

Synthesis and Characterization of LiFePO₄/CNT Composites with Variation of Calcination Time as Battery Cathode

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Abstract:- Synthesis of LiFePO₄/CNT composite with various calcination times as a battery cathode material has been successfully carried out. LiFePO₄ synthesis was obtained by the sol-gel method and the addition of CNT was carried out by the doctor blade method. The effect of variations in calcination time and the addition of CNT to the synthesis results were observed. Observations using SEM-EDS showed successful synthesis with a homogeneous surface morphology with the appropriate element content. The XRD results also showed standard-compliant nano crystalline peaks with increasing crystallinity by addition of CNT and duration of calcination. In addition, the conductivity also increased in the presence of CNT and the longer the calcination time. This shows that the resulting LiFePO₄/CNT has the potential as a battery cathode material.

Keywords:- LiFePO₄/CNT, Calcination, Battery.

I. INTRODUCTION

Batteries have been used for energy storage because they have the principle of storing electricity to produce energy. The need for compact, high-energy, environmentally friendly, and rechargeable batteries has been developed from lithium-ion battery concept. Currently, LiFePO₄ is studied extensively and is a good candidate for Li-ion battery cathode material, because of its high theoretical capacity (170 mAh/g), stability of charging cycle, low cost, and environmental friendliness [1,2].

However, the disadvantages remain that the low electronic conductivity and low lithium ion diffusion rate during the discharge process impair the performance of the diffusion rate, and cause the storage capacity to decrease rapidly. Important features responsible for the low-rate ability are considered to be intrinsically poor electronic conductivity (10^{-9} S cm⁻¹) and low Li⁺ ion diffusion due to its olivine crystal structure significantly limiting its performance at high charge and discharge rates [3–5].

To overcome this problem, many reports state that the electrical performance of LiFePO₄ can be improved by ion doping [6], particle size, cation doping, and modification of the phase surface [7]. Carbon materials such as graphite, graphene, and carbon black have been studied as cathode electrodes because of their corrosion resistance, and high conductivity. Recently, carbon nanotubes (CNTs) have been of interest for their increased conductivity, and high electron storage, which influences fast charging characteristics [8]. In this study the

preparation of the LiFePO₄ composite was carried out using the sol-gel method and the addition of CNT was carried out using the doctor's blade method and then calcined with various heating times. Furthermore, LiFePO₄/CNT characterization was carried out using SEM-EDS and XRD and its conductivity was measured to determine the maximum potential condition of the material as a battery cathode.

II. EXPERIMENTAL

A. Materials

The materials used in this study were copper sheet (MTI, Malaysia), LiOH p.a, FeCl₃.5H₂O p.a (Merck, Germany), distilled water, NH₄OH p.a (Merck, Germany), H₃PO₄. CNT powder prepared using the spray pyrolysis method as a result of previous studies[8] was used as an electrode material. Ethanol (Merck, Germany), terpineol (Sigma Aldrich, USA), ethylcellulose (Sigma Aldrich, USA), monoethanolamine (Merck, Germany), and iso-propanol (Merck, Germany) were used unrefined.

B. Synthesis of LiFePO₄/CNT

LiOH and Fe₂O₃ powders were mixed until homogeneous, and then the mixture was poured into H₃PO₄. The result is a gel powder heated by calcination at 400 °C in argon gas for 5 hours. Ethylcellulose was dissolved in ethanol (2% by mass) and stirred for 10 minutes, followed by mixing with 1.6 g of terpineol to form the binder. CNT and LiFePO₄ were dispersed into the binder with stirring for 10 minutes. Then, the paste was deposited onto the Cu foil substrate using the doctor blade method and dried at calcination heating temperature with different times of 2, 4, and 6 hours.

C. Characterization

The surface structure of the electrode was characterized by X-ray diffraction spectroscopy (XRD, Philip Analytical X-Ray BV) with Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV, Scanning Electron Microscopy (SEM), EDS (Energy Dispersive Spectroscopy), and a multimeter (SANWA-multimeter) was carried out to study the conductivity.

