INVESTIGATION OF THE STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF CARBON LiFePO$_4$ PREPARED BY USING CAROXYLON IMBRICATUM FORSSK EXTRACT AS A COATING AGENT

INVESTIGACIÓN DE LAS PROPIEDADES ESTRUCTURALES Y ELECTROQUÍMICAS DE LiFePO$_4$ RECUBIERTO DE CARBONO PREPARADO UTILIZANDO EXTRACTO DE CAROXYLON IMBRICATUM FORSSK COMO AGENTE DE RECUBRIMIENTO

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Abstract

This work evaluates the electrochemical performance of carbon-coated LiFePO$_4$ (LiFePO$_4$/C) using a plant extract of Caroxylon Imbricatum Forssk via a green synthesis route. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and cyclic voltammetry to investigate the phase, crystalline structure, morphology and electrochemical performance. Both samples, LiFePO$_4$ and LiFePO$_4$/C, exhibited an olivine LiFePO$_4$ structure and the obtained particle sizes were in the nanoscale. The effects of the carbon coating improved the electrochemical performances of carbon-coated LiFePO$_4$ via enhancing rate capability and electronic conductivity.

Resumen

Este trabajo evalúa el rendimiento electroquímico del LiFePO$_4$ (LiFePO$_4$/C) recubierto de carbono mediante un extracto vegetal de Caroxylon Imbricatum Forssk mediante una ruta de síntesis ecológica. Las muestras obtenidas se caracterizaron mediante difracción de rayos X (DRX), microscopía electrónica de barrido (MEB), espectroscopía Raman y voltamperometría cíclica para investigar la fase, la estructura cristalina, la morfología y el rendimiento electroquímico. Ambas muestras, LiFePO$_4$ y LiFePO$_4$/C, presentaron una estructura de LiFePO$_4$ de olivino y los tamaños de partícula obtenidos fueron a escala nanométrica. Los efectos del recubrimiento de carbono mejoraron el rendimiento electroquímico del LiFePO$_4$ recubierto de carbono al aumentar su capacidad de velocidad y la conductividad eléctrica.

Palabras clave: conductividad, caroxylon imbricatum, extracto, electroquímica, LiFePO$_4$ recubierto de carbono, nanopartículas.

Introduction

Global energy depletion has been significantly increasing at a critical rate due to various reasons, including the worldwide population growing, global economy rapid expansion, hybrid electric vehicles advancements, and the high demand for portable electronic devices [1–3]. The depletion of global energy reserves at this current consumption rate will become inevitably imminent. According to reports, the international requirements of energy will rise to double in the middle century and triple in the year 2100 [4]. To overcome the huge use of energy and the large global resources increasing shortage all over the world, there is a real need to protect the environment by considerably reducing both environmental pollution and the consumption of natural resources [5, 6].

Lithium-ion batteries (LIBs) had great interest in the past few decades and have been extensively used for numerous applications,

ranging from electric vehicles (EV) to portable electronics [7]. The LIBs application advantages in EV are long cycle life, energy density, and low CO_2 emission [8]. A battery is a source of electrochemical power able to convert chemical energy to electrical energy, and vice versa [9]. A battery consists of several cells, each composed of three main components: positive electrode (cathode), negative electrode (anode), and the electrolyte system [10]. In the electrochemical reaction, the reduction-oxidation (redox) process converts the chemical energy stored in the electrodes into electric current [11]. A rechargeable battery (storage battery or secondary cell) is a type of electrical battery, which can be charged and discharged into a load many times compared to a fully charged primary battery, which is discarded after use [12].

Among all types of rechargeable batteries, lithium-ion batteries (LIBs) are broadly used, especially in electric vehicles, unmanned aerial vehicles and portable electronic devices [13]. Compared with other common batteries, especially these containing metal elements, such as Ni-Cd and lead acid batteries [14, 15], LIBs are characterized by high specific and volumetric energy density [16, 17].

One of the promising cathodes is olivine-lithium iron phosphate ($LiFePO_4$); it exhibits different advantages such as high thermal stability, high theoretical capacity ($170\ mAh\ g^{-1}$), cycling stability, good safety features, and environmental friendliness [18–23]. However, the slow kinetics of lithium ion diffusion through the $FePO_4/LiFePO_4$ interface and low electronic conductivity ($\sim 10^{-9}\ S\ cm^{-1}$) are the main reasons for the poor rate performance of $LiFePO_4$, hence limiting its practical applications [24–28]. To overcome the poor rate performance of $LiFePO_4$, many efforts have been used, such as optimizing the synthesis processes [29–33], adding metal powders [34, 35], coating with supervalent ions [36–38], particle-size minimization [39–41], carbon nanocoating [40–46] and preparing composites of $LiFePO_4$ with other lithium extraction and insertion materials [47, 48]. Carbon conducting additives are often used to improve $LiFePO_4$ rate capability [49–56]. These additives not only enhance the rate capability of $LiFePO_4$

but also decrease the $LiFePO_4$ grain size and avoid impurity phases [57]. Almost all these methods have some disadvantages such as the produced material containing anion impurities, contaminated gases and increased the manufacturing costs [58].

