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# One-pot preparation of $LiFePO_4$/C composites

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**Abstract**−A convenient one-pot method, called high-temperature high-energy mechanical force (HTHEMF), was successfully developed for the preparation of $LiFePO_4$/C composites. Upon the combination of high-temperature with high-energy mechanical force, the whole synthesis process of this method is very simple and only involves two steps, the precursor preparation and the calcination step. The results of XRD, SEM, BET and electrochemical performance tests indicated that after calcination at 600 °C for 9 h, the $LiFePO_4$/C composites have the best properties. The discharge capacity of the composites was 150.3 mA h $g^{-1}$ at 0.1 C. After 30 cycles test, the reversible capacity was 147 mA h $g^{-1}$ and the retention ratio to the initial capacity was 97.8%. The results indicated that $LiFePO_4$/C composites with good properties can be obtained by one-pot HTHEMF method.

Keywords: $LiFePO_4$/C Composites, Cathode Material, High-temperature High-energy Mechanical Force, One-pot

## INTRODUCTION

$LiFePO_4$ is one of the most potential cathode materials for the replacement of traditional cathode materials of lithium ion batteries due to its excellent thermal stability, remarkable cycling stability and environmental friendliness [1]. However, the major limitations of $LiFePO_4$ for the commercial application are the high cost of the raw materials and the low utilization of its total capacity (caused by the low intrinsic electronic conductivity and the slow lithium ion diffusivity [2]). To reduce the cost of the $LiFePO_4$, some previous works [3,4] suggested the use of the low-cost ferric compounds (such as $FePO_4$ or $Fe_2O_3$) for the preparation of $LiFePO_4$. To improve the total capacity of $LiFePO_4$, many effective approaches have been reported, such as reducing particle size [5,6], doping conductive agents [7-9] or optimizing synthesis conditions of tradition methods [10-13]. Among them, carbon coating $LiFePO_4$ composites [14,15] and mechanical force (ball milling) are the effective ways to enhance the capacity of $LiFePO_4$/C composites with the homogeneous small particles. Usually, the mechanical force has been used as an auxiliary synthesis step at room temperature to reduce particle size by either grinding the precursors [11], or forming the precursor [12] or grinding the as-prepared $LiFePO_4$/C composites [16]. However, these approaches have some disadvantages, including long synthetic time, complex synthesis process and high synthesis temperature. A previous study [17] reported that these shortcomings might affect the electrochemical performance of the material.

High-energy mechanical force can decrease the temperature and the time of the chemical reaction [18-20] and prevent particle growth in the calcination steps, which is beneficial to obtaining fine and homogeneous composites at relatively low temperature for a short time. In our previous work, the preparation temperature of $BaMoO_4:Eu^{3+}$ was reduced from 1,000 to 600 °C [21] and the preparation time of $Li_4Ti_5O_{12}$ was only 3.5 h [22]. In this work, a one-pot high-temperature (350-650 °C) combined with high-energy mechanical force (HTHEMF) using $Fe_2O_3$ as the low-cost starting material and glucose as the carbon source was developed for the preparation of the $LiFePO_4$/C composites.

## EXPERIMENTAL

### 1. Preparation of $LiFePO_4$/C Composites

The HTHEMF furnace was made from the modification of conventional mechanical ball milling equipment by adding a controllable heating device. In the HTHEMF furnace, there is a mobile stainless-steel container with one small hole at each bottom and some stainless-steel spheres with different diameters (0.5, 1 and 2 cm). To avoid oxidation, $N_2$ is allowed passing from the small hole at the bottom of the container.

