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The Characteristics of $LiFePO_4$/Copper Nanoparticles/Carbon Nanotubes Composites Used as Lithium Ion Battery Cathode

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***Abstract*—Copper nanoparticles and carbon nanotubes (CNTs) have been used to form a LiFePO4/Cu nanoparticle/CNT (LFP/Cu/CNT) composites and applied as an active material in lithium ion battery cathode. The composites were prepared by mixing commercial LFP powders with a variation of copper nanoparticles and or CNT compositions in a vacuum mixer. The mixture was then applied onto an aluminium foil as a cathode current collector. For the characterization, X-ray diffraction (XRD) was used to confirm the phase, grain size and the presence of the impurities, whereas the morphology of the surface was characterized by using field emission scanning electron microscope equipped with energy dispersive X-ray spectroscopy (FESEM/EDX). The electrical conductivity of this cathode material was tested by using electrochemical impedance spectroscopy (EIS). XRD results showed that the composite has single phase LFP form and that the presence of copper nanoparticles and CNT were not detected in the crystal structure. Morphology and distribution of CNT and copper nanoparticle analysed using FE-SEM/EDX showed mixed materials in the variation of copper nanoparticles and CNTs with homogenous and even distribution of particle size in the range 100-300 nm. The electrical conductivity of LFP increased with the addition of copper nanoparticles at a certain level with 1-order of magnitude, whereas almost 3-order of magnitude with the addition of both copper nanoparticles and CNTs. The addition of CNTs alone, however, is more effective in increasing the conductivity as compared to the addition of copper nanoparticles due to the inevitable formation of secondary phase revealed by the EIS diagrams.**

***Keywords*— carbon nanotubes; copper nanoparticles; lithium ferro phosphate; lithium ion battery.**

I. INTRODUCTION

With the decrease of fossil fuel resource for energy, and the increase concern for environmental issues due to greenhouse effect from the use of fossil fuel, a lot of efforts have been stressed on the environmentally friendly energy alternatives resources. The key issues are the increasing demand for the renewable energy as an alternatives energy resources [1] and how to store the unused energy and use it later at a certain time and or condition. In this case, battery is one of the choices.

Battery comes with many advantages and offers suitable answer especially for the emission problems in many areas such as transportation and energy crisis. In addition, battery also has many advantages such as good performance, relatively high energy efficiency, and with combination with battery-electric vehicle, it is noiseless with less maintenance [2]. In this electrical vehicle use, however, the most challenging point in is that the limitation in the driving range since the battery-electric vehicle relies on battery as its sole energy source [3]. Hence, many efforts have been focused in developing sufficient energy to drive certain range and supply all loads needed by this battery-electrical vehicle.

As an electrochemical cell system, battery also offers many advantages in terms of portability and ease of replacement [4]. This stress has been emphasized even more with the increase use of hybrid electric vehicle (HEV) and electric vehicle (EV), and thus the demands for this kind of high capacity energy resources also increase [5].

Currently, lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMnO_2$), and lithium iron phosphate ($LiFePO_4$) have been widely used as cathode active materials in lithium ion batteries [6]. Of the three, $LiCoO_2$ has the highest theoretical capacity of 220 mAh/g, sufficiently high electrical conductivity of 10^{-3} S/cm, however, this material is quite expensive and has some issues on the safety consideration [7]. As for $LiMn_2O_4$, this material is easily made, environmentally friendly and affordable, but it has low capacity of 100 -120 mAh/g and other drawbacks on Mn mobility issue and oxygen release [8]. On the other hand, $LiFePO_4$ has the advantage of low manufacturing cost compared to those of $LiCoO_2$ and $LiMnO_2$ because of the abundance of the material in nature, non-toxic, and it has quite high theoretical capacity of 170 mAh/g, high charge-discharge cycles of > 3000 and environmentally friendly [6], [7]. The major problem with this material, however, is the slow lithium ions diffusion between the interface and thus impacting on low electrical conductivity in the order of 10^{-9} S/cm and thus low rate capability [8].

