Optimizing performance of Li$_4$Ti$_5$O$_{12}$ nanorod doped C@ZnO by hydrothermal synthesis as half-cell lithium-ion battery anode

B Priyono$^1$, M R Nugraha$^1$, A Z Syahrial$^1$, Faizah$^1$, A Subhan$^2$
$^1$Department of Metallurgy and Materials, Faculty of Engineering, Universitas Indonesia, Depok, 16424, Indonesia
$^2$Center for Research of Physics, LIPI, PUSPITEK, Tangerang, Banten, 15310, Indonesia

E-mail: bambang.priyono@ui.ac.id

Abstract. Lithium titanate, Li$_4$Ti$_5$O$_{12}$ (LTO) is a promising candidate as lithium ion battery anode material. In this investigation, LTO/C@ZnO was synthesized with LTO nanorod by hydrothermal method using TiO$_2$ xerogel that prepared by the sol-gel method, lithium hydroxide (LiOH), Activated carbon, and Zinc Oxide (ZnO) nanorod. Three variations of ZnO content addition in weight %, i.e., 4, 7 and 10%, labelled as sample LTO/C@ZnO-4, LTO/C@ZnO-7 and LTO/C@ZnO-10, respectively. The characterizations were made using XRD, FE-SEM, and BET testing. These were performed to observe the effect of ZnO addition on structure, morphology, and surface area of the resulting samples. Result showed that the optimum discharge capacity from each samples was 32.84 mAh/g in LTO/C@ZnO-4 with the crystallite size of 11.86 nm and the surface area of 348.736 m$^2$/g. In cyclic voltammetry testing, it shows a shift in reaction voltage and reduction in capacity that caused by the addition of C@ZnO and the lack of Li$_4$Ti$_5$O$_{12}$ that are formed.

1. Introduction
One of the most advanced technology development in secondary rechargeable batteries are Li-ion batteries. Li-ion batteries has one of the highest energy efficiency that allows it to be used in many applications that may increase energy sustainability [1]. Accordingly, Li-ion batteries is in high demand from industry and government funding agencies. About 96% of hybrid electric vehicles in the world market in present time use nickel metal hydride batteries. However, within 10 years, 70% of hybrids and 100% of plug-in hybrid and other electric vehicles are expected to use lithium-ion batteries [2].

The fact about lithium-ion battery is that the battery is relatively light and compacted which also give the properties of being able to have high energy output. In the application, the specific energy of lithium-ion batteries with the voltage of 4 V can be done and ranged between 100 Wh/kg to 150 Wh/kg [1]. This is also the consideration of choosing the lithium-ion batteries for future development and applications. Material development for Lithium-ion batteries has seen a bright future with LTO (Li$_4$Ti$_5$O$_{12}$ or Lithium Titanate) as base anode. LTO has been successful on the market because it can exhibit high rate and high cycle life despite the higher cost of Titanium, the reduced cell voltage, and lower capacity. This leads to LTO having high stability during charging and discharging process.
Development of other material for LIBs is promising, with LTO as base anode such as lithium titanate (Li4Ti5O12). Li4Ti5O12 has high lithium insertion/extraction voltage, approximately 1.55 V during intercalation, which has high stability during charging and discharging process [3]. Also compared with graphite which has tendency to pulverization, Li4Ti5O12 has higher safety concern due to their zero-strain property and proposed to be used in electric vehicle. During intercalation in Li4Ti5O12, every formula can accommodate three lithium ions, so theoretically it has the capacity of 175 mAh g⁻¹, compared than graphite (372 mAh g⁻¹) [4]. Despite their superiority, it has some drawbacks of low capacity and also low conductivity (10⁻³ S cm⁻¹). Researches has been conducted to improve its capacity and rate capability by conducting morphological optimization, doping other element, and nano-structuring of Li4Ti5O12 [5].

This research is conducted by fabricating spinel Li4Ti5O12/C@ZnO, with C@ZnO as doping of other element, with sol-gel and hydrothermal method for TiO2 nanorod, solid state method for Li4Ti5O12, and mixing the carbon with ZnO. Difference of ZnO concentration is observed in this research and its effect to the material.