In this work, carbon-coated particles of $LiFePO_4$ were synthesized using Caroxylon Imbricatum Forssk plant extract as a carbon-coating source. The morphology, structure, and electrochemical properties of carbon-coated $LiFePO_4$ are investigated carefully.

Materials and Methods

Chemicals

Fresh Caroxylon imbricatum plant was collected from the local area of Al-Islah, Iraq. Lithium nitrate ($LiNO_3$), iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and ethanol were purchased from Sigma Aldrich and used without further purification.

Preparation of caroxylon Imbricatum Forssk extract

The fresh Caroxylon imbricatum Forssk plant was washed thoroughly with deionized water to remove any dust particles. The plant dried at 60°C in an oven until completely dry. The dried plant was grinded into a fine powder using a mortar and pestle. Afterward, the crushed plant was weighed and dispersed in deionized water in the ratio 1g: 100 ml. The dispersion was sonicated for 1 hour and then centrifuged. The obtained solution was further filtered using filter paper, and the resulting plant extract was stored in the refrigerator (4°C) for utilization in the synthesis of $LiFePO_4$.

Synthesis of $LiFePO_4$

Stoichiometric amount (0.21 mol) of $Fe(NO_3)_3 \cdot 9H_2O$, $LiNO_3$ and $NH_4H_2PO_4$ were prepared separately by dissolving 8.08 g, 14.48 g, and 2.31 g in 50 mL of plant extract respectively. The

precursor solutions were mixed and stirred continuously using a magnetic stirrer at room temperature for 1 hour to ensure uniform distribution of the extract and thorough mixing of the precursors. Transfer the mixed solution into a crucible and dry the mixture at 80°C in an oven to evaporate the water and obtain a dry powder. Once dried, grind the precursor powder to ensure homogeneity. Place the obtained powder in a muffle furnace and calcine the powder under an inert atmosphere at 800°C for 6 hours. After cooling to room temperature, the obtained $LiFePO_4/C$ composite powder was collected and washed with deionized and ethanol several times and then dried at 80°C for 1 hour. For comparison, the $LiFePO_4$ was prepared by the same procedure using 50 mL of deionized water instead of plant extract.

$$LiNO_3 + Fe(NO_3)_3 \cdot 9H_2O + NH_4H_2PO_4 + C(\text{from plant extract}) \rightarrow$$
$$LiFePO_4/C + \text{byproducts}$$
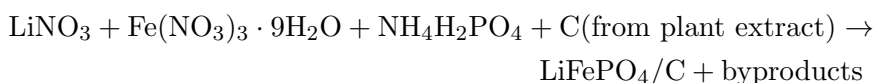
Characterization

The phase and crystalline structure of the $LiFePO_4$ samples were characterized by an X-ray diffractometer (Philips X'pert) using Cu Kα radiation (λ=1.54056 Å) and Raman spectroscopy (Witec Alpha 300RAS). The microstructures and morphologies were examined using scanning electron microscopy (JSM-7600TFE). The carbon content of the $LiFePO_4$ samples was estimated by a carbon analyzer (LECO Co., CS 400). The electrochemical performance has been studied by measuring the coin-type cell CR2025 made of the $LiFePO_4/C$ and $LiFePO_4$ samples.

Results and Discussion

The structural identification of the synthesized $LiFePO_4/C$ and $LiFePO_4$ was characterized by XRD analysis and shown in Figure 1. As shown in Figure 1, both $LiFePO_4/C$ and $LiFePO_4$ display well crystallized and sharp peaks of olivine type structure patterns (JCPDS, No. 81-1173). Also, the sharp peak observed at 26.53° corresponds to the (002) graphitic carbon plane which indicates the successful carbon coating of $LiFePO_4/C$. Additionally,

the average crystallite sizes of both LiFePO$_4$/C and LiFePO$_4$ were calculated using Scherrer's equation and found to be 75.3 nm and 46.5 nm for LiFePO$_4$ and LiFePO$_4$/C respectively.