Many efforts have been conducted by many researchers to improve the conductivity of this LFP such as metal doping [9], [10] and carbon coating [11]. This carbon coating is usually performed during the synthesis and is expected to form a composite of LFP/C with more conductivity [12]. Cu doping and carbon coating LFP had also been performed and the results showed that the material has a promising activity for use as cathode material in lithium ion battery [13]. The use of carbon and or carbon nanotubes as anode active materials has been explored by many investigators and it has proven to increase the performance of LFP-based lithium ion battery [14]–[20].

In this work, in an effort to improve the conductivity of LFP active material used as a cathode in lithium ion battery, copper nanoparticle and carbon nanotube (CNT) have been used to form a LFP/Cu/CNT composites and the results are presented and discussed.

II. MATERIAL AND METHOD

A. Materials

The materials were LiFePO4 powders (LFP), copper nanoparticles (Cu), and carbon nanotube (CNT). Binder is polyvinylidene fluoride (PVDF) whereas the solvent is n-methyl pyrrolidone (NMP). Other materials for battery assemblage including polymer battery case, separator, anode active material in the form of graphite single side coated copper foil for anode current collector, positive and negative terminals, aluminium foil for cathode current collector, and electrolyte (LiPF6). All of these materials were purchased from MTI Corporation with no further treatment and or purification.

B. Cathode Preparation

Composite material in the form of cathode sheet was made by using LFP with the addition of various copper nanoparticles compositions, i.e. 0, 1, 3, 5, and 7 % at two CNT compositions, i.e. 0 and 5 %. Polyvinylidene fluoride served as a binder plus NMP as a solvent to make a slurry. Detail of the composition along with the sample coding is given in Table 1.

This slurry was prepared in a vacuum mixer before casting it onto cathode current collector of aluminium foil by using a film applicator. The sheet was allowed to cool and dry for 24 h before putting it into calendaring process and then ready for conductivity measurement.

TABLE I
SAMPLE CODING

Sample	%Cu	%PVDF	%CNT	%$LiFePO_4$
1A	0	10	0	90
1B	1	10	0	89
1C	3	10	0	87
1D	5	10	0	85
1E	7	10	0	83
2A	0	10	5	85
2B	1	10	5	84
2C	3	10	5	82
2D	5	10	5	80
2E	7	10	5	78

C. Characterization

The structural characteristic of cathode active material was examined by using x-ray diffraction (XRD, Panalytical) with Cu Kα radiation (λ = 1.5406 Å), morphology was examined by using field emission electron microscopy (FE-SEM, FEI Inspect F50) equipped with energy dispersive X-ray spectroscopy (EDX), whereas the conductivity was examined by using electrochemical impedance spectroscopy (EIS, Hioki LCR 3532-50).

III. RESULT AND DISCUSSION

The morphology of the as-received materials, Cu, CNT and LFP are given in Fig. 1. As can be seen in Fig. 1, for the as-received Cu and LFP powders, they have a spherical shape with a particle size of around 200-300 nm, quite homogenous and distributed uniformly. For the carbon nanotube morphology, as can be seen in the figure, it has cylindrical wire-shape with a diameter of around 50 nm and a length of up to 3 microns. The shape and size are also homogenous and distributed uniformly.

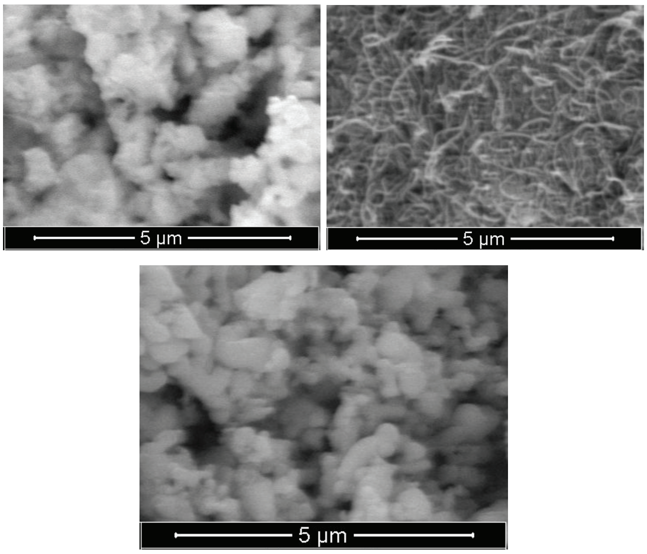

Fig. 1 Morphology of the as-received copper nanoparticle (top left), carbon nanotube (top right) and LiFePO4 (bottom)