2. Materials and Methods
Preparation and synthesis of Li4Ti5O12/C@ZnO is done through several processes before it is ready to be characterized under XRD, BET, SEM, and EDS. Processes that will be done consists of sol-gelling, hydrothermal, calcination, ball-milling, sintering, and mixing.

2.1. Synthesis of LTO nanorod
It begins by preparing primary solution which is 20 ml ethanol (pH 3) with the addition of 3.40 gram of Titanium (IV) Butanate, and secondary solution which is 5 ml ethanol (pH 3) + H2O which were later go through titration process with RW 3.5.

Gelling process is done using magnetic stirrer and magnetic spin bar until gel is produced from the process. The formed gel will be dried overnight to evaporate the moisture inside the gel and proceed the evaporation process for one week to evaporate the moisture content inside the gel. After evaporation process is done with no moisture content inside the gel left, it proceeds to the next process which is calcination. Calcination process is done inside a furnace with 300 °C temperature and is done in 2 hours. Calcination process is done to obtain TiO2 anatase, to evaporate moisture content inside the gel, and enhance crystallinity.

Next process will be hydrothermal to achieve the TiO2 nanorod structure. First it begins with mixing the TiO2 with NaOH 10M solution and 10ml of water in beaker glass, then stirred in the magnetic stirrer for 30 minutes long. After the mixing is done, it will be put inside the autoclave for heating process in the furnace at temperature of 180 °C for 24 hours. The use of autoclave here is to have the highest purity result. Then the precipitated need to be filtered with membrane filter and dried in hot plate at 80 °C temperature until all the moisture evaporated. Sintering process was done in tube furnace with temperature 750 °C for 3 hours to increase the crystallinity, achieve the spinel structure and remove the impurities.

Next process is ball-milling where the lithium hydroxide will be mixed with TiO2 nanorod using high energy ball-mill (HEBM). Ball-milling process is aimed to obtain optimum surface area.

2.2. Synthesis of ZnO nanorod
Zinc oxide nanorods synthesis process involves several stages before being mix with the activated carbon. First, Zinc oxide (ZnO) nanorods that will be produced in this research will have 0.05 M concentration obtained from 0.05 M concentration of Zinc nitrate tetrahydrate (Zn(NO)3·4H2O, Merck) and Hexamethylenetetramine (HMTA) (C6H12N6, Merck). Both of them are dissolved in cold water in a beaker glass by putting the beaker glass inside the cooler box with crushed ice blocks covering all the beaker glass, then keep the cooler box closed for about 1 hour. After being cooled from the cooler box, the beaker glass will be moved into the oven for heating process in 90°C temperature for about 3 hours.
After the heating was done, the precipitated need to be strained using membrane filter paper and dried it in petri dish for approximately 1 day. Then it needs to be heated again in 80 °C for 30 minutes to ensure that all the water content inside the powder already disappeared.

2.3. Synthesis of activated carbon
The activation process of carbon is carried out to produce carbon with specific surface area. In this study, carbon activation was performed using NaOH because NaOH is more advantageous and can produce high specific surface area. The carbon used in this study is commercial carbon from PT Brataco.

Commercial carbon sources that used are still in the form of granules with ununiform size, so it need to be reduced into smaller size to achieved uniform grain. Reducing the size of carbon is done by using high energy ball mill and involves the use of zirconia balls. The fine carbon of the milling results is then heated to the furnace. Carbon is placed on a combustion boat located on a metal buffer and inserted into a tube furnace. Heating is carried out in temperature of 500° C with a heating rate of 20 °C min⁻¹ and holding time about 2 hours. The heating carbon is then mixed with NaOH pellets. The ratio of the amount of NaOH pellets with carbon is 3:1 (3 grams of pellet NaOH : 1 gram of carbon) followed by the addition of 10 mL of distillated water. Mixing between carbon and NaOH pellets is done using the help of magnetic stirrer for 2 hours. First, NaOH pellet was mixed with 10 mL of water until it homogenized in a beaker glass and then it added with carbon. The mixture which has been stirred for 2 hours then will be heated in an oven at 130° C for about 4-24 hours until the carbon is completely dried.

