on the morphology of products. FePO_4 is neutral and lauric acid is acidic, so compared with other lithium source, lithium hydroxide with strong alkaline can mix with FePO_4 and lauric acid well to reach the homogeneity of molecular level. At the same time, the rheological phase method integrates the advantages of solid-phase method and liquid-phase method, which makes the homogeneous system with certain viscosity to decrease the particle size.

2.2 Electrochemical cycling test

Fig.3 shows the initial charge-discharge curves of LiFePO_4/C synthesized with different lithium sources at 0.1C. From the curves, all the samples have stable charge-discharge platform located at 3.45/3.4 V, corresponding to the redox plateau potentials of $\text{Fe}^{2+}/\text{Fe}^{3+}$, the charge capacity of samples A, B and C is

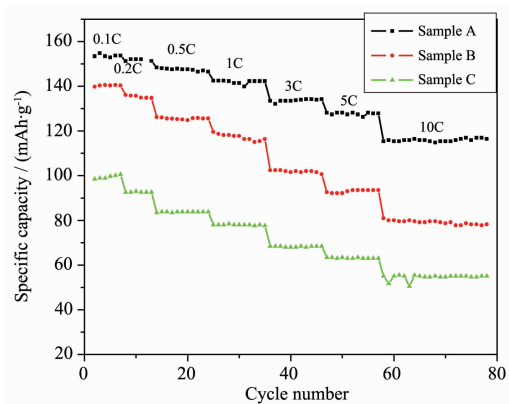


(a) $\text{LiOH} \cdot \text{H}_2\text{O}$; (b) Li_2CO_3 ; (c) $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$

Fig.3 Initial charge-discharge curves of LiFePO_4/C with different lithium sources at 0.1C

155.8 $\text{mAh} \cdot \text{g}^{-1}$, 157.2 $\text{mAh} \cdot \text{g}^{-1}$ and 113.5 $\text{mAh} \cdot \text{g}^{-1}$, the discharge capacity of samples A, B and C is 153.4 $\text{mAh} \cdot \text{g}^{-1}$, 139.7 $\text{mAh} \cdot \text{g}^{-1}$ and 98.4 $\text{mAh} \cdot \text{g}^{-1}$, coulomb efficiency is 98.2%, 88.9% and 86.7%, respectively. It can be seen that the sample synthesized with lithium hydroxide shows the highest discharge capacity and coulomb efficiency, i.e. sample A has the best reversibility. The charge-discharge process of LiFePO_4 occurs in the mutual transformation process of FePO_4 and LiFePO_4 : lithium ions extract from LiFePO_4 and get into electrolyte when charging; on the contrary, lithium ions insert into $\text{Li}_{1-x}\text{FePO}_4$ from electrolyte when discharging. The uniform and regular particle morphology of sample A would mean a more stable structure, so after the delithiation, nearly all the lithium ions can insert into the materials again, which leads to high coulomb efficiency. However, there is a certain amount of impurities in sample C by XRD analysis result. The existence of impurities does not only decrease the content of electrochemical active substance, but also impedes the extraction/insertion of lithium, which causes a part of lithium ions can not join in electrochemical reaction and thus leading to lower specific capacity.

Fig.4 shows the discharge cycling curves of three samples at different current rates. Seeing from the chart, sample A shows the best cycling performance and its specific capacity decays slowly with current density increasing. At 0.1C, the specific capacity is 153.4 $\text{mAh} \cdot \text{g}^{-1}$ and maintains 116.4 $\text{mAh} \cdot \text{g}^{-1}$ at high



(a) $\text{LiOH} \cdot \text{H}_2\text{O}$; (b) Li_2CO_3 ; (c) $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$

Fig.4 Discharge cycling curves of three synthesized samples at different current densities

rate of 10C, with capacity retention rate of 76%. However, the specific discharge capacity of sample B and C at 0.1C is $139.7 \text{ mAh} \cdot \text{g}^{-1}$, and $98.4 \text{ mAh} \cdot \text{g}^{-1}$, respectively, their capacity retention rates are both only 56% at 10C. Liu Youyong et al^[17] synthesized nanospheres- LiFePO_4 composite by PEG based sol-gel synthesis, the specific capacity is $113 \text{ mAh} \cdot \text{g}^{-1}$ at 5C; Wu Yongming et al^[18] successfully developed a facile method to synthesize the hierarchical LFP/C NMs, the specific capacity of LFP/C NMs decreased from 150 to $85 \text{ mAh} \cdot \text{g}^{-1}$ with an increasing current rate from a value of 0.1C to 5C. Compared with the data of the two documents, our sample displays an excellent rate capability.