The $LiFePO_4$/C composites were prepared by using $LiH_2PO_4$, $Fe_2O_3$ in stoichiometric ratio. Glucose was used as the reducing agent and the carbon source. All the raw reactants and some stainless-steel spheres were added into the stainless-steel container. The container was put into the HTHEMF furnace, and then the preparation process was accomplished in it. In the preparation process, the HTHEMF method includes two steps: synthesis step and calcination step. Two chemical reactions are involved in the synthesis step, glucose pyrolysis and the synthesis of $LiFePO_4$ as follows:

$$C_6H_{12}O_6 \rightarrow 6C+6H_2O \tag{1}$$

$$2LiH_2PO_4+Fe_2O_3+C \rightarrow 2LiFePO_4+2H_2O+CO \tag{2}$$

The calcination step is involved in the crystallization of $LiFePO_4$ and the formation of carbon-coating. In this step, a part of carbon from the glucose pyrolysis (occurring during the synthesis step) is coated

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on the surface of the $LiFePO_4$ particles, and then the $LiFePO_4$/C composites are synthesized.

In the calcination step, the process parameters, such as temperature and time, have strong influence on the properties of $LiFePO_4$/C. To test the relationship between the parameters of the preparation and the properties of the composites, the calcination step was carried out at various temperatures from 580 to 650 °C and time from 6 to 10 h. The ball-to-power ratio was 10 : 1 and the flow rate of $N_2$ gas was 1 ml $min^{-1}$.

### 2. Structural and Physical Characterization

The crystallographic structure of the samples was evaluated by X-ray diffraction (XRD, RINT2000) with CuK$\alpha$ radiation ($\lambda$=0.152 nm). The powder morphologies were determined by scanning electron microscopy (SEM, XL-30FEG) and transmission electron microscopy (TEM, JEOLJEM). The specific surface area was measured by specific surface area analysis instrument (BET, 3H-2000BET-A). The residual carbon content of the samples was measured by an elemental analyzer (EA, Elementar Vario Micro Cube).

### 3. Fabrication of Electrochemical Cells and Electrochemical Characterization

$LiFePO_4$/C composites, carbon black and polyvinylidene fluoride (PVDF) binder (80 : 10 : 10 in mass%) were mixed together, then stirred in 1-methyl-2-pyrrolidinone (NMP) for 9 h. The mixture was spread uniformly onto a thin aluminum foil then dried at 120 °C in vacuum oven for 6 h. Circular discs were cut from the aluminum foil as cathode and the metallic lithium as anode for coin-type cell CR2025, and then the cells were assembled in an argon-filled glove box. The electrochemical property measurements of the coin-type cells CR2025 were performed using Land-CT2001A (Land, Wuhan) and electrochemical workstation CHI600 (Chenhua, Shanghai).

## RESULTS AND DISCUSSION

### 1. Preparation Flowchart of $LiFePO_4$/C by HTHEMF Method

The flowchart for the preparation of $LiFePO_4$/C composites is shown in Fig. 1. The first step was at 350 °C for 1 h, aiming at the precursor preparation. The second step involved various temperatures from 580 to 650 °C and time from 6 to 10 h, allowing for the formation of $LiFePO_4$/C. The whole synthesis process of the HTHEMF method is very simple and only involves two steps. However, in some previously reported methods, complex preparation steps are often employed, such as dispersion in solvent, ball milling of starting material, pre-treatment, ball milling of precursors, calcination and so on, which easily lead to the waste of energy and the extension of production time. In addition, the simple process reported here also help avoids the transfer step and increases the yield, making it suitable for the large-scale industrial production.