The next stage in the process of carbon activation is heating the carbon in the furnace with nitrogen gas flow. The heating is carried out in temperature of 700 °C at a 20 °C min⁻¹ heating rate and a nitrogen gas flow rate of 100 cm³ min⁻¹. The result of this step is to produce carbon with very dry conditions and minimize the volatile substances that still exist from the previous stage.

Then the heated carbon will be washed using a 0.1 M HCl solution and hot distillated water until it achieved 6.5 pH. The purpose of this washing is to remove residues or inorganic species formed during the process. Sufficient quantity of carbon is fed into a beaker glass and poured 0.1 M HCl solution then stirred. The pH measurement of the solution was performed using pH indicator paper. This step is repeated until the pH of solution achieved 6.5 then washed with hot distillated water. Filtered the solution are necessary with the membrane filter paper to get the carbon precipitate. The heating is done in the oven with the filtered carbon placed inside the beaker glass. The purpose of this heating is to remove or evaporate water that may still be contained in carbon.

2.4. Synthesis of LTO/C@ZnO composite
The concept of this LTO/C@ZnO composite is to have the ZnO nanorod particle encapsulate into the porous of activated carbon. This phenomena called ballistic effect [6]. In order to have that, the composite mixing need to be done step by step from the ZnO nanorod and the carbon first. After that, the C@ZnO powder being mixed again with LTO nanorods. The mixing of these substances is carefully carried out with certain composition that shows in table 1. The percentage of ZnO addition in this research are 4%, 7%, and 10% followed by 5% of activated carbon in all variables.

Table 1. Weight of each material for composite mixing.

| No | Sample       | LTO (g) | Carbon (g) | ZnO (g) |
|----|--------------|---------|------------|---------|
| 1  | LTO/C@ZnO-4 | 1.82    | 0.1        | 0.08    |
| 2  | LTO/C@ZnO-7 | 1.76    | 0.1        | 0.14    |
| 3  | LTO/C@ZnO-10| 1.70    | 0.1        | 0.2     |
2.5. Coin cell fabrication
In the battery fabrication process, the initial stage which had to be done is slurry making. In this stage, the active material which obtained from previous synthesis process was prepared with other substances of PVDF and acetylene black. The ratio of each substance of active material, PVDF and acetylene black respectively are 8:1:1. All material mixed together along with DMAC 5 gram using a magnetic stirrer. The mixture was stirred for 3 hours with hot plate temperature 80°C. Slurry results were coated to Cu-foil and dried for 1 hour in 80°C with doctor blade as the media. The coated material then assembled inside a glove box with a argon atmosphere.

The electrochemical analyses were performed using using a CR2032-type coin cell in which lithium metal chip was the counter electrode and LiPF₆ as an electrolyte. EIS (Electrochemical impedance spectroscopy) was conducted in a range from 0.10 Hz to 20 kHz using the HIOKI RM3544 instrument. The CV (cyclic voltammetry) test was performed between 0.01 and 3.0 V with the scan rate of 0.1 mVs⁻¹. The charge–discharge (CD) performance was conducted from a low-current (C/5) to a high-current (12C) discharge rate using the WonATech WBCS 2000 instrument.

3. Results and Discussion

3.1. Brunauer–Emmett–Teller
The pores formed in the sample would make the gas flow easily through it. The higher the pores present in the sample, the higher the surface area value of the sample. From BET result on the Table 2, It shows with the addition of 4% ZnO, the surface area in the compound was 348.736 m²/g which is higher than the other variables. Along with the addition of the ZnO composition, the surface area has decreased due to the pores that blocked by the substances [7].

| Sample          | Surface Area (m²/g) |
|-----------------|---------------------|
| LTO/C@ZnO-4     | 348.736             |
| LTO/C@ZnO-7     | 98.786              |
| LTO/C@ZnO-10    | 88.246              |

3.2. FE-SEM

3.2.1. LTO nanorod

![Figure 1. FE-SEM result of LTO nanorod powder with 10,000 X magnification.](image-url)
From figure 1, the morphology of the sample has a rough morphology and has a non-uniform particle size, the structure of the sample slightly different from the structure of nanorod, the structure of the sample is more similar with damaged nanorod samples in the process, although the basic form of the sample still appears to look like a rod despite the damage, this may be due to mechanical treatment in this study in the form of a ball mill or due to process temperature. From the particle size measurement, the particle have a size 200-400 nm for diameter, and has a length from 700 nm – 1 μm [8]. This proves that the rod structure still exists even if it is damaged, on generally the nanorod structure has a diameter of nanometer and length micrometer size, this indicates that the mechanical treatment to mix TiO₂ nanorod, damages the structure of nanorod so that the length of the micron-sized particles becomes nano sized. On the sample observation with 500x magnification as in the picture will be seen a lot of agglomerates from nanorod LTO samples. Agglomeration is common in nano-sized particles because of their high surface energy, so to reduce this surface energy, the particles will agglomerate.