Carbon coating in the LiFePO$_4$ structure was also confirmed by Raman spectra. As shown in Figure 2, LiFePO$_4$ sample displays a strong band at 985 cm^{-1} related PO$_4^{-3}$ anion stretching vibrations, while LiFePO$_4$/C exhibits strong bands at 1339, 1579, and 2679 cm^{-1}, which are ascribed to defects in the graphene structure, graphite carbon and second order of two phonon processes respectively [3–59].
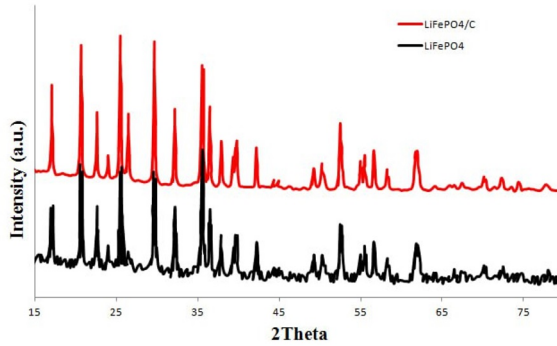

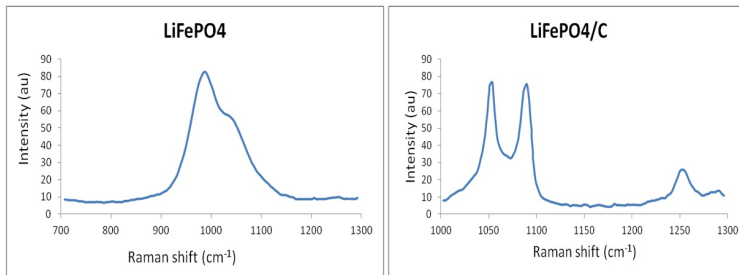FIGURE 1. *XRD patterns of synthesized samples*

FIGURE 2. *Raman spectra of synthesized samples*

Figure 3 shows the SEM images of LiFePO$_4$ samples prepared in the presence and absence of plant extract. In both SEM images, the morphology of LiFePO$_4$ and LiFePO$_4$/C displays agglomerated spherical shaped particles, and the particles sizes were 85.7 nm and

62.3 nm for $LiFePO_4$ and $LiFePO_4/C$ respectively. In comparison with $LiFePO_4$, the $LiFePO_4/C$ shows a clear regular and spherical shape, which is expected to make the $LiFePO_4/C$ sample more favorable for the electrochemical performance. From XRD and SEM analysis, it is found that the sample with a high carbon content ($LiFePO_4/C$) has smaller crystallite and particle sizes therefore have high specific surface area, hence best electrochemical performance [60–62].
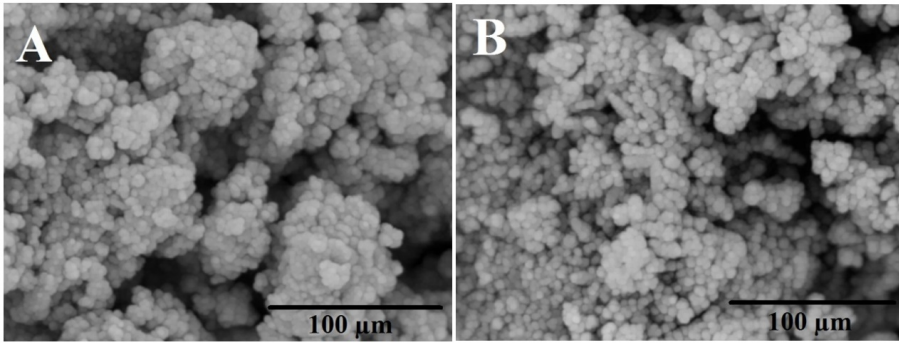

FIGURE 3. *SEM images of synthesized samples, (A) LiFePO$_4$ (B) LiFePO$_4$/C*

Sample	Average crystallite size (nm)	Particle size (nm)	Carbon content
LiFePO$_4$	75.3	85.7	0.8
LiFePO$_4$/C	46.5	62.3	13.6

TABLA 1. *Average crystallite sizes, particles size and carbon content of synthesized samples*

Figure 4 shows the cyclic voltammetry (CV) curves of $LiFePO_4/C$ and $LiFePO_4$ performed at 2.3–4.3 V and 0.1 mV s^{-1} voltage range and rate respectively. The CV profile of $LiFePO_4/C$ shows sharper redox peaks compared with $LiFePO_4$ and the voltage difference between oxidation and reduction peaks was 302 mV and 173 mV for $LiFePO_4$ and $LiFePO_4/C$ respectively. As a result, the observed redox curves indicate that the $LiFePO_4/C$ possess lower polarization than that of the $LiFePO_4$ which could be resulted of kinetics enhancement by reduction of the lithium ion diffusion path and electronic conductivity improvement by carbon coating.