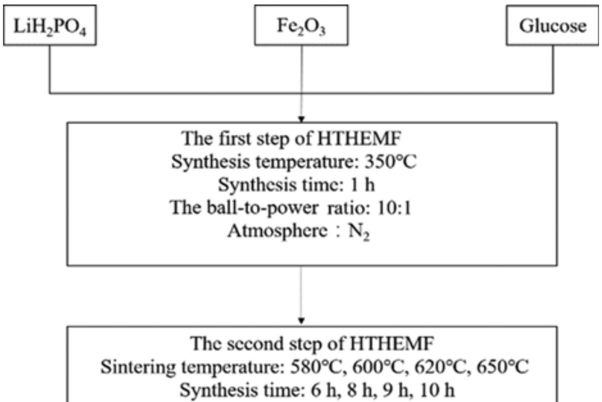

**Fig. 1. Flowchart of $LiFePO_4$/C preparation by the HTHEMF method.**

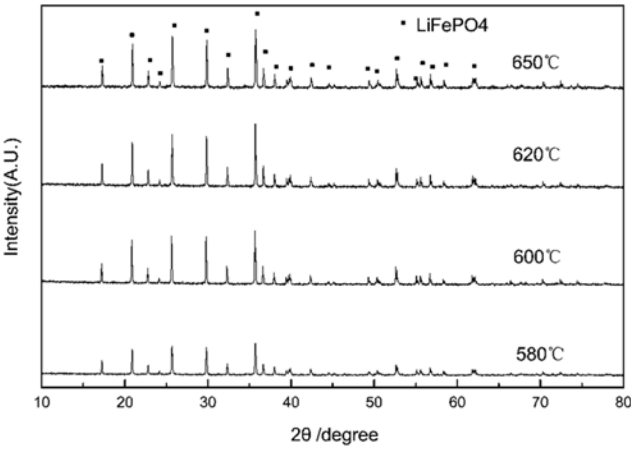

**Fig. 2. XRD patterns of the samples synthesized at various temperatures.**

### 2. Characterization of $LiFePO_4$/C Obtained at Various Temperatures

Fig. 2 shows the XRD patterns of $LiFePO_4$/C samples obtained at various temperatures from 580 to 650 °C for fixed time of 8 h. All patterns have the space group Pnmb of orthorhombic structure and confirm the formation of the olivine-type $LiFePO_4$ (JCPDS, No. 40-1499). The main diffraction peaks of the samples are sharp and without any impurities. It indicates that the pure $LiFePO_4$/C composites can be successfully synthesized at 580 °C, which is very close to the $LiFePO_4$ crystallization temperature of ~567 °C [23], and much lower than the temperatures ranging from 680 to 850 °C by other methods [6,9,11]. Perhaps, it is because the high-energy mechanical force refines the reactants and increases the reaction rate, which boosts the synthesis reaction at low temperature. Compared with the others, the sample obtained at 580 °C shows the weakest diffraction peaks, namely, the lowest crystallinity. With the increase of temperature, the diffraction peaks of the samples increase obviously, indicating that the increase of temperature is beneficial to obtaining $LiFePO_4$/C composites with good crystallization, which is in accordance with the previous literature [24].

The SEM images of the samples are shown in Fig. 3. From the images, it is easy to find that the particle size increases slightly with the increase of temperature. It could be that the increasing calcination temperature promotes the particles' growth. The results prove that the temperature plays a critical role in controlling particle size, and the conclusion is consistent with traditional solid-state method

