

Microstructural and Electrochemical Investigation of Carbon Coated Nanograined LiFePO₄ as Cathode Material for Li-Batteries

Rinlee Butch M. Cervera, Princess Stephanie P. Llanos

Abstract—Lithium iron phosphate (LiFePO₄) is a potential cathode material for lithium-ion batteries due to its promising characteristics. In this study, pure LiFePO₄ (LFP) and carbon-coated nanograined LiFePO₄ (LFP-C) is synthesized and characterized for its microstructural properties. X-ray diffraction patterns of the synthesized samples can be indexed to an orthorhombic LFP structure with about 63 nm crystallite size as calculated by using Scherrer's equation. Agglomerated particles that range from 200 nm to 300 nm are observed from scanning electron microscopy images. Transmission electron microscopy images confirm the crystalline structure of LFP and coating of amorphous carbon layer. Elemental mapping using energy dispersive spectroscopy analysis revealed the homogeneous dispersion of the compositional elements. In addition, galvanostatic charge and discharge measurements were investigated for the cathode performance of the synthesized LFP and LFP-C samples. The results showed that the carbon-coated sample demonstrated the highest capacity of about 140 mAhg⁻¹ as compared to non-coated and micrograined sized commercial LFP.

Keywords—Ceramics, microstructure, electrochemical measurements, energy storage, transmission electron microscope.

I. INTRODUCTION

THE depleting supply and harmful effects to the environment of fossil fuel as power source have forced the development and utilization of renewable energies. However, due to the intermittent nature of these renewable energy sources, energy storage systems such as batteries are crucial. And one of the top battery technologies is Lithium-ion batteries (LIB) due to its promising battery chemistry and versatility in its applications. In order to address the demands of LIB related applications, alternative materials for electrodes and electrolytes and synthesis processes must be developed [1], [2].

It is generally recognized that the development of electrode materials strongly affects the performance of the battery. The energy density of the battery is mainly governed by the capacity of the electrode. Thus, the use of electrode materials that offer larger capacity will increase and improve the performance of a lithium-ion battery, specifically, the type of cathode materials [1]. In recent years, studies have focused on identifying new materials that are suitable for use as positive electrode material in rechargeable LIB. Since its discovery in

1999, olivine LiFePO₄ is considered to be one of the most competitive cathode materials due to its several promising characteristics. It has a high theoretical capacity of 170 mAhg⁻¹, an acceptable operating voltage of 3.45 V vs Li⁺/Li, high cycling performance, and long cycle life. It is nontoxic and it can be synthesized at a low cost [3]. Despite the highly desirable properties of LiFePO₄, it has been difficult to utilize its full potential due to its poor electronic conductivity (~10⁻⁹ Scm⁻¹) and low lithium ion diffusion coefficient (~10⁻¹⁴ cm²/s). In order to address these limitations, different parameters to enhance its properties have been investigated [4]-[8]. Hence, LiFePO₄ (LFP) and carbon coated nanograined LiFePO₄ (LFP-C) have been synthesized via wet chemistry method and we investigated its electrochemical performance as a cathode in Lithium battery.

II. EXPERIMENTAL

A. Synthesis of Carbon Coated Nanograined LiFePO₄

The LFP cathode material was synthesized via wet chemistry method. Pre-dried FePO₄·2H₂O and LiOH·H₂O precursors were mixed in a stoichiometric ratio in a hot ethanol solution of stearic acid under vigorous stirring. For the LFP-C, 50% more excess stearic acid was used. After it forms into a slurry, the mixture was dried at 150 °C for 5h. The sample was then ground and pressed into pellet using a uniaxial hydraulic press. Finally, the pellet was sintered at 400 °C under inert argon gas flow environment and ground afterwards to obtain the final powder sample.

B. Characterization of Samples

The samples have undergone different material characterization techniques to verify if the method was able to synthesize LFP and LFP-C. Thermogravimetric analysis (TGA) of the precursor mixture was performed using TA Q500 in the temperature range of 25 °C to 700 °C at 5 °C/minute heating rate under Ar gas flow. X-ray diffraction (XRD) patterns were recorded on Siemens Kristalloflex 760 X-ray generator with a Cu X-ray tube (λ=1.5418Å) and a Philips 1080 vertical goniometer. The surface morphology and elemental composition were determined through SEM-EDS (JEOL JSM-5310) and TEM (JEOL JEM-2100F and Oxford Instrument X-max 80). The electrochemical performance was evaluated using coin cells assembled in an argon-filled glove box. The working electrode was prepared by mixing the synthesized LiFePO₄ with carbon black as conducting agent and polyvinyl difluoride as binder in a weight ratio of 80:15:5.

