Improving Performance of LiFePO$_4$ by addition of Carbon Nano Tube for Lithium Ion Battery

W. Honggowiranto$^{1*}$, E. Kartini$^1$, Sudaryanto$^1$, R. N. S. Rofika$^2$, E. Hutamaningtyas$^1$, A. Subhan$^3$, A. Sudjatno$^1$

$^1$Center for Science and Technology of Advanced Material, National Nuclear Energy Agency, Serpong, South Tangerang, Banten, 15314, Indonesia.
$^2$Department of Physics, Faculty of Mathematics and Sciences, Bandung Institute of Technology, Ganesh, 10, Bandung, 40132, Indonesia.
$^3$Research Center of Physics, Indonesia Indonesian Institute of Sciences, Serpong, South Tangerang, Banten, 15314, Indonesia.

wagiyo@batan.go.id

Abstract. LiFePO$_4$ (LFP) cathode material has been synthesized with hydrothermal method. The reaction was done by reacting a mixture of FeSO$_4$.7H$_2$O, H$_3$PO$_4$, LiOH and CNT. In order to improve performance of LFP, the carbon nano tube (CNT) was added with the variation of 5, 10 and 15 mmol, before hydrothermal process. The material was stirred using a magnetic stirrer for 30 minutes, and then autoclave was heated at 180°C for 6 hours then sintered at 700°C for 6 hours. The results were characterized by X-ray diffraction (XRD), and Scanning Electron Microscope (SEM), and Impedance Spectroscopy (EIS). The X-ray data shows that the crystal structure of synthesized LiFePO$_4$ has a group of Pmn with a space (olivine structure) which is in agreement with the LFP standard material. The addition of CNT does not change the crystal structure. This shows in SEM images that the crystallite size of LiFePO$_4$ particles does not have much effect on the composite. The battery cell performance was measured by Impedance Spectroscopy and charge / discharge Battery Analyzer BST-8. The EIS data, showed the decreasing of battery impedance total from LiFePO$_4$ material without CNT to addition of 5, 10 and 15 mmol CNT namely 214; 128.1; 88.6 and 70.1 Ω, and the specific capacity 0.1C are 38.78; 51.53; 106.84; 92.79 mAh/g, respectively. It is shown that the maximum specific capacity was obtained for LFP composite with the addition of 10mmol CNT. It can be concluded that the addition of CNT increases the conductivity and specific capacity, thus improving performance of lithium ion battery.

Keywords : LiFePO$_4$, Hydrothermal, CNT, Lithium ion battery

1. Introduction
The lithiump iron battery has been considered to be an attractive power source not only for small electronic devices, such laptop, cell phones, flash light, but also for large scale applications like energy storage for photo voltage, electric vehicles (EV), hybrid electric vehicles (HEVs). The lithium ion battery cell has been regarded as one of promising power source candidates for electric vehicles in recent years [1,2]. LiFePO$_4$ batteries have become a main of research related to the fact that they are relatively safe and low manufacturing cost. In theories, LFP have a high capacity of 170 mAh/g,
good cycling ability and good stability during charge-discharge [3-5]. The limitation of this materials are the inherent low electronic conductivity (10^{-9}-10^{-10} S cm^{-1} at room temperature). However the wide commercialization are limited by its low electronic conductivity and low lithium ion diffusivity [3].

Many researches had been done to improve the performance of LFP[3]. Metal doping and carbon coating were conducted to increase the electronic conductivity [6]. As for the low ionic conductivity, the reduction of particle size may be improved it. LFP can be synthesized by solid state method, sol-gel, precipitation and also hydrothermal synthesis [7,8]. One of the most relevant methods to reduce particle size was reported to be hydrothermal method. In order to reduce the energy usage and costs of synthesizing LFP cathode materials (at high temperature), the hydrothermal synthesis can indeed be used at low temperature and it is favourable method [9,10]. Carbon coating is used to improve the weak performance and electrical conductivity of LFP [11]. In order to get the maximum electrochemical performance, carbon as active material must be in nano particle size with high crystallinity and uniform size distribution [12,13]. The nano size carbon related to support the ionic transport and electronic conduction of LFP [14-16]. Currently, carbon nanotube (CNT) are the strongest and offer superior electrical and thermal conductivities. The addition of CNT on LFP has no effect on the structure of pure LFP, and also exhibits high discharge capacity[9].

