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# Microwave synthesis of copper network onto lithium iron phosphate cathode materials for improved electrochemical performance

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## HIGHLIGHTS

- An efficient route was used to prepare Cu/$LiFePO_4$ (LFP) hybrid as cathode material.
- The Cu/LFP cathodes exhibit an improved performance as compared to fresh LFP one.
- The microwave approach can deposit Cu network, fully covered the LFP powders.
- The Cu network ensures LFP to get electrons, alleviating electrode polarization.

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## ABSTRACT

Herein reported is an efficient microwave-assisted (MA) approach for growing Cu network onto $LiFePO_4$ (LFP) powders as cathode materials for high-performance Li-ion batteries. The MA approach is capable of depositing highly-porous Cu network, fully covered the LFP powders. The electrochemical performance of Cu-coated LFP cathodes are well characterized by charge/discharge cycling and electrochemical impedance spectroscopy (EIS). The Cu network acts as the key role in improving the specific capacity, rate capability, electrode polarization, as compared to fresh LFP cathode without the Cu coating. The EIS incorporated with equivalent circuit reveals that the completed Cu network obviously suppresses the charge transfer resistance. This result can be attributed to the fact that the Cu network ensures the LFP crystals to get electron easily, alleviating the electrode polarization in view of one-dimensional $Li^+$ ion mobility in the olivine crystals. Based on the analysis of Randles plots, the relatively higher $Li^+$ diffusion coefficient reflects the more efficient $Li^+$ pathway in the LFP powders through the aid of porous Cu network.

## 1. Introduction

So far, there are two main challenges of lithium-ion batteries for transportation including cost down and safety issue [1]. It is generally recognized that the development of electrode materials is capable of overcoming the above obstacles. In this regard, olivine $LiFePO_4$ (LFP) has shown great potential to meet these two challenges due to its relatively low cost of raw materials, long cycle life, thermal stability, flat voltage plateau (~3.4 V vs. $Li^+/Li$), moderate theoretical specific capacity (~170 mAh $g^{-1}$), and most importantly, environmental friendliness and abundance of Fe resources in nature [2,3]. Although LFP cathode has become a commercially relevant cathode material, the insulating character of olivine LFP limits its use as a cathode material for high-power Li-ion batteries [4,5]. A loss in specific capacity with increasing *C* rate is caused by the hindered transfer of Li ions upon lithium insertion/extraction due to intrinsic low electronic conductivity ($10^{-9}$ S $cm^{-1}$), associated with diffusion controlled kinetics of the delithiation/lithiation process [2]. Accordingly, several strategies have been proposed to resolve the above problems, including surface coating or mixing with conductive layers (e.g., carbon or metal) [6–9] and reducing LFP particle size [2,5,10]. Owing to their great success, the LFP composites have been taken into account as promising cathode materials for high-power and high-energy Li-ion batteries. This achievement directs us to develop an efficient surface coating technique for improving the electrochemical performance of LFP cathodes.

Recently, our pervious studies have proposed a facile

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microwave-assisted (MA) technique to prepare metallic nanoparticles (e.g., Pt–Sn alloy and Ag nanorod) onto carbon supports [11,12] and ZnO layer over spinel lithium titanate powders [13]. Generally, the MA method is capable of depositing metallic nanoparticles with good uniformity on different supports due to its energy efficiency, uniformity, and simplicity in execution [14,15]. In this work, the MA method is applied for growing copper layer over the surface of LFP powders within a short period of 10 min, forming Cu-coated LFP composites. The Cu nano-coating with highly electronic conductivity could repair incomplete electronic network on the LFP powders, thus facilitating the lithium insertion/extraction kinetics [4,9]. The Cu-coated LFP cathodes were systematically characterized by structural analysis, charge–discharge cycling at various *C* rates, and electrochemical impedance spectroscopy (EIS). This present study aims at the influence of Cu layer on the specific capacity, cyclic stability, equivalent series resistance ($R_{ES}$), and apparent diffusion coefficient in the Cu-coated LFP cathodes. As a result, the Cu-coated LFP cathodes display superior electrochemical performance as compared with fresh LFP one. This satisfactory result is beneficial for the development of LFP cathodes in practical use of Li-ion batteries.

## 2. Experimental

In a typical procedure supplied by Ubiq Technology Co., Taiwan, a solid-state reaction has been employed to synthesize fresh carbon-coated LFP powder. The carbon content in the LFP powders was approximately 2–3 wt%. Herein one-stage procedure of pulse MA method for depositing Cu layers on the LFP powders could be described as follows. The as-derived LFP powders (10 g) were chemically impregnated with a Cu-containing solution (100 mL) in a beaker. The ionic solution consisted of 0.01 M $Cu(CH_3COO)_2$, 0.04 M KOH, and ethylene glycol (EG). The beaker was then placed at the center of a household microwave oven and then heated under microwave power of 900 W. With the help of a temperature controller the maximal temperature was maintained at *ca.* 150 °C. The parameter setting of power-on:power-off period was 3 s:3 s and total cycle number was 100 cycles, respectively. The Cu-coated LFP powders were then separated from the solution and then dried at 105 °C in a vacuum oven overnight. The $Cu^{2+}$ concentration was selected as controlling factor in tuning the atomic composite of Cu layer over the LFP powders. The other two ionic solutions (i.e., 0.02 and 0.03 M $Cu(CH_3COO)_2$) were separately prepared and then added into each aqueous solution. Subsequently, the MA depositions were carried out under the same operating condition. The LFP powder without any Cu coating was designated to LFP-BK, and the Cu-coated LFP samples were denominated to LFP-C1, LFP-C2, and LFP-C3, according to the sequence of $Cu^{2+}$ ionic concentration, i.e., 0.01, 0.02, and 0.03 M.

