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$LiFePO_4/C$ Composite Prepared by Coal Based Carbon Sources

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A novel carbon source which was obtained from coal has been successfully applied to prepare $LiFePO_4/C$ composite for the first time. The $LiFePO_4/C$ composite was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM), Thermal Gravimetric (TG), Raman spectra and electrochemical techniques. TG curves indicated that the coal had a high carbon-containing (32 wt. %). TEM images showed that the surface of $LiFePO_4$ was covered with a carbon layer of ~3 nm. The electrochemical performance was greatly improved by coating with coal based carbon source due to the enhanced electronic conductivity. It exhibited high initial capacity of 156.7 mAh/g at 0.1 C-rate and 96.5 mAh/g at 2 C-rate, which were higher than the pure $LiFePO_4$. The R_{ct} of the $LiFePO_4/C$ composite and pure $LiFePO_4$ were 270 Ω and 450 Ω, respectively. Thus, the approach for the preparation of $LiFePO_4/C$ composite by using coal as carbon source may open new prospects for utilization of coal in lithium ion batteries.

Keywords: Coal, Carbon, $LiFePO_4/C$ composite, Acid treated.

1. INTRODUCTION

Lithium ion batteries have been applied as the power sources for electric vehicles and hybrid Evs. However, its wide applications in industry are severely limited by the cost, lifetime and safety. Recently, intensive efforts have been put into exploring the costly and relatively unsafe cathodes. Among various lithium-ion batteries, $LiFePO_4$ has attracted great attention as one of the prospective cathode material due to its low cost, good safety and high theoretical specific capacity (170 mAh/g). Nevertheless, the pure $LiFePO_4$ electrode suffer from poor electronic conductivity (10^{-8}~10^{-10} Scm^{-1})[1] and low Li-ion diffusion in the solid phase leading to high initial capacity losses and poor rate capacities. To overcome these problems, several strategies have been adopted, such as particle size reduction[2-3], metal doping[4-6] and carbon coating[7-9]. Among them, carbon coating is considered as the most effective way due to its convenience and effectiveness to improve the capacity and rate performance of $LiFePO_4$[10].

So far, various carbon sources have been used to prepare $LiFePO_4$/C composites, such as glucose, sucrose, Phenol-formaldehyde resin, graphene, polypyrrole and polyethylene glycol etc. J. K. Kim prepared a $LiFePO_4$/C composite by using sucrose as carbon source could exhibit a capacity of 165 mAh/g at 0.1 C-rate and 145 mAh/g at 1 C-rate[11]. A $LiFePO_4$/C composite using a mixture of 30% Phenol-formaldehyde resin and 70% sucrose as carbon sources was prepared by Rao[12], which exhibits a capacity of 162 mAh/g at a 0.1 C-rate. Zhou reported that a $LiFePO_4$ /graphene prepared by spray-drying and annealing process could exhibit a capacity of 148 mAh/g at 0.1 C-rate and 143.3 mA/g at 1 C-rate[13]. Though all the carbon sources that already reported to prepare $LiFePO_4$/C composite could greatly enhance the electrochemical performance, but most of them are not economic and can not be easily available. Consequently, exploring a carbon source which has a rich source and low cost is essential.

Coal, as one of the most widely used traditional fuels, has been commonly used for cooking and heating. However, several ways have been developed to employ the coal in recent years such as energy product and storage materials[14]. In this paper, we report a novel way to employ the coal. The coal-based carbon was used as carbon source to prepare $LiFePO_4$/C composite due to its low cost, high carbon-containing and abundant source. Firstly, coal was treated by using a mixture of concentrated sulfuric acid and nitric acid, and the acid treated coal can be dissolved in ethanol. Thus, ethanol solution with various carbon-containing precursors was obtained. After the impurities were removed, the $LiFePO_4$ prepared already was added to the solution. In the process of impregnation in the ethanol solution for hours, the organic precursors can be evenly adsorbed on the surface of the $LiFePO_4$. By high temperature treatment, the organic precursors were carbonized. Hence, $LiFePO_4$/C composite was obtained. Compared to pure $LiFePO_{4,}$ the $LiFePO_4$/C composite has higher capacity and better rate performance. This work can greatly improve the utilization rate of coal.