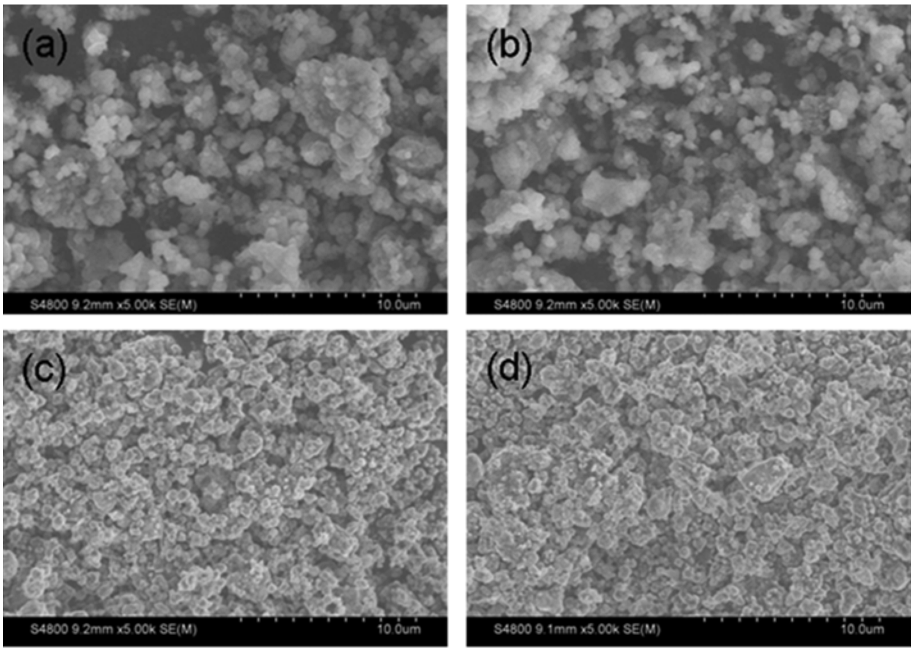

**Fig. 3. SEM images of the samples synthesized at (a) 580 °C, (b) 600 °C, (c) 620 °C and (d) 650 °C.**

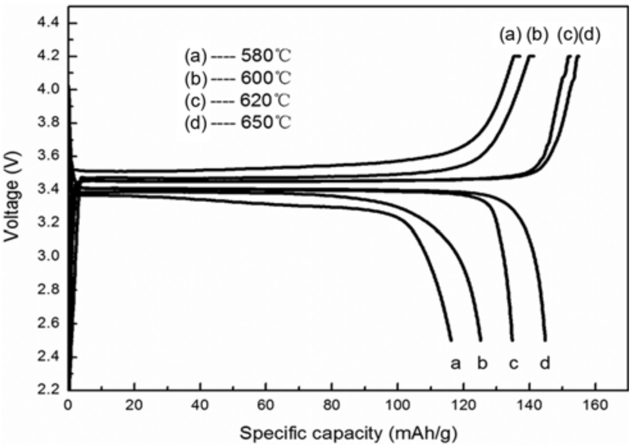

**Fig. 4. Charge-discharge curves of the samples synthesized at various temperatures.**

[25].

### 3. Charge/Discharge of $LiFePO_4$/C Obtained at Various Temperatures

Fig. 4 shows the initial charge/discharge profiles at 0.1 C of $LiFePO_4$/C composites obtained at different temperatures. The discharge voltage plateau of the samples ranges from 3.2 to 3.4 V. With the increase of temperature, the discharge capacities of the samples increase initially and decrease subsequently. The sample obtained at 580 °C delivers the lowest discharge capacity of 116.1 mA h $g^{-1}$, while the sample obtained at 600 °C delivers the maximums value of 144.7 mA h $g^{-1}$. The significant enhancement of discharge capacity may be due to its higher crystallization and smaller particles. Padhi et al. [1] proved that large particles can cause the reduction of capacity, because lithium ions cannot successfully insert in the core region of large particles. Besides, the larger particles simply lead to a longer route of lithium ion diffusion and bigger polarization of the cell. The results of XRD, SEM and charge/discharge capacities imply that the optimum temperature of the HTHEMF method is 600 °C.