Aim of this work is to synthesize LFP by hydrothermal method with addition of CNT during the process in order to improve performance of lithium ion battery. The crystal structure and microstructure of the LFP will be characterized, including the electrochemical and battery performance.

2. Experimental method

Cathode materials of LiFePO4 were prepared by hydrothermal process. The main precursors were FeSO4·7H2O (Sigma-Aldrich, 99.0%), H3PO4 (Aldrich, 85.0%), LiOH (Merck, 98.0%). In addition, variations of carbon nano tube (CNT) with 5 mmol, 10 mmol, 15 mmol were added to the precursors before hydrothermal. The LiOH was dissolved in 60 mL of deionized water, then was added subsequently into FeSO4·7H2O suspension under vigorous stirring, then, the H3PO4 were dropped into it and CNT with stirring to get suspension for 30 minutes. After stirring the mixed solution was transferred into a 90 mL Teflon lined stainless steel autoclave. It was sealed off tightly followed by heating in an electric muffle oven at temperatures of 180°C for 6 hours, then cooled down to room temperature. Details of the hydrothermal method has been described elsewhere [15]. The solid grey precipitates was filtered and washed with demineral water several times with ethanol and distilled water. It was dried at vacuum oven at 120°C for 10 hours, then annealed in tubular furnace at 700°C for 6 hours in atmospheric argon.

All the samples are marked as LFP1, LFP2, LFP3 and LFP4 (respectively, 0 mmol, 5 mmol, 10 mmol, and 15 mmol CNT). The crystal structure of those LiFePO4 were characterized by X-ray diffraction (XRD) using a with Cu Kα target, scan range from 10° to 80°. The morphology of the samples was observed by using scanning electron microscopy.

The cathode was prepared by mixing the active materials with acetylene black and then was grounding the mixture for 30 minutes and heated in vacuum oven at 120°C for 2 hours. Polyvinylidene fluoride (PVDF) was mixed with active materials for 15 minute, then N-methyl-2-pyrrolidinone (NMP) was added to make slurry while mixing for 30 minutes. The weight ratio of active materials with acetylene black and PVDF was 85:3:5. The slurry was pasted onto an aluminum current collector using doctor blade. It was dried on oven vacuum at 120°C for 10 hrs. A half-cell battery was prepared under the glovebox. The electrochemical performance and charge-discharge of the lithium ion battery was done using an impedance spectroscopy and a battery analyzer.
3. Results and discussion

The SEM image and XRD pattern of multiwall carbon nano tube (CNT) commercial are shown in Figure 1(a) and (b), respectively. The microstructure of CNT shows circular porous and some agglomerations. The diffraction peaks at 2θ~ 25.944, 72.703 and 43.095 corresponds to CNT standard.

![Figure 1](image1.png)

**Figure 1.** (a) SEM image and 1(b) X-ray diffraction of Carbon Nano Tube commercial.

Figure 2(a) shows image of the LiFePO₄ (LFP) prepared by hydrothermal method without any additional CNT. Figures 2(b), 2(c) and 2(d) are the images of LFP prepared by hydrothermal with the addition of CNT 5, 10 and 15 mmol, respectively.

![Figure 2](image2.png)

**Figure 2.** The SEM images of (a) LFP1, (b) LFP2, (c) LFP3 and (d) LFP4.

The distribution of LFP particles without CNT are dispersed homogenously, with the particle size between ~ 0.3-1.3 μm. The addition of CNT made agglomeration, and the sizes increased to ~0.4-1.7 μm and ~0.4- 1.5 μm, for LFP2 and LFP3, respectively. Further increasing CNT the size decreased again to 0.2-1 μm for LFP4.
Figure 3. X-ray diffraction patterns of LFP1, LFP2, LFP3 and LFP4.