2. EXPERIMENTAL

2.1. Preparation of materials

(1) All the chemical reagents used in this paper were analytically pure grade. Firstly, 10 mmol $LiOH·H_2O$ and 5 mmol $NH_4H_2PO_4$ were dissolved in mixed solvent of 20 ml EG and 20 ml deionized water stirring for 30 minutes at 35 ºC. Subsequently, 5 mmol $FeSO_4·7H_2O$ was added to the solution and the reaction mixtures were stirred for 2 hours under AR atmosphere to prevent the conversion of Fe^{2+} to Fe^{3+}. Then the mixture was transferred into a 50ml Teflon-lined stainless steel autoclave, followed by heat treatment at 180 ºC for 8 hours. After the autoclave was cooled to room temperature, the mixture was filtrated and washed by deionized water and ethanol. Finally, the powder obtained was dried in avacuum drying oven at 80 ºC for 12 hours.

(2) Coal was obtained from Heishan, Xingjiang, China. Firstly, the raw coal was pulverized and sieved with a 200 mesh standard sieve. Then the obtained powders were treated by HNO_3 (63%)

and H_2SO_4 (98%) with a volume ratio of 1:3. 5 g of the raw coal was added into the beaker containing 240 ml of the mixed acid. After reaction for 24 hours, the solution was diluted with deionized water and then filtrated. The obtained powder was washed with deionized water several times until the pH value approached neutral. Subsequently, 0.1 g of the raw coal and acid treated coal were dispersed in 100 ml ethanol respectively to explore the solubility. After 30 days' standing, the raw coal precipitated, while the acid treated coal remained a homogeneous dispersion. Then the solution of acid treated coal was filtrated to remove the impurity composition such as SiO_2. Finally, the pure solution with various carbon-containing precursors was prepared.

(3) The $LiFePO_4$/C composite was prepared by impregnation method. 1 g pure $LiFePO_4$ synthesized before was added into the acid treated coal solution impregnating at 60 ºC. With the evaporation of the solvent, the organic precursors were deposited. The organic precursors deposited could be evenly adsorbed on the surface of the $LiFePO_4$. After drying, the mixture was sintered at 350 ºC for 2 hours and 700 ºC for 6 hours in a flowing of Ar gas with a heating rate of 5 ºC/min to carbonize the organic precursors. Then the coal-based carbon source was successfully applied to prepare $LiFePO_4$/C composite.

2.2 Characterization of sample

The crystalline phases of the samples were analyzed by X-ray diffraction (XRD, D/MAX) using Cu $K\alpha_1$ radiation. Raman spectra were recorded on a J-Y Lab Ram-IB spectrometer using 3 mW of 632.8 nm radiation from a He-Ne laser. Thermal gravimetric (TG) analysis was carried out on an STA 449C instrument (NETZSCH, Germany) using a heating rate of 5 ºC/min under Ar atmosphere. Scanning electron microscopy (SEM) images were obtained on a Nova Nanosem 430 microscope (FEI, USA), operated at 20 kV. Transmission Electron Microscope (TEM, Tecnai F30) was used to investigate the carbon layer of the $LiFePO_4$/C composite.

2.3 Electrochemical characterization

The electrochemical performances of the samples were tested using CR2016 coin-type cells. The cathode was prepared by mixing the fabricated powder as active material (80 wt.%), acetylene black (10 wt.%) as well as polyvinylidene fluoride (PVDF) (10 wt.%) dissolved in N-methyl-pyrrolidone (NMP). The cells were assembled in an Ar-filled glove box, using lithium metal as anode and Celgard 2400 membrane as separator with 1M LiPF6 in ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1,v/v). The charge/discharge tests were evaluated on a LAND battery tester (Wuhan LAND Electronics Co. Ltd., China) at room temperature (20~25 ºC). Cyclic voltammetry (CV) and electrochemical impedance spectroscopic measurement (EIS) were carried out on an electrochemical workstation (SP1, ZIVE, Korea).