X-ray diffraction patterns of LFP at various copper nanoparticles and no CNT compositions are shown in Fig. 2, whereas the diffraction patterns of LFP at various copper nanoparticles and 5 wt.% CNT compositions are given Fig. 3.

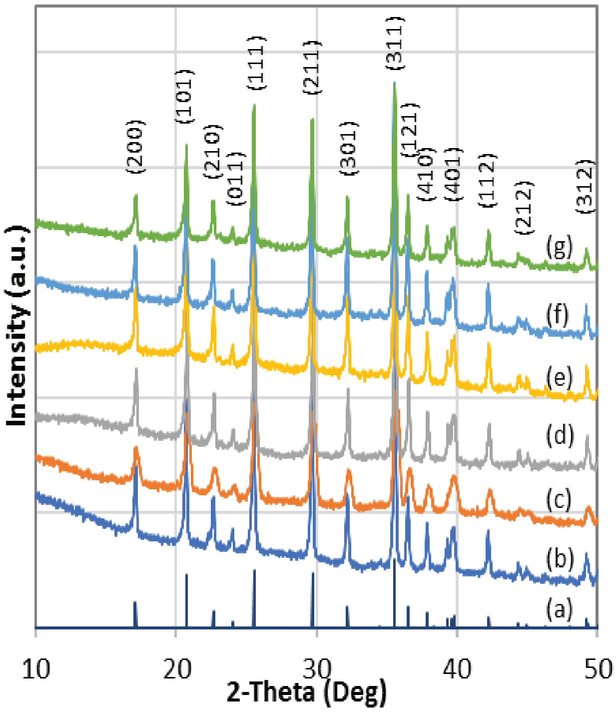

Fig. 2 X-ray diffraction patterns of (a) JCPS 083-2092, (b) as-received LiFePO4, (c) sample 1A, (d) sample 1B, (e) sample 1C, (f) sample 1D, and (g) sample 1E

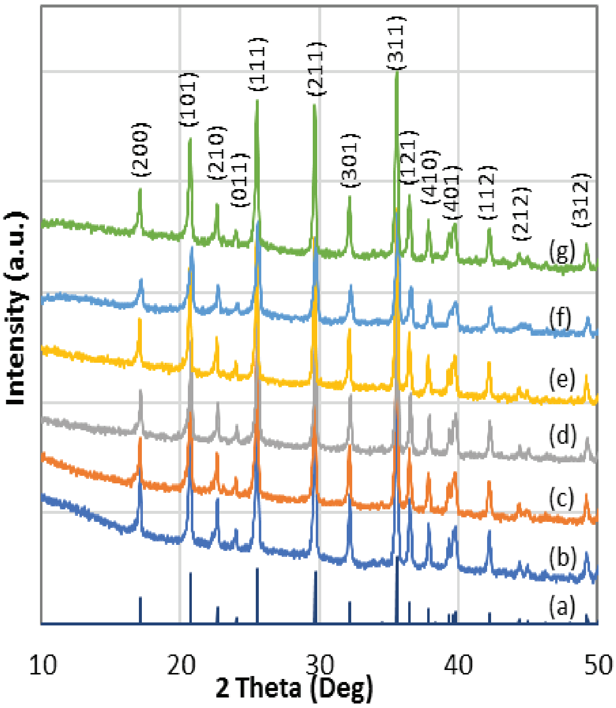

Fig. 3 X-ray diffraction patterns of (a) JCPS 083-2092, (b) as-received LiFePO4, (c) sample 2A, (d) sample 2B, (e) sample 2C, (f) sample 2D, and (g) sample 2E

As seen in both Fig. 2 and 3, the entire diffraction peaks of the LFP composite at these various copper nanoparticles and CNT compositions are still in agreement with that of LFP standard indexed to the orthorhombic Pnma space group (JCPDS No.083-2092).