Further examination of the LFP shape, they did not change with addition of CNT. These implied that the addition of CNT did not give the impact to the physical and structural of LFP as observed by x-ray diffraction, as shown in Figure 3. The refinement results of diffraction data showed that all LFP can be indexed as the orthorhombic phase with space group *Pnma* 62 which belongs to LiFePO₄. This means that LFP prepared by the hydrothermal process has been done successfully. There is no change in the crystal structures of LFP2, LFP3 and LFP4 after the addition of CNT with 5, 10 and 15 mmol. Similar result by Feng et al. identified that no characteristic peaks from CNT are observed, due to the low content of CNT, which show that the additions have no obvious impact on the structure of LFP [13]. There is a slightly change in the crystallite sizes namely 1000.2Å, 1413.8Å, 1506.7Å and 952.3Å, for LFP1, LFP2, LFP3 and LFP4, respectively. The refinement results of the diffraction patterns are listed in Table 1.

The impedance spectroscopy (EIS) of the half-cell was measured at SOC (0%) before charge and discharge process. The EIS results of LFP1, LFP2, LFP3 and LFP4 are shown in Figure 4. The intercept on x-axis in the high frequency region indicates an internal resistance of the cell, and the diameter of the semicircle represents the effect caused by charge transfer and electrochemical double layer. As shown in Figure 4, the equivalent diagram reflecting the process internal process. The total impedance could be regarded as the electrolyte resistance R1 and the charge transfer resistance R2, for LFP1, LFP2, LFP3 and LFP4 were 214;128.1; 88.6 and 70.1Ω (at SOC 0%). This result indica-
Table 1. Refinement Results of X-ray diffraction from LFP1, LFP2, LFP3 and LFP4.

|                | LFP1       | LFP2       | LFP3       | LFP4       |
|----------------|------------|------------|------------|------------|
| Formula /Unit Crystal | O16P4Fe4Li4 | O16P4Fe4Li4 | O16P4Fe4Li4 | O16P4Fe4Li4 |
| Formula mass (g/mol) | 631.0376   | 631.0376   | 631.0376   | 631.0376   |
| Calculate Density (g/cm3) | 3.5942     | 3.5942     | 3.5991     | 3.6025     |
| R (expected)/% | 2.87967    | 2.56783    | 2.63627    | 2.62593    |
| GOF          | 1.11669    | 1.06554    | 1.05008    | 1.17499    |
| R(weighted profile)/% | 3.04305   | 2.65064    | 2.70147    | 2.84642    |
| Weight Fraction (%) | 100        | 100        | 100        | 100        |
| Space group (No.) | P n m a (62) | P n m a (62) | P n m a (62) | P n m a (62) |
| Lattice Parameters : |            |            |            |            |
| a (Å) | 10.3299(5) | 10.3323(6) | 10.3286(4) | 10.3248(4) |
| b (Å) | 6.0065(3)  | 6.0081(3)  | 6.0061(2)  | 6.0035(3)  |
| c (Å) | 4.6929(3)  | 4.6957(3)  | 4.6926(2)  | 4.6919(2)  |
| alpha (°) | 90         | 90         | 90         | 90         |
| beta (°) | 90         | 90         | 90         | 90         |
| gamma (°) | 90         | 90         | 90         | 90         |
| Preferred orientation direction /hkl | 0.00 0.00 1.00 | 0.00 0.00 1.00 | 0.00 0.00 1.00 | 0.00 0.00 1.00 |
| Preferred orientation parameters | 1.000000 | 1.000000 | 1.000000 | 1.000000 |
| Crystallite Size (Å) | 1000.2     | 1413.8     | 1506.7     | 952.3      |

The addition of CNT decreased the charge transfer polarization resistance which related to the unique CNT network allowed easy electronic transfer, thus maximizing the efficiency of current collection and increased the mobility of lithium ions [9, 17]. As for the double-layer capacitance in form of CPE and Ws is the Warburg impedance that reflects the diffusion of lithium-ion in the solid. The simulation results are tabulated in Table 2.