3. RESULTS AND DISCUSSION

The solubility test was made to explore the solubility of raw coal and acid treated coal in ethanol. As shown in Fig 1, at first, there was no significant difference between the states of the two solutions. After 30 days' standing, the raw coal precipitated, while the acid treated coal remained a homogeneous dispersion. The solubility of the coal treated by acid can reach 3 wt.%. Referring to the literature reported by Guo[14], the dissolution mechanism can be explained as follows: according to the coal structure model, aromatic units consist of the organic structure connected by aliphatic and ether bond. After treated by mixed acid, the aliphatic and ether bonds between the aromatic units were broken down. During the treating process, some oxygen-containing functional groups such as carboxyl, nitro, hydroxyl or sulfonic groups were introduced, making the acid treated coal soluble in some polar organic solvents.

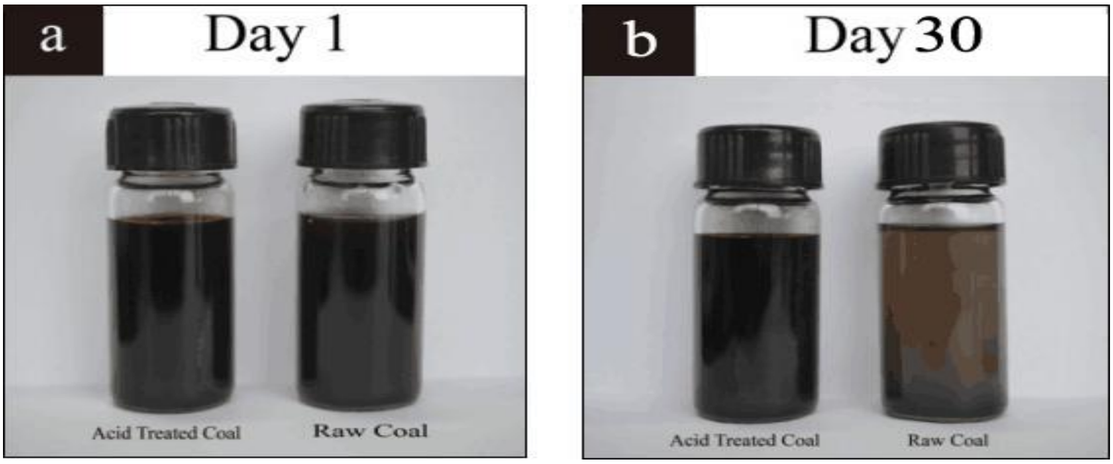


Figure 1. Solubility test of raw coal and acid treated coal in ethanol. (a) The initial state of acid coal and raw coal dispersed in ethanol. (b) The state of the acid treated coal and raw coal in ethanol after standing for 30 days.

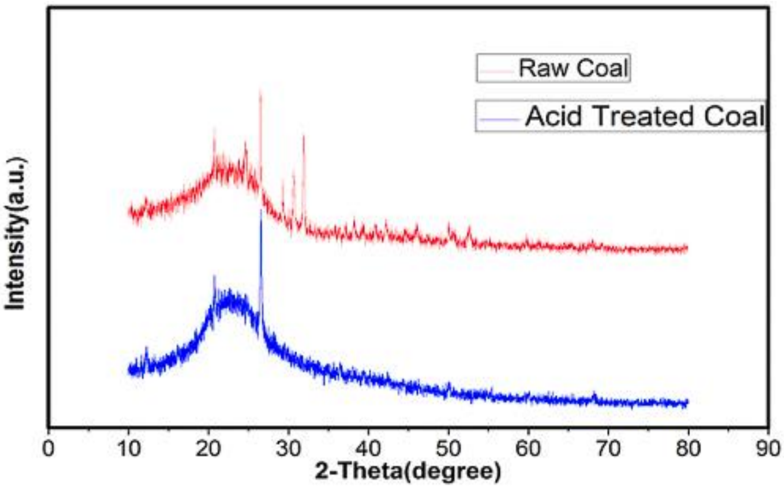


Figure 2. XRD patterns of the coal and acid treated coal

XRD patterns of the raw coal and acid treated coal are shown in Fig 2. It can be seen from the XRD patterns that both of the samples exhibit the peaks around 21° and 26° indicate the presence of SiO_2 (JCPDS 65-04667). Since the SiO_2 is poorly soluble in organic solvents, it can be removed after filtered. Compared to the raw coal, the peaks at 29°, 31° and 32° have disappeared after acid treated. The peaks around 29° and 32° indicate the presence of the $3CaO\cdot 2SiO_2\cdot xH_2O$ (JCPDS 33-0306), and the peak at 32° repents the $CaCO_3\cdot MgCO_3$ (JCPDS 36-0426). Therefore, most of impurity compositions were removed during the acid treated process.