3.2.2. ZnO nanorod

![Figure 2. FE-SEM result of ZnO nanorod powder with 10,000 X magnification.](image)

From figure 2 it shows hexagonal crystal structure of ZnO in good accordance with the reference ZnO nanorod (JCPDS no. 01-080-0075) [9]. The structure of ZnO nanorod that formed are still very few and can be seen there are still many agglomeration in it. It is supported by XRD data that showing the low peak of ZnO nanorod. Therefore, it can be said that the ZnO nanorod purity are still low.

3.2.3. Activated Carbon

![Figure 3. SEM result of carbon (a) before activation (b) after activation.](image)
From the figure 3, the morphology of the carbon before activation was not have enough porous compare to carbon after activation. The porous in the structure can greatly enhance the surface area of the carbon [7].

3.2.4. LTO/C@ZnO

![Figure 4. FE-SEM result of LTO/C@ZnO (a) 4% (b) 7% (c) 10% powder with magnification 25.000X.](image)

3.3. X-Ray Diffraction

From the figure 5, it shows the XRD patterns of LTO/C@ZnO with the 4%, 7% and 10% composition of ZnO addition. The presence of the Li$_4$Ti$_5$O$_{12}$ compound in the sample are indicated by 3 highest peaks at an angle of 18.509° in plane (111), 35.708° in plane (311), and 66.486° in plane (440) (JCPDS No. 00-049-0207). This is has slightly different with reference [10], where the second highest peak is the plane (400) and (111) is the third highest. This is due to the presence of Li$_2$TiO$_3$ in the sample which also has a high peak at an angle of 18.514°, 43.676°, and 35.967° (JCPDS 00-033-0831), the result of the Scherrer equation shows that the crystallite size of Li$_4$Ti$_5$O$_{12}$ nanorod have a size of 11.86nm (LTO/C@ZnO-4), 29.82nm (LTO/C@ZnO-7) and 29.82nm (LTO/C@ZnO-10). This shows that the synthesized Li$_4$Ti$_5$O$_{12}$ nanorod spinel have small size of crystallite size but low in degree of crystallinity because the intensity in xrd peak was still low.

For ZnO nanorods in the samples are also indicated by 2 highest peaks at an angle of 36.47° and 56.71°. It confirmed from the intensity of 3 diffraction graphs that, along with the addition of ZnO, the intensity in each sample are slightly increased. For the activated carbon, the phase are shows in angle 15.95° and 28.97°.

![Figure 5. Phases indicated of samples (a) LTO/C@ZnO-4, (b)LTO/C@ZnO-7, (c) LTO/C@ZnO-10.](image)
3.4. Electro Impedance Spectroscopy

Based on the EIS test, it could be seen in figure 6 that the sample of LTO/C@ZnO-4 has the lowest charge transfer resistivity (Rct) compare to other samples. In this case, the optimal ZnO content is 4% in which the conductivity is better than other three samples. As seen on the table 3, the LTO-K/C@ZnO-10 having the moderate resistivity among the other samples.

Figure 6. Graph of EIS result and the equivalent circuit.

The equivalent Randle’s circuit was obtained by fitting the EIS graph using the software EISSA with the component containing Rs for solution resistance with series connection to the two component in parallel components containing Rct (charge transfer resistance) and Cdl (Capacity double layer) representing the impedance in the porous electrode. The Warburg impedance in semi-infinite diffusion then connected to said parallel system.