Figure 4. Impedance plots of half cells of LFP1, LFP2, LFP3 and LFP4.
Table 2. Electrochemical performance of LFP batteries.

| Sample | R1 (Ω) | R2 (Ω) | Ws (Ω) | CyL1 Specific Capacity (mAh/g) | CyL10 Specific Capacity (mAh/g) | Retention after 10th cycle |
|--------|--------|--------|--------|-------------------------------|--------------------------------|----------------------------|
| LFP1   | 4.0    | 210.0  | 1284.7 | 38.78                         | 27.12                          | 69.881                     |
| LFP2   | 3.8    | 124.3  | 274.9  | 51.53                         | 39.50                          | 76.654                     |
| LFP3   | 12.4   | 76.2   | 122.7  | 106.84                        | 104.50                         | 97.809                     |
| LFP4   | 3.4    | 66.7   | 85.9   | 92.79                         | 90.49                          | 97.521                     |

Figure 5 shows the charge-discharge analysis of all LFP batteries at 0.1C rate measured at room temperature. The specific capacity for both cycle 1 and 10 increased with the addition of CNT as for LFP1, LFP2, and LFP3, then decreased at LFP4. The discharge capacity of LFP3 is observed at 106.84 mAh/g, which exhibited the highest initial discharge capacity, with the capacity retention of 97.8% after 10th cycles. Similar results was done for mesoporous LFP microspheres embedded homogeneously with 3D CNTs conductive networks, where the initial discharge capacity is 150 mAh/g [17]. The lower discharge capacity of LFP4 relative to LFP3 show that the current density is large and reducing the discharge capacity in charge-discharge process as the result of the excess CNT as active material at LFP4 [13]. The first discharge capacity of LFP4 is observed at 92.79 mAh/g with retention is 97.5% after 10th cycle.

![Graph showing specific capacity](image_url)

Figure 5. (a). Specific capacity of (a) LFP1, (b) LFP2, (c) LFP3 and (d) LFP4.

4. Conclusion
LiFePO4 as cathode material for Li-ion battery was successfully synthesized by hydrothermal method. The addition of CNT before the hydrothermal has reduced the internal resistance, thus increased the mobility of lithium ions due to the existing of CNT. The charge–discharge results show good performance of the lithium ion battery, and the highest specific capacity was 106.84 mAh/g obtained for LFP3 (CNT 10mmol)
Acknowledgment
This work is financially supported by the Ministry Research Technology and Higher Education through the Research Grant of National Innovation System Consortium (INSINAS) with the contract no. IRPK-042-2018.