Strong and sharp diffraction peaks as seen in the figure indicate that LFP/C sample is highly crystalline with no typical diffraction patterns of other phases. The non-existence of other diffraction patterns reveals that copper nanoparticles and CNT have been dissolved to form composite solid solution with no change in the crystal structure [21]. This finding agrees with that found by others in which the addition of Cu metal powders did not affect the crystal structure of LFP [22].

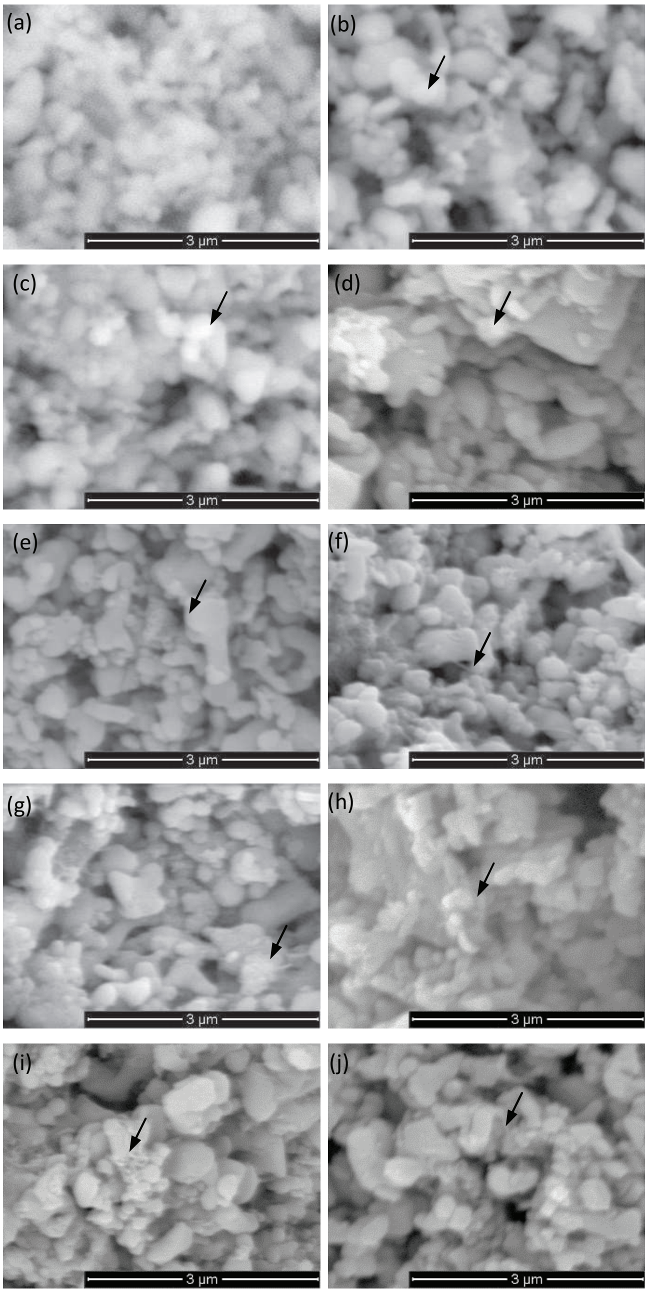

Fig. 4 Morphology of (a) sample 1A, (b) sample 1B, (c) sample 1C, (d) sample 1D, (e) sample 1E, (f) sample 2A, (g) sample 2B, (h) sample 2C, (i) sample 2D, and (j) sample 2E

Morphology of the composites on the surface was revealed using a scanning electron microscope and the results are given in Fig. 4(a) – 4(e) for LFP at various copper nanoparticles with no CNT and Fig. 4(f) – 4(j) for LFP at various copper nanoparticles and selected 5 wt.% CNT.