The carbon content of the acid treated coal, Phenol-formaldehyde resin and glucose were estimated by thermal gravimetric (TG) measurement in Ar atmosphere at a heating rate of 5 ºC and the curve is shown in Fig.3. After samples were processed at high temperature under inert gas, the organic components of the carbon source could be carbonized. Herein, the carbon-containing could be calculated. Considering the 6 wt.% of ash content in coal such as SiO_2[15], the percentage of the remaining carbon could be calculated to 32 wt.%. While, the remaining carbon of phenol formaldehyde resin and glucose were 20 wt.% and 8 wt.% respectively. Obviously, compared to the traditional carbon sources such as glucose and phenol formaldehyde resin, the carbon content of coal is the highest. Due to the high carbon-containing, we could greatly reduce the waste of materials and energy consumption. Thus, the carbon-coating efficiency was greatly improved.

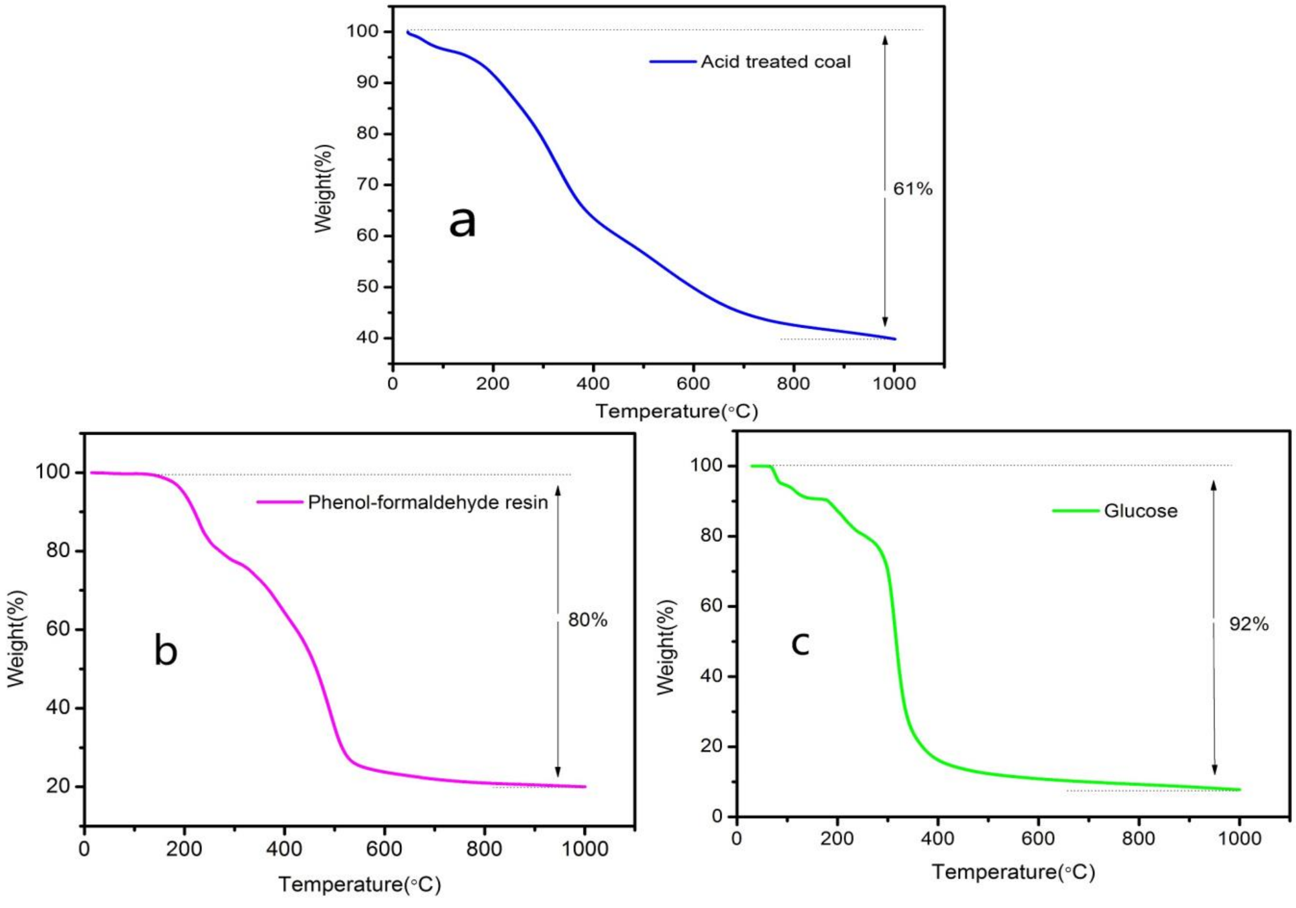


Figure 3. TG curve of the carbon source. (a) Acid treated coal. (b) Phenol-formaldehyde resin. (c) Glucose.

The X-ray diffraction patterns of the $LiFePO_4/C$ are shown in Fig 4. As can be observed in the figure, all the diffraction peaks can be indexed to olivine-type structure with a space group of Pmnb (JCPDS NO. 40-1499) and there are no peaks belong to the impurity phase.

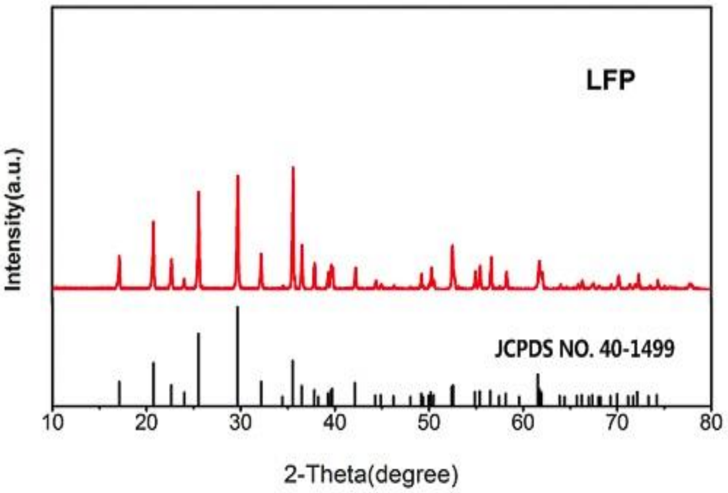


Figure 4. The XRD patterns of LiFePO4 prepared by solvothermal method.