Figure 5 shows the rate capability of LiFePO$_4$/C and LiFePO$_4$ samples. The LiFePO$_4$/C sample exhibited a rate capability of 152.2, 139.8, 122.7, 99.5, and 78.2 mAh g^{-1} at 0.2, 1, 5, 10, and 15 C, respectively. For LiFePO$_4$, the corresponding capacities were 144.6, 129.9, 111.3, 82.5 and 49.7 mAh g^{-1}.
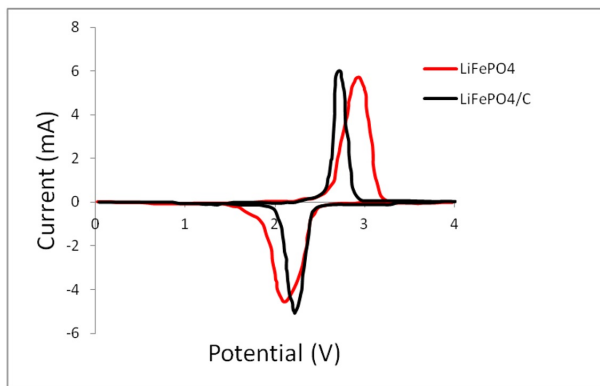

FIGURE 4. *Cyclic voltammetry curves of LiFePO$_4$ and LiFePO$_4$/C*

The best rate capabilities of LiFePO$_4$/C compared to LiFePO$_4$ should be related to the nanoscale lithium ion diffusion path and superior electrical contact between current collector and the particles resulting from the doped carbon.
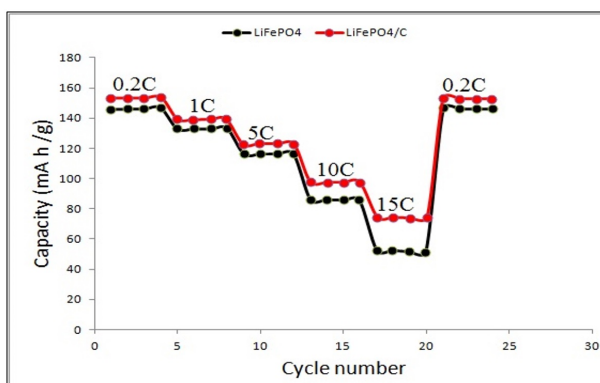

FIGURE 5. *Capability of LiFePO$_4$ and LiFePO$_4$/C*

Figure 6 represents the spectra of LiFePO$_4$/C and LiFePO$_4$ obtained by electrochemical impedance spectroscopy (EIS) in

aqueous electrolyte. In Nyquist plot, the impedance semicircle diameter in medium high frequency represents the lithium ion charge-transfer resistance R_{ct} between the active $LiFePO_4$ samples and the electrolyte. Based on the EIS results, the $LiFePO_4/C$ sample has smaller charge transfer resistance thereby better electrode performance compared with $LiFePO_4$ sample.
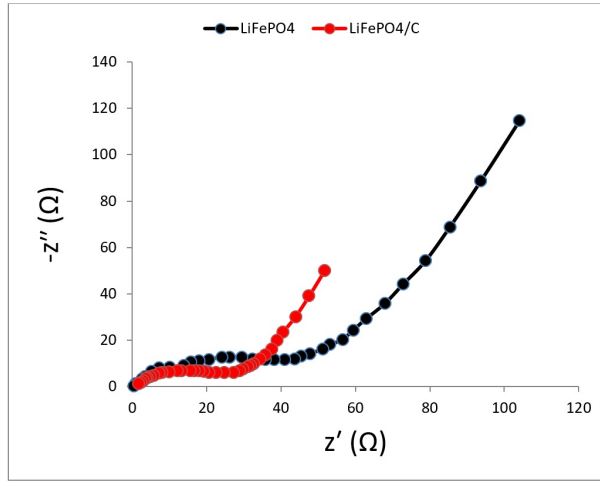

FIGURE 6. *Nyquist plot of $LiFePO_4$ and $LiFePO_4/C$*

Conclusion

This study demonstrated the successful synthesis of carbon-coated $LiFePO_4$ with superior structural and electrochemical properties using Caroxylon Imbricatum Forssk plant extract as a carbon source. X-ray diffraction analysis confirmed that the proper $LiFePO_4$ Olivine phase was achieved successfully. The as-prepared $LiFePO_4/C$ and $LiFePO_4$ materials morphology were investigated via SEM technique and the results confirm the formation of agglomerated spherical shaped particles. The electrochemical measurements indicated that the electrochemical performance of $LiFePO_4$ coated by carbon was improved, compared with $LiFePO_4$. The electrochemical results also indicated that the coating by carbon not only reduced the size of $LiFePO_4$ but also decreased

lithium ion diffusion path, improved the electronic conductivity, enhanced the rate capability and reduced charge transfer resistance.

Conflict of Interest

The authors declare no conflict of interest.

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