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The mixture was pressed onto a mesh which served as a current collector and dried at 150 °C to partially melt the binder. The cell consisted of lithium foil as counter electrode, Hipore ND525 polyolefin separator, and 1 M LiPF₆ (EC:DMC = 1:1, v/v) as electrolyte. The testing was done using VMP 300 (Biologic) Multi-channel Potentiostat/Galvanostat. Galvanostatic charge and discharge tests between 2.2 V and 4.2 V versus lithium were performed at different C rates. Cyclic voltammetry measurements were performed at a scan rate of 0.1 mVs⁻¹ in the same potential range.

III. RESULTS AND DISCUSSION

Fig. 1 shows the stacked XRD patterns of the synthesized LFP and LFP-C. The diffraction peaks can be indexed to an orthorhombic LiFePO₄. No distinct carbon peaks were found and it may just exist in amorphous form. A small impurity peak of Li₃PO₄ as indicated by asterisk can be observed. The calculated lattice parameters are $a=10.33\text{\AA}$ $b=5.995\text{\AA}$ $c=4.694\text{\AA}$, and $a=10.32\text{\AA}$ $b=6.005\text{\AA}$ $c=4.694\text{\AA}$ for LFP and LFP-C, respectively. The crystallite size is about 63 nm for LFP-C as calculated using Scherrer's equation. The results show that as the amount of carbon increases, the average grain size decreases. This decrease can be attributed to the carbon layer formed during the sintering which inhibits the growth of LiFePO₄ particles.

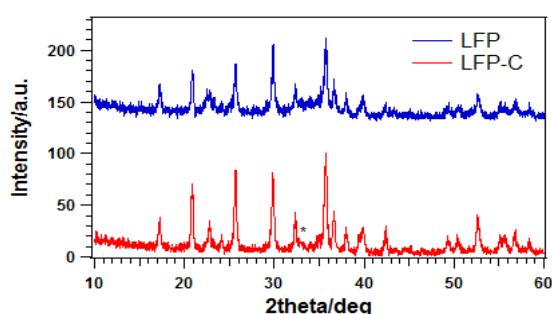


Fig. 1 XRD stack pattern of samples sintered at 400 °C for 3h for LFP and LFP-C

The TEM microstructure images of carbon-coated LFP are shown in Fig. 2. The LFP crystallites appear as the darker regions with the carbon coating surrounding it as the lighter region. It can be deduced that the LFP crystallites are coated by a carbon layer and connected by a carbon network. Lattice fringes are evident, which suggest the crystallinity of LFP structure with a d-spacing of 0.259 nm. The absence of fringes in the lighter region confirms the amorphous form of the carbon coating of about 3 nm to 9 nm in thickness. The presence of the carbon matrix is believed to inhibit the growth of LFP as supported by the XRD and SEM results wherein the sample with excess carbon has smaller grain size. This would be beneficial to the shortening of Li⁺ ions diffusion path. Furthermore, it can be seen that the carbon network links the nanoparticles together, thereby ensuring good electronic contact between the crystallites and increases the electronic conductivity [9], [10].

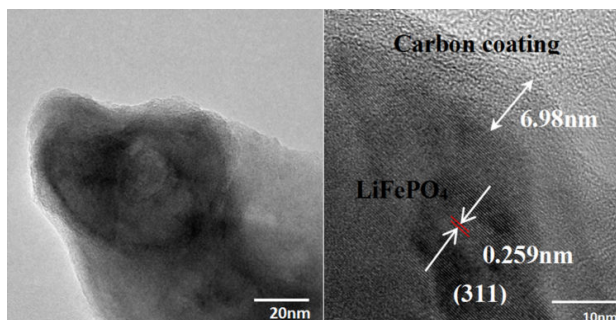


Fig. 2 TEM images of the LFP-C sample

The synthesized samples were subjected to 0.1 C, and the charge-discharge profiles are shown in Fig. 3. The LFP sample showed 44.6 mAh/g and 51.6 mAh/g charge and discharge specific capacities, respectively. On the other hand, the LFP-C sample revealed specific capacities of 108.4 mAhg⁻¹ and 108.9 mAhg⁻¹ for the charge and discharge, respectively. The curves show a plateau at around 3.45 V corresponding to the lithium extraction and insertion between LiFePO₄ and FePO₄. It can be said that the addition of carbon or carbon coating in the LFP increases the capacity by enhancing the electronic conduction and thereby enhancing the overall electrode.