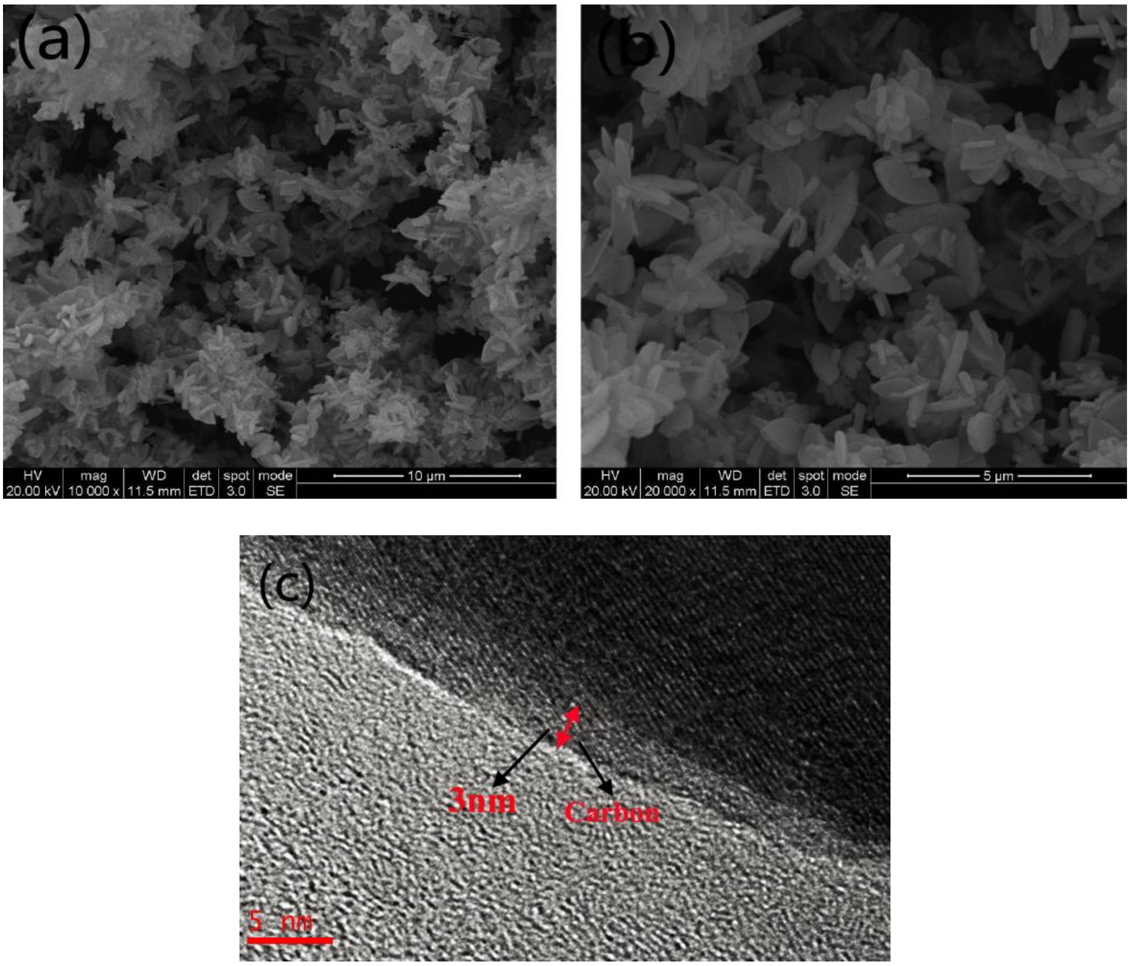


Figure 5. (a, b) SEM images of the $LiFePO_4/C$ composites. (c) TEM images of the $LiFePO_4/C$ composites.

The peaks are strong and narrow, indicating high crystallinity of the as-synthesized sample. The morphology of $LiFePO_4$ is shown in Fig 5a-b. It can be seen that the $LiFePO_4$ exhibits nanosheet morphology with a average thickness of about 100 nm. The nanosheet is very neat. In order to understand morphology and microstructure of the $LiFePO_4$ after carbon coating, TEM observation was performed. The TEM images were shown in Fig 5c, it can be observed that the surface of $LiFePO_4$ were evenly wrapped by a thin film of carbon. The thickness of the carbon coating layer is about 3~4 nm, which can greatly improve the electronic conductivity and facilitate the properties of $LiFePO_4$[16].

To further explore the carbon species of the $LiFePO_4/C$ composite, Raman spectra (shown in Fig.6) were presented to identify the degree of graphitization of the carbon in the composite. It can be observed that there are two broad bonds at about 1350 cm^{-1} and 1595 cm^{-1} for the samples, which represent the D-band and G-band respectively. The intensity of D-band corresponds to the sp^3 hybridized carbon atoms, while the G-band corresponds to the sp^2 hybridized carbon atoms. The intensity ratio (I_D/I_G) of the $LiFePO_4/C$ composite could be used to calculate the degree of graphitization of the carbon materials[17]. According to the literature[18] reported before, the carbon layer with higher degree of graphitization is more beneficial to increase the electron conductivity than amorphous carbon. Based on Fig.6, the value of I_D/I_G for $LiFePO_4/C$ composite is about 1.02, indicating that the carbon layer has a high degree of graphitization.