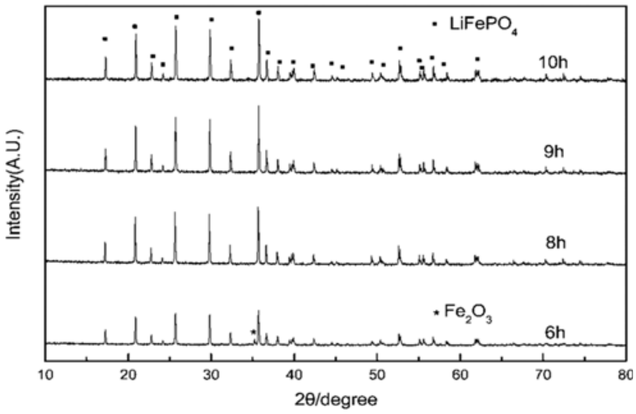

**Fig. 5. XRD patterns of the samples synthesized for various time.**

### 4. Characterization of $LiFePO_4$/C Obtained for Various Time

Fig. 5 displays the XRD patterns of the samples obtained at 600 °C for the various preparation times from 6 to 10 h. As can be observed, the $LiFePO_4$/C composites are successfully obtained for 6 h; however, a small amount of $Fe_2O_3$ can be found. When the time is increased up to 8 h, the diffraction peaks of $Fe_2O_3$ disappear, and all diffraction peaks are matched with the orthorhombic olivine $LiFePO_4$, implying that pure $LiFePO_4$/C composites can be obtained at 600 °C for 8 h. The calcination time of $LiFePO_4$/C composites using HTHEMF is obviously less than that by other methods previously [25,26]. While, the intensity diffraction peaks of the sample obtained for 8 h are weaker than the samples obtained for 9 h and 10 h. The result indicates that the preparation time of the

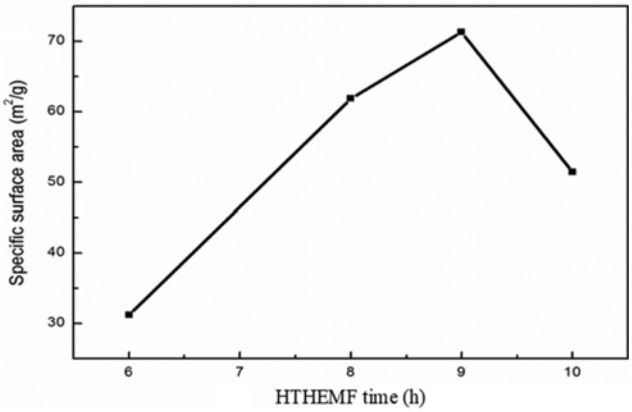

**Fig. 6. Effect of high energy mechanical force time on the specific area of the samples.**

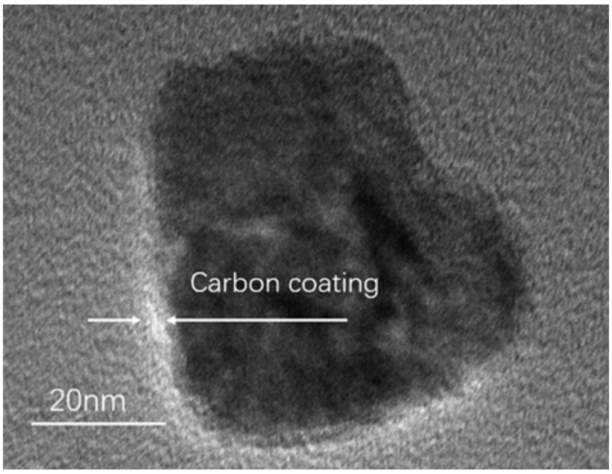

**Fig. 8. HRTEM image of the sample synthesized for 9 h.**

proposed method plays an important role in the preparation of LiFePO$_4$/C with good crystallization.

LiFePO$_4$ composites with large specific surface area can possess good electrochemical performance [25]. Previous literature has shown that the increase of calcination time easily leads to the growth of the LiFePO$_4$/C particles and the decrease of the specific surface area [25]. However, the HTHEMF method can decrease the particles and increase the specific surface area during the calcination step within a reasonable time. Therefore, the effect of calcination time on the specific surface area of LiFePO$_4$/C is investigated in Fig. 6. The specific surface area of the samples increases dramatically with the increase in time from 6 to 9 h, and is found to be 31.2, 61.9 and 71.3 m$^2$ g$^{-1}$, respectively. And then the specific surface area decreases to 51.4 m$^2$ g$^{-1}$ for 10 h. From Fig. 6, it can be concluded that the calcination time of HTHEMF plays an important role in obtaining the LiFePO$_4$/C composites with small size and large specific surface area. Therefore, the optimum calcination time was 9 h. The TEM images of the samples are shown in Fig. 7. It can be seen that the particle sizes of the LiFePO$_4$/C composites decreased with increased calcination time from 6 to 9 h, and then increased up to 10 h. This phenomenon also proved that 9 h of calcination time was beneficial to obtaining the LiFePO$_4$/C composites with small particles sizes.