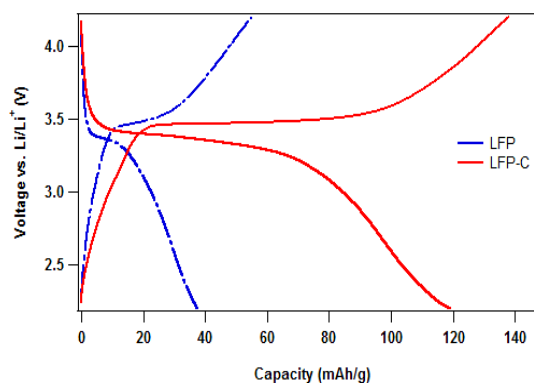


Fig. 3 Charge-Discharge curves of synthesized LFP and carbon coated LFP (LFP-C) at 0.1C rate

The SEM images in Fig. 4 show agglomerated particles. Using Image J software, the particle sizes were approximated to be 259 nm and 218 nm for the LFP and LFP-C sample, respectively. The trend agrees with the XRD results that the carbon-coated sample has a smaller grain size. On the other hand, EDS analysis revealed homogeneous dispersion of Fe, P, O, and C as also shown in Fig. 4. The weight percent carbon in the carbon-coated LFP is 12.7% performance. The sample without carbon coating showed a lower capacity which may be due to lower electronic conductivity [11]. This is in addition that the carbon-coated LFP has smaller grain size which may promote easier lithium-ion extraction and insertion due to shorter diffusion path. This is further supported with the results obtained for the charge and discharge characteristics of a micrograined size commercial LFP sample as compared to the nanograined size carbon-coated LFP.

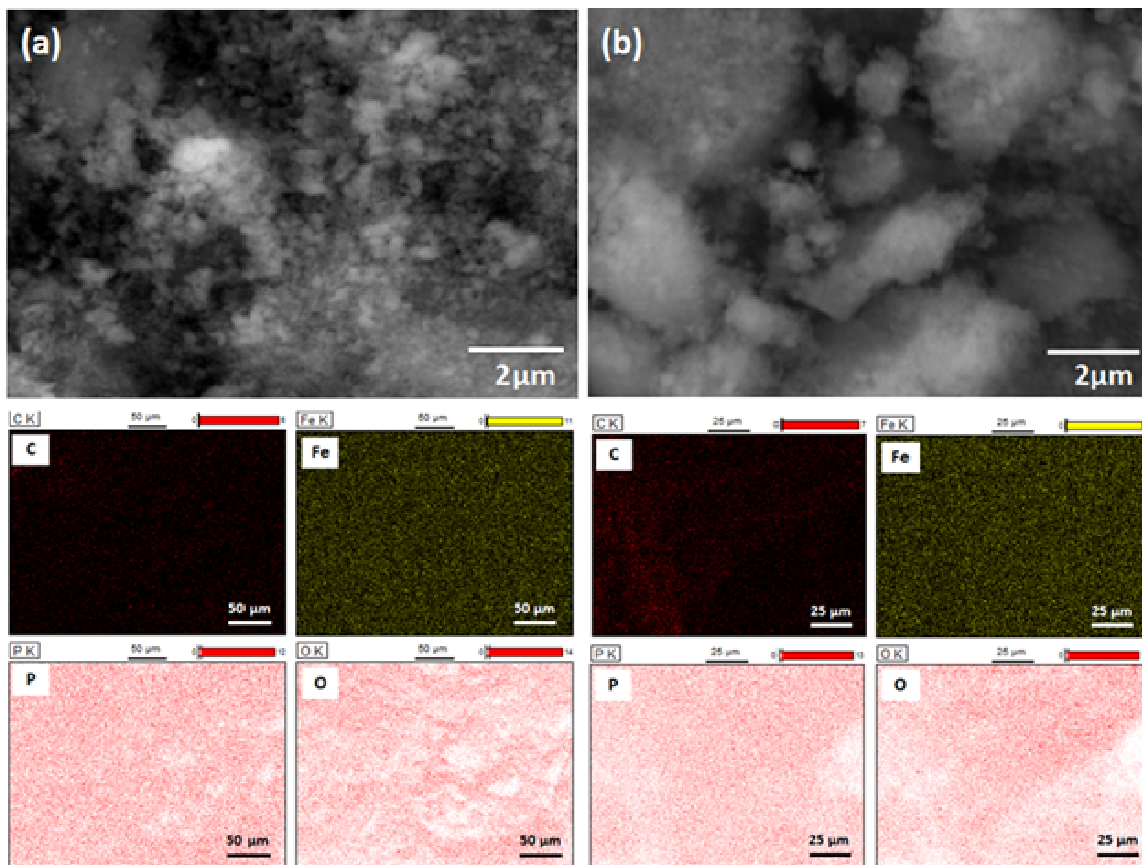


Fig. 4 SEM micrographs and EDS mapping of samples sintered at 400 °C for 3h (a) LFP and (b) LFP-C