References
[1] B. Scrosati and J. Garche, “Lithium batteries: Status, prospects and future,” J. Power Sources, vol. 195, pp. 2419–2430, 2010.
[2] E. Kartini, A. Purwanto, S. Sudaryanto, H. Honggowiranto, and R. N. S. Rofika, “Indonesian consortium of lithium ion battery for solar street lamp,” in IOP Conf. Series: Materials Science and Engineering, 2018, vol. 432, pp. 012063–1.
[3] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, “Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries,” J. Electrochem. Soc., vol. 144, no. 4, pp. 1188–1194, 1997.
[4] Y. Xu, S. Chung, J. T. Bloking, and Y. Chiang, “Electronic Structure and Electrical Conductivity of Undoped LiFePO₄,” Electrochem. Solid-State Lett., vol. 7, no. 6, pp. 131–134, 2004.
[5] U. K. Muhsin Mazman, Omur Cuhadar, Davut Uzun, Ercan Avci, Emre Bicer Tevhit Cem Kaypmaz, “Optimization of LiFePO₄ synthesis by hydrothermal method,” Turkish J. Chem., vol. 38, pp. 297–308, 2014.
[6] Y. Dai, L. Ma, H. Zhang, Y. Chen, Y. Chen, and W. Wang, “Hydrothermal Synthesis of Spindle-Like Nanostructured LiFePO4 Powders Mediated by Organic Acid,” Int. J. Electrochem. Sci., vol. 11, pp. 1730–1737, 2016.
[7] Y. Yin, X. Li, X. Mao, X. Ding, and S. Yang, “Solid State Reaction Preparation of LiFePO₄/(C D Cu ) Cathode Material and Its Electrochemical Performance,” J. Mater. Sci. Technol., vol. 29, no. 10, pp. 937–942, 2013.
[8] Q. Jiang, X. Wang, and H. A. N. Zhang, “One-Pot Hydrothermal Synthesis of LiMn₂O₄ Cathode Material with Excellent High-Rate and Cycling Properties,” J. Electron. Mater., vol. 45, no. 8, pp. 4350–4351, 2016.
[9] S. R. Rao and U. V Varadaraju, “Hydrothermal synthesis of LiFePO₄ nanorods composed of nanoparticles from vivianite precursor and its electrochemical performance for lithium ion battery applications,” Bull. Mater. Sci., vol. 38, no. 5, pp. 1385–1388, 2015.
[10] W. Honggowiranto, Sudaryanto, E. Kartini, and A. Purwanto, “Electrochemical Performance of LiFePO₄ Cylinder Cell Battery,” AIP Conf.Proc. 6th Nanosci. Nanotechnol. Symp., vol. 1710, no. 030042, pp. 1–7, 2016.
[11] H. Wu, Q. Liu, and S. Guo, “Composites of Graphene and LiFePO₄ as Cathode Materials for Lithium-Ion Battery : A Mini-review,” Nano-Micro Lett., vol. 6, no. 4, pp. 316–326, 2014.
[12] L. Yu, D. Cai, H. Wang, and M. Titirici, “Synthesis of Microspherical LiFePO₄-Carbon Composites for Lithium-Ion Batteries,” Nanomaterials, vol. 3, pp. 443–452, 2013.
[13] W. Feng, Y. Cao, X. Zhao, J. Gang, and W. Su, “Effect of Carbon Nanotubes on the Electrochemical Performance of LiFePO₄ Particles in Lithium Ion Batteries,” Int. J. Electrochem. Sci., vol. 12, pp. 5199–5207, 2017.
[14] K. P. Abhilash, P. C. Selvin, B. Nalini, H. Xia, and S. Adams, “Electrochemical Analysis of the Carbon-Encapsulated Lithium Iron Phosphate Nanochains and Their High-Temperature Conductivity Profiles,” ACS Omega 2018, vol. 3, pp. 6446–6455, 2018.
[15] C. P. Supriadi, E. Kartini, W. Honggowiranto, and K. T. Basuki, “Synthesis and Characterization of Carbon Material Obtained From Coconut Coir Dust by Hydrothermal and Pyrolytic Processes,” IJTech 2017, vol. 8, pp. 1470–1478, 2017.
[16] W. Honggowiran and E. Kartini, “Characterization of LiFePO₄ Cathode by Addition of Graphene for Lithium Ion Batteries,” AIP Conf.Proc. 6th Nanosci. Nanotechnol. Symp., vol. 1710, no. 030045, pp. 1–6, 2016.
[17] Z. S. Guan Wu, Ran Ran, Bote Zhu, Yujing Sha, Chao Su, Yingke Zhou, “3D-amorphous-carbon-and-graphene-co-modified-LiFePO₄-composite-derived-from-polyol-process-as-electrode-for-high-power-lithium-ion-batteries_2014_Jour.pdf,” J. Energy Chem., vol. 23, pp. 363–375, 2014.