III. RESULT AND DISCUSSION

The results of Scanning Electron Microscopy (SEM) are to find out the morphology of pure LiFePO₄ and LiFePO₄/CNTs as shown in figure 1. The surface area morphology of pure LiFePO₄ indicated that the material had homogeneous particle sizes (Fig. 1a), further addition of CNT (Fig. 1b) morphologically patched LiFePO₄ material onto the

CNTs. However, the morphology of LiFePO₄/CNT is not limited, based on the composite material results.

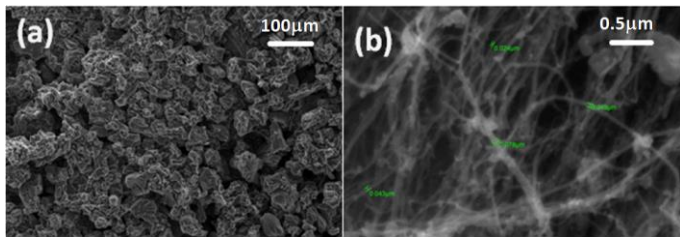


Fig 1. SEM for pure LiFePO₄ (a), LiFePO₄/CNT (b).

Testing using EDS (Energy Dispersy Spectroscopy) is to identify the composition of the sample. The EDS of pure LiFePO₄ as shown in Figure 2a is dominated by the elements Li, Fe, P, and O with a composition of 41.01, 27.63, 18.41, and 12.68% respectively. Furthermore, the EDS yield of CNT-doped LiFePO₄ as a whole is dominated by carbon, namely 83.73% (figure 2b).

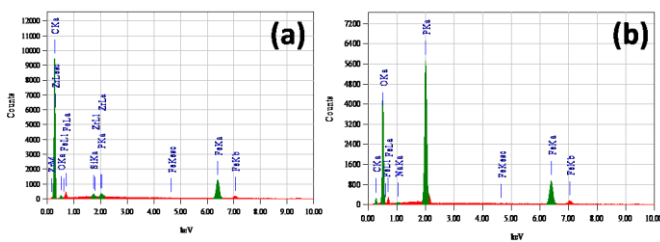


Fig 2. EDS for pure LiFePO₄ (a), LiFePO₄/CNT (b).

Figure 3 shows the adjusted diffraction pattern with reference to the powder Diffraction Standard program. The carbon type detected in the reference (JCPDS number 020-456) seems to be dominated by the peak at 2θ from 26.29° - 26.39°. It exhibits a type of carbon with (002) oriented hexagonal structure of graphite. The diamond structure is dominated by a peak at 2θ from 43.44° - 43.91° with reference number JCPDS 060 675 with orientation (111) [8]. The crystalline phase of LiFePO₄ is olivine. LiFePO₄ material and its peaks were detected by JCPDS card no. 40-1499. The peak of LiFePO₄ is shown at 2θ slightly less than 30° and (211) and (020) reflection of FePO₄ is shown at 2θ slightly greater than 30°. This peak can be used to distinguish these two phases and the fractions of the different phases present in a multiphase mixture (311) reflection phase LiFePO₄ (35.6°) phase FePO₄, reflection (121) phase LiFePO₄ (36.5°) indicates FePO₄ phase (36.7°). The peak area of crystal orientation is used for calculations in determining crystal size by using dominant and strong peaks with high-intensity peaks. Crystallite size was calculated using the Scherer equation [9] as in equation 1.

$$L = \frac{K \lambda}{\beta \cos \theta} \quad (1)$$

where L is nano crystallite size (nm), λ is the X-ray wavelength in nanometer (nm), β is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and K is a constant related to crystallite shape, normally taken as 0.9.

The crystal size of pure LiFePO₄ is 101.6 nm and decreases when CNT is added. Then the decrease in crystal size was directly proportional to the calcination time, the results at 2, 4, and 6 hours were 60.07; 34.74; and 15.93 nm, respectively. The crystal sizes obtained are summarized in table 1. It is known that the effect of addition of CNT and increasing the calcination time decreases the crystal size.