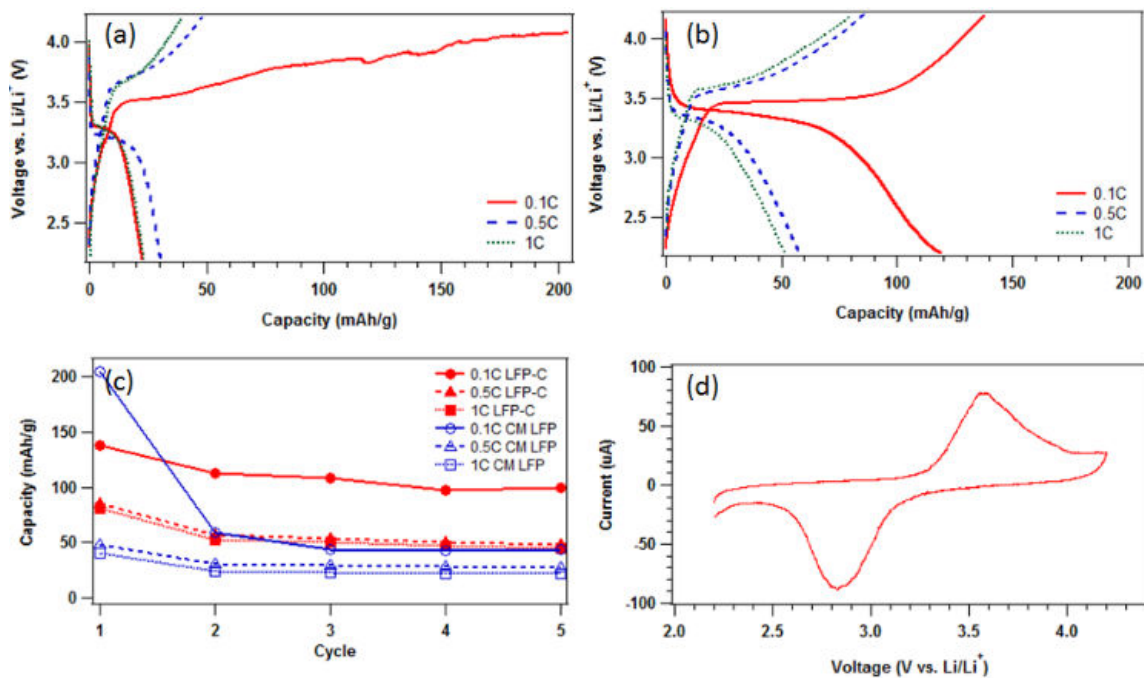


Fig. 5 (a) Charge-Discharge curves of (a) commercial LiFePO₄ and (b) LFP-C at 0.1C, 0.5C, and 1C; (c) Cyclability of commercial and LFP-C; (d) Cyclic voltammetry curve of LFP-C at 0.1mVs⁻¹

Fig. 5 shows the charge and discharge capacity of the commercial LFP (Fig. 5 (a)) and LFP-C (Fig. 5 (b)) at different C-rates (1 C, 0.5 C, and 0.1 C). It can be observed that the LFP-C showed higher capacities than the commercial LFP. At 0.5 C rate, the LFP-C revealed about 90 mAh/g charging capacity while only about 50 mAh/g for the commercial LFP. It can also be observed that the LFP-C has better coulombic efficiencies than the commercial sample. In addition, the cyclability as shown in Fig. 5 (c) also revealed better cycling performance of the LFP-C. On the other hand, Fig. 5 (d) revealed the cyclic voltammetry curve of the LFP-C samples at 0.01 mVs^{-1} from 2.2 V to 4.2 V. The profile shows two distinguishable peaks at around 3.60 V and 2.83 V. The oxidation and reduction peaks correspond to the two-phase charge-discharge reactions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, corresponding to lithium insertion and extraction in the LiFePO_4 structure.

IV. CONCLUSION

LFP-C as cathode material was successfully synthesized using wet chemistry method at 400°C sintering temperature. The XRD patterns showed an orthorhombic LFP. SEM images revealed a particle agglomeration, while TEM images confirmed the crystallinity of LFP and presence of amorphous carbon coating. The carbon coated LFP sample delivered a high charge capacity of about 140 mAhg^{-1} with good coulombic efficiency as compared to the commercial LFP. Hence, in this study, the observed good electrochemical properties of synthesized sample can be ascribed to the successful incorporation of carbon which enhances electronic conduction as well as with the smaller grain size which enhances electrode performance.

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