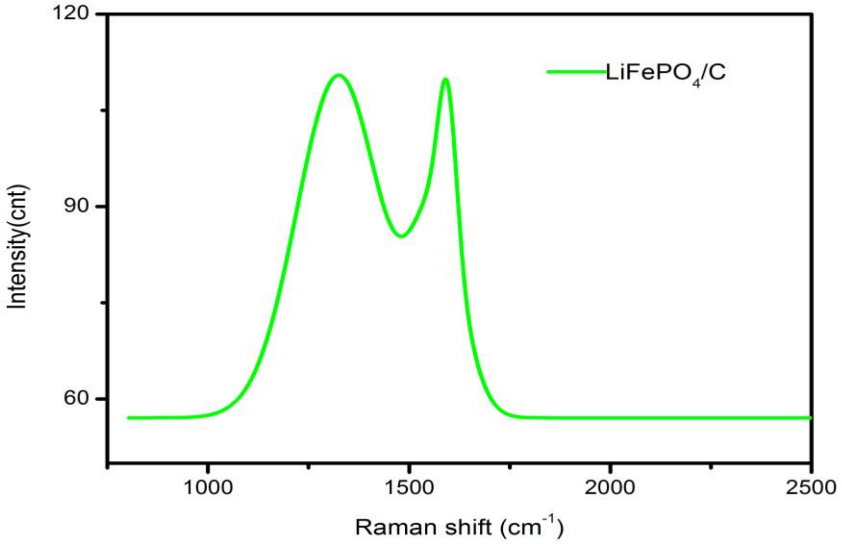
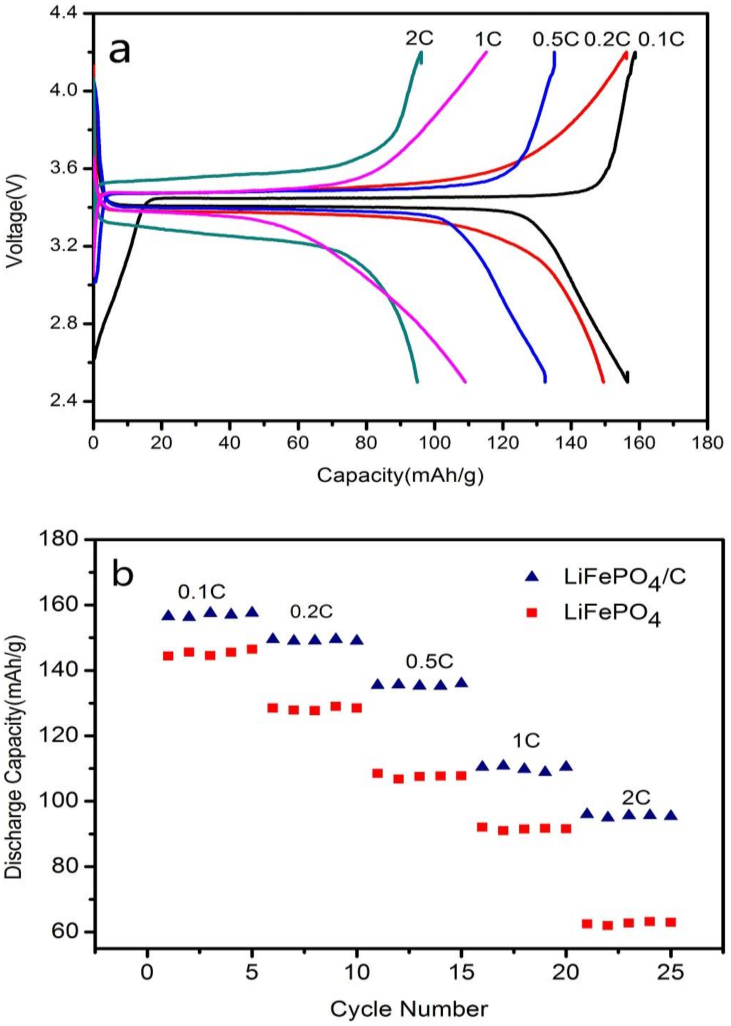


Figure 6. Raman spectra of $LiFePO_4/C$ composite.