Contrasting the SEM images with the electrochemical performance of samples, we can also see that there is a close connection between electrochemical performance and the morphology of the samples. The sample A has the smallest particle size of 200 nm and without blocky particles, Li^+ can rapidly extract/insert from LiFePO_4 owing to the shorter diffusion distance of lithium ions, which improves its rate capability. The reason why sample C exhibits bad rate capability is that the purity of the target product and morphology mentioned in the XRD and SEM results are not beneficial to the extraction/

insertion of Li^+ . Dong et al^[19] considered that pH value could affect the dispersion of water system and cell performance of LiCoO_2 cathodes, when the pH value of the slurry was $\text{pH} \leq 7.0$ or $\text{pH} \geq 11.6$, the adhesive force between slurry covering and aluminum foil, conductivity and charge-discharge performance of LiCoO_2 cathodes decreased obviously. Hence, we presume that the above situation may be suitable for LiFePO_4 in this work. In other words, when the system of mixed materials is alkaline, it can be obtained LiFePO_4 electrode with fine dispersion and excellent electrochemical performance. Only the material system of sample A is alkaline, so its electrochemical performance is the best.

2.3 Analysis of the optimum sample

2.3.1 Analysis of particle size

The particle size distribution of sample A and its precursor are given in Table 1. The particle size of sample A is small, the average particle size is only $1.942 \mu\text{m}$, D_{10} , D_{50} , D_{90} value and the average particle size of sample A are close to its precursor, which represents particles without growing much during calcination, the result is in accordance with SEM, which shows that the reaction system composed of $\text{LiOH} \cdot \text{H}_2\text{O}$, FePO_4 and lauric acid can suppress particle growth, thus the small particles obtained.

Table 1 Particle size distribution of sample A and its precursor

Sample	$D_{10} / \mu\text{m}$	$D_{50} / \mu\text{m}$	$D_{90} / \mu\text{m}$	Average particle size / μm
Precursor of A	0.224	0.891	4.667	1.881
A	0.227	0.873	4.892	1.942

2.3.2 Cycling stability test

Fig.5 shows the cycling curve of sample A at 10 C, its specific capacity basically keeps at about $115 \text{ mAh} \cdot \text{g}^{-1}$, the capacity retention rate after 800 cycles is still 96%, which indicates that sample A has an excellent cycling stability. All the results show that the nanoparticles of sample A is stable, even at high rate, the reversibility of lithium extraction/insertion is also good.

2.3.3 Cyclic voltammetry test

Fig.6 shows the cyclic voltammetry curve of sample A for the 1st, 2nd and 5th cycles at scanning