As can be seen in Figure 4, the spherical shape of the LFP is still intact covered by Cu marked by arrow in Figure 4(b) – 4(e) and or CNT marked by arrow in Figure 4(f) – 4(j). The tendency of the LFP particles to agglomerate also decreases with more concentration of Cu and or CNT additions.

The prepared cathode sheets were examined for their electrical conductivity using EIS at 3.7V and a frequency range of 5-100 kHz. The results in the forms of Cole plots are shown in Fig. 5 and Fig. 6 with a summary is presented in Table 2.

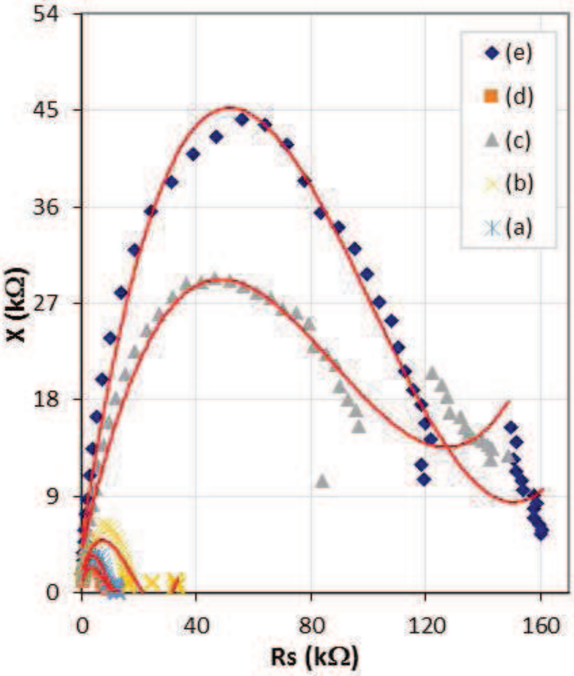

Fig. 5 Room temperature AC impedance spectra of (a) sample 1A, (b) sample 1B, (c) sample 1C, (d) sample 1D, and (e) sample 1E at 4 V. Semicircle of each sample is shown

The impedance measurement was performed by providing a bias voltage of 4V DC and a 10-mV signal permutation superimposed on the bias voltage at a frequency range between 4 Hz – 1 MHz. As seen in Fig. 5, the sample in this variation is dominated by the grain boundary resistance shown by the radius of the semicircle curve at the low frequency region.

The addition of copper nanoparticles at 3 wt.% shows a large semicircle size, but at 5 wt.% the semicircle size shrinks. Meanwhile, the semicircle size goes up at the addition of 7 wt.% copper nanoparticles. In general, all the treatment by copper nanoparticles addition shows the formation of a non-single semicircle. In Fig. 6, the Cole plot is even more complicated with non-single semicircle. The absence of the semicircle in the spectra indicates that the composite formed a non-single phase and or structure. When associated with the XRD results given previously, the phase may not be detected, however, these EIS spectra reveal the possibility of other phases presence in the LFP composite such as copper oxide.