To certify the structure of the LiFePO$_4$/C composites synthesized for 9 h, the HRTEM image of the sample is shown in Fig. 8. It can be seen that a uniform thin layer of carbon with a thickness of about 3 nm was coated on the surface of the particles. The result of the EA showed that the residual carbon weight content of the sample is 2.5%. Utilization of the LiFePO$_4$ composites with smaller and uniform carbon-coating particles can enhance the charge and discharge capacities of the material.

## 5. Electrochemical Properties of LiFePO$_4$/C Obtained for Various Time

The electrochemical properties of the cathode material, such as charge/discharge capacity, cycling performance and electrochemical impedance spectroscopy, are an important index to determine its performance. Therefore, the electrochemical properties have been studied by measuring the coin-type cell CR2025 made of the LiFePO$_4$/C composites.

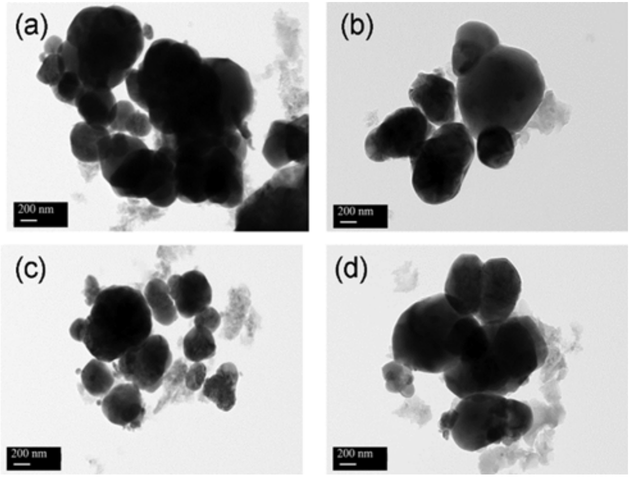

**Fig. 7. TEM image of the samples synthesized for (a) 6 h, (b) 8 h, (c) 9 h and (d) 10 h.**

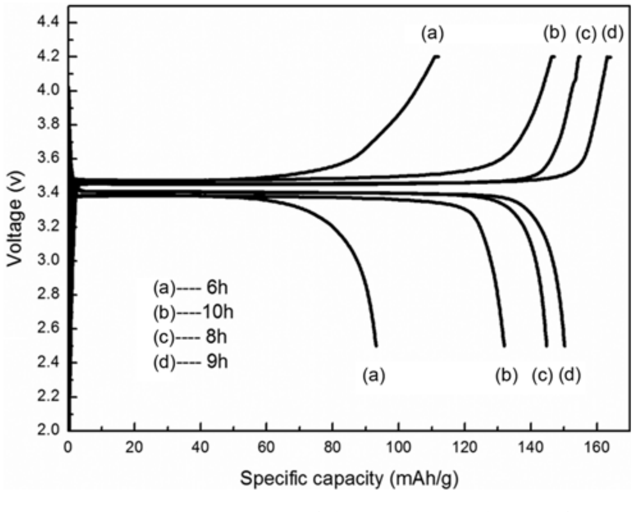

**Fig. 9. Charge-discharge curves of the samples synthesized for various times.**

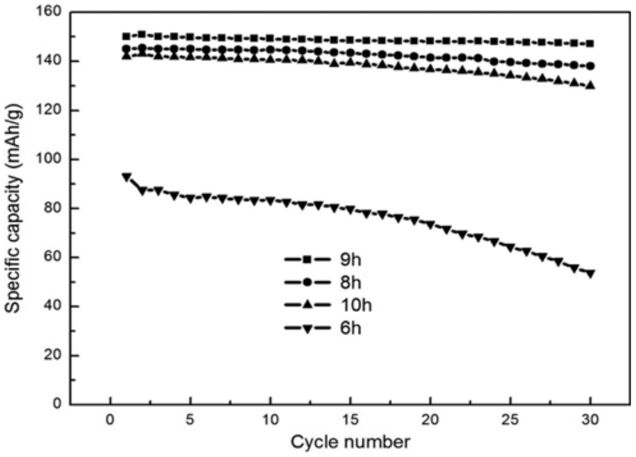

**Fig. 10. Cycle performance of the samples synthesized for various times.**

Fig. 9 shows the charge/discharge profiles of the composites at 0.1 C obtained at 600 °C for various times. The first discharge capacity of the samples obtained for 6, 8, 9 and 10 h was found to be 93.1, 144, 150.3 and 131 mA h $g^{-1}$, respectively. The maximal discharge capacity of the sample obtained for 9 h may be attributed to its largest specific surface area and smallest particle size.

Fig. 10 shows the cycling performance of the electrochemical cells at 0.1 C for 30 cycles. The sample obtained for 9 h with the best microstructure delivers the best long-term cycling stability, while the sample obtained for 6 h shows to the worst. For the two samples, after 30 cycles test, compared to their initial discharge capacities, the