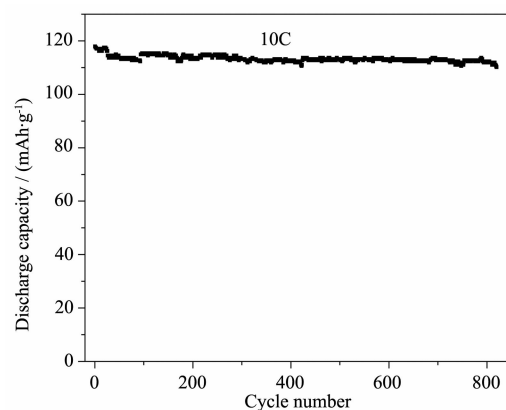


Fig.5 Cycling performance of sample A at 10C

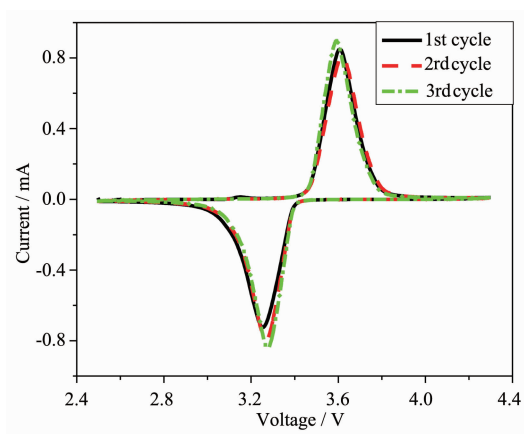


Fig.6 Cyclic voltammetry curve of sample A

rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$. The reduction and oxidation peak positions for the 1st, 2nd and 5th cycles are the same, it proves that the structure of the sample A is very stable during the charge/discharge processes. Seeing from the chart, the CV curves exhibit symmetrical and sharp shape of the anodic/cathodic peaks at 3.27 V and 3.62 V, respectively, the redox potential interval is small only 0.35 V, which demonstrates the higher electrochemical reactivity and lower electrode polarization. The nearly equal area of anodic/cathodic peaks indicates well lithium insertion/ extraction reversibility of the LiFePO_4/C , which is in well agreement with the good performance showed in galvanostatic charge/discharge results.

2.3.4 Electrochemical Impedance analysis

Fig.7a shows the impedance spectra of LiFePO_4 composites with different lithium sources. As can be seen from the figure, all spectra have an intercept at the Z' axis, a semicircle and a straight line in the high-, middle- and low-frequency regions. An intercept at the Z' axis in high frequency corresponds to the ohmic resistance, which represents the

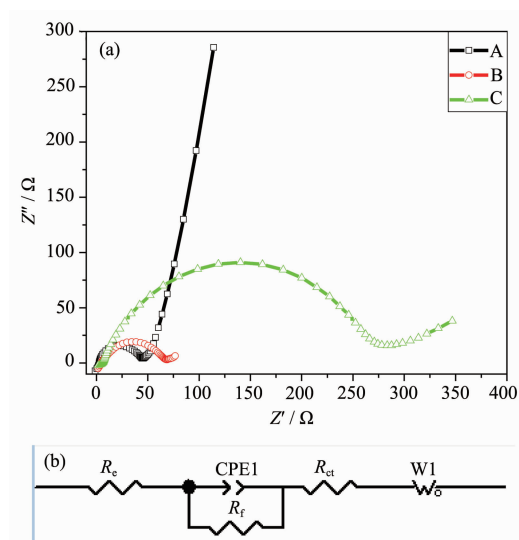


Fig.7 (a) Impedance spectra of samples with different lithium sources; (b)Equivalent circuit model for fitting the experimental AC data

resistance of the electrolyte and LiFePO_4/C thin film. The middle frequency semicircle indicates the charge-transfer resistance of electrochemical reaction. The slow frequency line is attributed to the diffusion of the lithium ions into the bulk of the electrode material. An equivalent circuit model of EIS was constructed to analyze the resistance of LiFePO_4/C electrode (Fig.7b), which can explain the impedance spectra through the ohmic resistance R_e , charge-transfer R_f and the diffusion resistance R_{ct} . The parameters of the equivalent circuit by computer simulations are shown in Table 2. Seeing from the table, the resistance of the electrolyte and sample A thin film is only 2.673Ω , the charge-transfer resistance of electrochemical reaction is 41.05Ω , the diffusion resistance is 40.43Ω . all the resistance of sample A is the lowest, which leads to the highest electrical conductivity and the optimum electrochemical performance of sample A.

Table 2 Numerical values of the elements from equivalent circuit

Samples	R_e / Ω	R_f / Ω	R_{ct} / Ω
A	2.673	41.05	40.43
B	4.524	64.35	59.04
C	5.945	269.2	227.4

3 Conclusions

In this work, LiFePO_4/C composite was

synthesized by rheological phase method with lauric acid as carbon source and surfactant. It is found that all the composites are olivine-type LiFePO_4 with high

crystallinity, and the energy consumption of calcination process decreases. Using $\text{LiOH} \cdot \text{H}_2\text{O}$ as lithium source can get LiFePO_4/C with excellent electrochemical performance and rate capability, specific capacity of $153.4 \text{ mAh} \cdot \text{g}^{-1}$ at 0.1C, and $116.4 \text{ mAh} \cdot \text{g}^{-1}$ at high rate of 10C, The good performance is mainly due to the small particle size of only 200 nm. Through analyzing the optimum sample in detail, we found using rheological phase method with the raw material system of $\text{LiOH} \cdot \text{H}_2\text{O}$, FePO_4 and lauric acid to synthesize LiFePO_4/C can restrain the particles growing and get the sample with outstanding cycling stability and reversibility at high rate.

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