The X-ray diffraction (XRD) patterns of LFP powders were collected by an automated X-ray diffractometer (Shimadzu Labx XRD-6000) with Cu-K$\alpha$ radiation ($\lambda$ = 1.5418 Å). Field-emission scanning electron microscopy (FE-SEM) measurements were performed using a JEOL 2010F microscope. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-2100 TEM with an acceleration voltage of 200 kV. An energy diffraction spectroscopy (EDS) was adopted to analyze the atomic Cu ratio in the LFP composites. The chemical composition of LFP powders was analyzed using X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded with a Fison VG ESCA210 spectrometer and Mg-K$\alpha$ radiation.

The electrochemical properties of LFP powders were evaluated by assembling CR2032 coin-type cells in an Ar-filled glove box. First, the Cu-coated LFP samples were dried at 105 °C overnight in a vacuum oven before assembling the coin cells. The dried LFP powders were then well mixed with polyvinylidenefluoride (PVdF) and conducting media (Super-P and KS-6) in the weight ratio of 85:10:5 by blending in *N*-methyl pyrrolidinone (NMP). The slurry was blended by a 3D mixer using Zr balls for 3 h, ensuring homogeneous slurry. Afterward, the prepared slurry was coated on Al foil with a doctor blade, followed by evaporating the solvent, NMP, with a blower dryer. The prepared cathode sheet was dried at 135 °C in a vacuum oven for 12 h and pressed under a pressure of approximately 200 kg $cm^{-2}$. The thickness of cathode sheets was adjusted to have a thickness of 100 μm. In the test cells, Li metal and porous polypropylene film (Celgard separator #2400) served as counter electrode and separator, respectively. The electrolyte solution was 1.0 M $LiPF_6$ in a mixture of ethylene carbonate, propylene carbonate, and dimethyl carbonate, with a weight ratio of 3:2:5. The charge/discharge cycling test of assembled coin cells at various *C* rates (from 0.1 to 5*C*) was carried out within the voltage range of 2–4 V vs. Li/$Li^+$ at ambient temperature. The EIS measurement was performed in the frequency range of 100 kHz to 0.01 Hz at open circuit potential (OCV) with an alternating current perturbation of 5 mV. The EIS analysis of LFP cathodes was carried out using an impedance analyzer (CH Instrument, Inc., CHI 608) and the equivalent circuit was analyzed using computer software (*Z*-view).

## 3. Results and discussion

Fig. 1 shows typical XRD patterns of Cu-coated LFP powders, prepared by the MA method at 150 °C. For comparison, the XRD pattern of LFP-BK sample was also provided. It has shown that all the diffraction peaks can be indexed to orthorhombic lattice of LFP, referring to the JCPDS No. 83-2092: $a$ = 10.334 Å, $b$ = 6.010 Å, and $c$ = 4.693 Å [16,17]. Herein the intense reflection peaks reveals that the as-prepared LFP powders are well crystallized. It is worth noting that almost no Cu reflections can be observed, indicating that the Cu content is less than the detection limit of XRD analysis.

XPS analysis was performed on the Cu-coated LFP samples to figure out the Cu content onto the surface of LFP powders. Fig. 2(a) shows survey XPS spectra of Cu-LFP powders, confirming the presence of Cu content. The intensity of Cu 2p peak, consisted of two distinct primary peaks for Cu $2p_{1/2}$ and Cu $2p_{3/2}$, is an

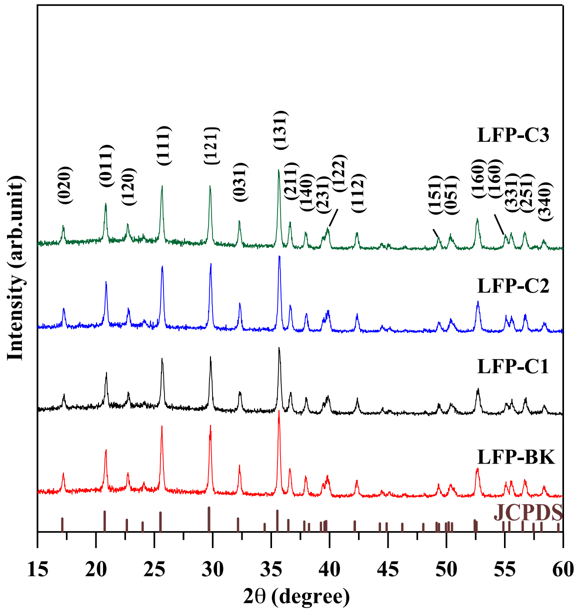

**Fig. 1.** Typical XRD patterns of fresh LFP and Cu-coated LFP powders.