Fig 7a is the initial charge/discharge performance of $LiFePO_4/C$ composite at various C-rates. The charge/discharge capacity of the composite is 156.7 mAh/g at a low rate of 0.1 C, which is close to the theoretical capacity(170 mAh/g). With the increase of the current rate, the discharge capacities decrease from 151 mAh/g from 0.2 C to 139, 113 and 96 mAh/g for 0.5 C, 1 C and 2 C rates, respectively. The comparison of cycling performance between $LiFePO_4$ and $LiFePO_4/C$ are shown in Fig 7b. Obviously, the $LiFePO_4/C$ composite exhibits excellent rate cycling performance and higher charge/discharge capacities than pure $LiFePO_4$. What's more, the capacities of pure $LiFePO_4$ decays rapidly in the high current rates. It decreases from 144.1 mAh/g at 0.1 C to 61.5 mAh/g at 2 C, while the $LiFePO_4$/C composite still remains a high capacity of 96 mAh/g at a rate of 2 C. The above results suggest that the $LiFePO_4$/C composite prepared by coal based carbon source has excellent electrochemical performance. It also indicates that a new utilization way of coal has been found in this paper.

The electrochemical impedance spectroscopy spectra of $LiFePO_4$/C and $LiFePO_4$ after 50 cycles are shown in Fig 7c. Both of the two spectras are composed of a semicircle in the high-to-medium frequency region and a slope line in the low frequency region. The semicircle and slope line correspond to charge transfer resistance in cathode–electrolyte interface and the Li ions diffusion in $LiFePO_4$ crystal, respectively. The diameter of the semicircle represents the charge transfer resistance R_{ct} and the R_{ct} of the $LiFePO_4$/C and $LiFePO_4$ are 270 Ω and 450 Ω, respectively. It is apparently that the R_{ct} decreased after carbon coating using acid treated coal as the carbon source.



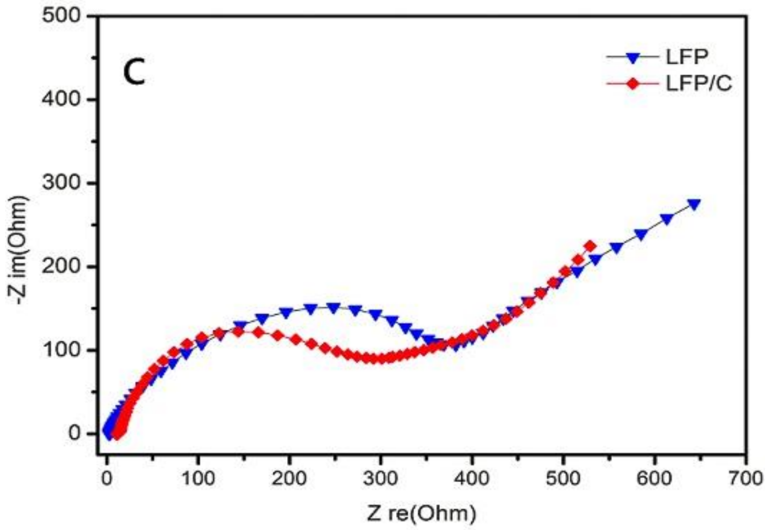


Figure7. (a) Charge and discharge curves of $LiFePO_4$/C at various rates. (b) Rate performance of $LiFePO_4$/C and $LiFePO_4$. (c) Nyquist plots of $LiFePO_4$/C and $LiFePO_4$.

4. CONCLUSION

In this paper, $LiFePO_4$/C composite has been successfully prepared by impregnation method using coal as carbon source. SEM images show the morphology of the $LiFePO_4$/C composite was nanosheet. The surface of $LiFePO_4$ was evenly covered with carbon layer observed from the TEM images. The TG curves indicates that the coal has the highest carbon content (32 wt.%) , compared to the traditional carbon source such as glucose (8 wt.%) and Phenol formaldehyde resin (20 wt.%). The electrochemical performance was apparently improved after carbon coating due to the enhanced electric conductivity and Li-ion diffusion rate. It exhibits high capacities of 156.7 mAh/g at 0.1 C-rate and 149.5 mAh/g at 0.2 C-rate. The capacities are considerable even at the high rate. Therefore, the above results reveal that the coal holds great potential as carbon source for lithium ion batteries due to its low cost and abundant source. Thus, a new utilization way of coal has been found.

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