capacity retention rates of the cells are 98% and 64%, respectively. Fig. 11 shows the typical Nyquist plots of the samples. All Nyquist plots have similar shapes, and the semicircle impedance at the medium high frequency represents the charge-transfer resistance of $Li^+$ ions at the interface of the electrode/electrolyte. Based on the results from Fig. 11, the $LiFePO_4$/C composites obtained for 9 h have the smallest charge-transfer resistance, showing the best electrode performance.

The optimum preparation process of $LiFePO_4$/C composites by the HTHEMF method was carried out at 350 °C for 1 h, then sintered at 600 °C for 9 h. The total production time of the method was 10 h, much shorter than that employed by other methods ranging from 20 to 48 h [27,28]. Compared with the other methods [4,9, 15,25], the preparation time and temperature of HTHEMF method are relatively short and low when the discharge capacities of the $LiFePO_4$/C composites show no significant difference (130-158 mA h $g^{-1}$). In addition, the synthesis steps of HTHEMF are simple. The low-cost ferric compounds ($Fe_2O_3$), fewer steps, low temperature and short time of method could reduce the energy consumption and cost of the $LiFePO_4$/C composites.

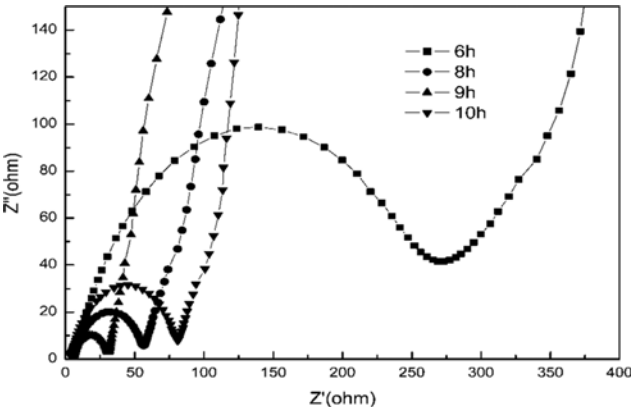

**Fig. 11. Nyquist plots of the samples synthesized for various times.**

## CONCLUSIONS

By optimizing the operation parameters of temperature and time of the calcination steps, $LiFePO_4$/C composites with the best performances were obtained by the HTHEMF method at 350 °C for 1 h and 600 °C for 9 h. At 0.1 C, the composites show good properties with the discharge capacity of 150.3 mA h $g^{-1}$ and the retention ratio to the initial capacity as 97.8% after 30 cycles test. The HTHEMF method with relatively simple procedure, short preparation period and relatively low energy consumption can be an alternative method for the large-scale industrial production of the $LiFePO_4$/C composites.

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