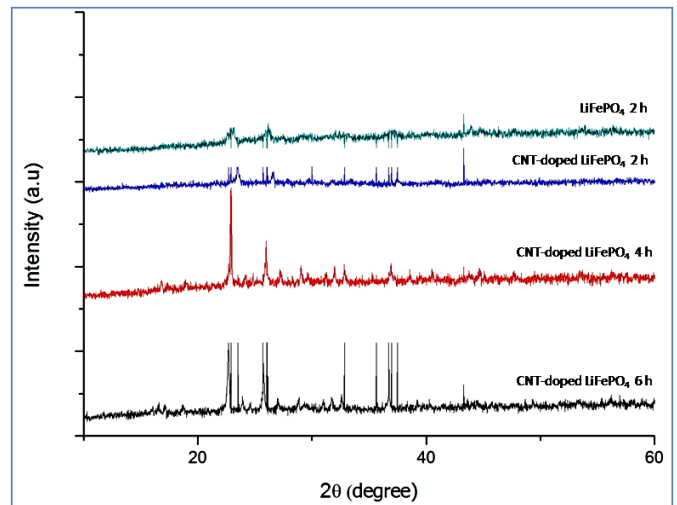


Fig 3. LiFePO₄/CNT XRD results at various calcination times.

Conductivity measurements were measured on a battery prototype with a voltage of 0.2 V used and tested using a multimeter to identify resistance (R). Conductivity can be calculated by equation 2.

$$\sigma = \frac{t}{R.A} \quad (2)$$

where t, R and A are the thickness, resistance and surface area of the electrode[8]

Table 1 and Figure 4 show the relationship between temperature variations during heating and conductivity. From Figure 4 it can be seen that increasing the linear conductivity value of LiFePO₄ doped with CNT is the highest conductivity value. Therefore, a longer time for the heat of calcination will have an impact on increasing conductivity of CNT-doped LiFePO₄ [10–12]. The addition of CNT in LiFePO₄ makes the crystal size smaller because during the calcination process the decrease in LiFePO₄ crystals is affected by porous carbon materials, so it will disturb the smallest size [13,14]. Furthermore, the addition of calcination time will generate activation energy in crystal vibrations and also release boundary atoms to diffusion motion and substitution for other atomic lattice transformations. The increase in conductivity will affect the increase in fast charging characteristics of lithium-ion batteries.

Table 1. Crystallization size and conductivity (pure LiFePO₄ and LiFePO₄/CNT heated at various times).

Sample	Crystal size (nm)	Conductivity (S/m) (10 ⁻⁷)
LiFePO ₄ pure (2h)	101.64	1.881
LiFePO ₄ /CNT (2h)	60.07	2.451

LiFePO ₄ /CNT (4h)	34.74	2.744
LiFePO ₄ /CNT (6h)	15.93	3.602

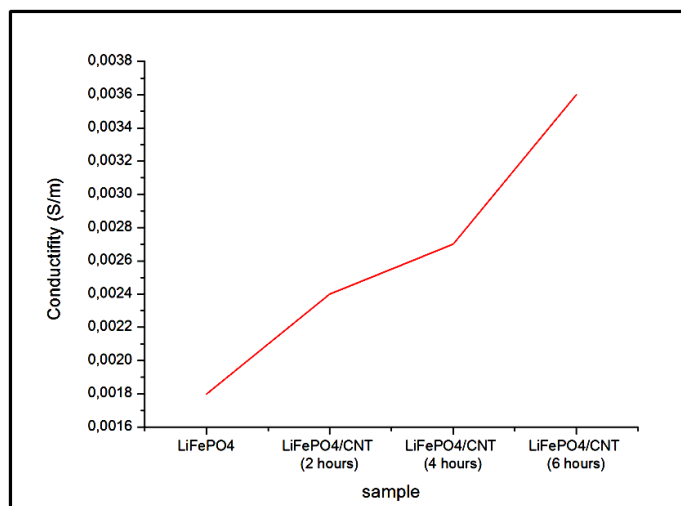


Fig 4. The relationship between conductivity and the type of LiFePO₄ sample

IV. CONCLUSION

LiFePO₄ were prepared by the sol-gel method from LiOH and Fe₂O₃ powder and variations in the ratio of H₃PO₄ mol CNT/LiFePO₄ were successfully made as composite electrodes. The morphology of the surface area on the SEM results showed that the material was homogeneous in particle size, and the morphology of the LiFePO₄ material was further patched with CNT. However, the morphology of LiFePO₄/CNT is not limited, based on the result that a material is a composite. The longer time for calcination heating will have an impact on decreasing crystal size and increasing conductivity. The highest conductivity will affect the improvement of fast charger characteristics.

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