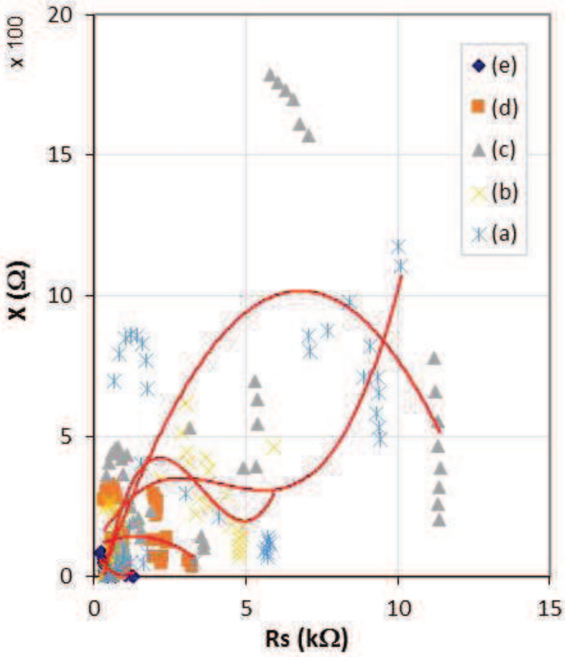

Fig. 6 Room temperature AC impedance spectra of (a) sample 2A, (b) sample 2B, (c) sample 2C, (d) sample 2D, and (e) sample 2E at 4 V. Semicircle of each sample is shown

The summary of the Cole plots discussed previously are presented in Table 2. As seen in Table 2, the electrical conductivity of pure $LiFePO_4$ (sample 1A) shows a value of 7.0×10^{-8} S/cm. This conductivity value is in agreement with that found by another investigator [8]. The conductivity increases with the addition of copper nanoparticles and reached a maximum value at 3 wt.% copper nanoparticles with a conductivity of 5.4×10^{-7} S/cm after then the conductivity decreases with the addition of more copper nanoparticles. The logical explanation of this decrease that yet has to be confirmed is that, at high concentration, copper nanoparticles tend to agglomerate. Moreover, due to its inherent reactivity, copper nanoparticles will react with oxygen to form coper oxides that is almost impossible to avoid, as has also been found by other investigators [13].

TABLE II

ELECTRICAL CONDUCTIVITY OF THE COMPOSITES

	Sample 1 (S/cm)	Sample 2 (S/cm)
A	7.00×10^{-8}	2.05×10^{-5}
B	2.10×10^{-7}	1.60×10^{-5}
C	5.40×10^{-7}	1.40×10^{-5}
D	6.20×10^{-8}	8.40×10^{-5}
E	4.46×10^{-8}	1.92×10^{-5}

Furthermore, the electrical conductivity increased by almost 3 orders of magnitude with the addition of 5 wt.% CNT. This conductivity value was almost stable along with the addition of copper nanoparticles concentration with only a little change. The highest conductivity was observed in the addition of 5 wt.% copper nanoparticles and 5 wt.% CNT. This can be explained by the fact that, at an appropriate concentration, CNT will play a role in keeping both LFP and copper nanoparticles from oxidation, and at the same time keeping the path for the electron movement and thereby increase the value of electrical conductivity [16]. It then can be seen that the addition of CNT alone has sufficed in increasing the electrical conductivity without the need more addition of copper nanoparticles.

IV. CONCLUSIONS

In this work, the electrical conductivity of pure LFP is 7.00×10^{-8} S/cm. The addition of copper nanoparticle, at certain concentration, has an effect in increasing of LFP electrical conductivity of about 1-order in magnitude, however, the increase in conductivity is lower than the expected value due to an inevitable oxidation of copper nanoparticle at high concentration. In the variation of CNT addition, there is an increase in conductivity of about 3-order of magnitude as compared to the pure LFP. The electrical conductivity of LFP with the addition of CNT is 1.6×10^{-5} S/cm, whereas on the variations of both copper nanoparticles and CNT additions, the maximum electrical conductivity at the composition of 5 wt.% copper nanoparticles and 5 wt.% CNT is 8.4×10^{-5} S/cm. It then can be concluded that the addition of CNT alone is more effective in increasing the electrical conductivity as compared to the addition of copper nanoparticles.

NOMENCLATURE

σ	conductivity	S sm^{-1}
ρ	resistivity	Ω
λ	wavelength	Å
θ	Bragg's angle	deg
CNT	carbon nanotubes	
EDX	energy dispersive X-ray spectroscopy	
EIS	electrochemical impedance spectroscopy	
EV	electric vehicle	
HEV	hybrid electric vehicle	
LFP	lithium ferro phosphate	
NMP	n-methyl pyrrolidone	
PVDF	polyvinylidene fluoride	
SEM	scanning electron microscope	
XRD	X-ray diffraction	

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