Table 3. Rs, Rct, Cdl and W impedance values of the experimental with variation ZnO content.

| Sample          | Rs (ohm) | Rct (ohm) | Cdl (F)     | W          |
|-----------------|----------|-----------|-------------|------------|
| LTO/C@ZnO-4     | 13.40    | 103.95    | 1.00 E-06   | 221.62     |
| LTO/C@ZnO-7     | 26.83    | 145.87    | 7.19 E-07   | 247.87     |
| LTO/C@ZnO-10    | 23.15    | 107.76    | 9.54 E-07   | 174.5      |
| LTO-K/C@ZnO-10  | 11.37    | 105.07    | 1.21 E-06   | 175.12     |

The correlation between charge transfer resistance and active surface area in terms of heterogeneous electron transfer constant (Ks) is that the higher active surface area will facilitate the electron transfer and make the Ks value become higher and thus lowering the charge transfer resistance (Rct). It can be seen in sample LTO/C@ZnO-4 which has the highest surface area, the Rct value of this sample is the lowest. According to Zeng, et. al, the impedance of porous electrode is inversely proportional to the interfacial surface area of the particle per unit volume of electrode [11].

Further, the Rct value of sample LTO/C@ZnO-7 is the highest among other sample which seems correlate to the result in the specific capacity value obtained in the Cyclic Voltammetry result below.

3.5. Cyclic Voltammetry

The discharge capacity which could be observed on Table 4, the sample of LTO/C@ZnO-4 has the capacity of 32.84 mAh/g. For LTO/C@ZnO-7 has 28.54 mAh/g and LTO/C@ZnO-10 for 31.55 mAh/g. As seen on the figure, the trend of the discharge capacity of every samples decrease with the addition of
ZnO nanorods 7 wt. % concentration to the LTO. It has a significant decrease compared with the other samples. This could indicate the agglomeration and pulverization which happened in the LTO/C@ZnO-7 and LTO/C@ZnO-10 samples having capacity fade. Compare with the samples using the commercial LTO (LTO-K/C@ZnO-10), it has the highest discharge capacity of 123.4 mAh/g. The use of non-nanorod commercial LTO can achieved higher capacity than the LTO nanorods. This also means the LTO nanorods that have been synthesized is still not successful enough because there are not enough Li$_4$Ti$_5$O$_12$ that formed in the process, which can be seen from low peak of LTO in CV graph result.

Figure 7. Result of cyclic voltammetry of the samples with different variables (a) LTO/C@ZnO-4, (b) LTO/C@ZnO-7, (c) LTO/C@ZnO-10.

Table 4. Result of CV of different samples.

| No. | Sample                 | Charge - Discharge Capacity (mAh/g) |
|-----|------------------------|-------------------------------------|
|     |                        | C+   | C-    |
| 1   | LTO/C@ZnO-4           | 26.54 | 32.84 |
| 2   | LTO/C@ZnO-7           | 27.06 | 28.54 |
| 3   | LTO/C@ZnO-10          | 4.24  | 31.55 |
| 4   | LTO-K/C@ZnO-10        | 120   | 123.4 |

3.6. Charge-Discharge
It can be seen in figure 8, for all the variables of ZnO, the charge and discharge capacity for each variable has shown decrement of capacity. As seen on the current rate from C/5 to 20C the LTO/C@ZnO-4 the charge capacity is 27.45 mAh/g into 2.75 mAh/g and 29.42 mAh/g into 2.67 mAh/g for the discharge capacity. For the LTO/C@ZnO-7, the charge capacity is 25.6 mAh/g into 4.88 mAh/g and the discharge capacity from 25.81 mAh/g and 4.72 mAh/g. In the LTO/C@ZnO-10 having the same decrement for the charge and discharge capacity with the charge capacity of 26.12 mAh/g decrease to be having the lowest compared to other variables to be 1.91 mAh/g. For the discharge capacity from 27.87 mAh/g and decrease to be 3.01 mAh/g but it only reach up to 15C. For the sample with commercial LTO (LTO-
K/C@ZnO-10) it reach the highest charge capacity of 113.17 mAh/g into 6.28 mAh/g. for the discharge it has the capacity of 115.4 mAh/g into 14.38 mAh/g in 15C current rate.

![Graphs](image)

**Figure 8.** Result of charge-discharge of the samples with different variables (a) LTO/C@ZnO-4, (b) LTO/C@ZnO-7, (c) LTO/C@ZnO-10.

### 4. Conclusions

For the active material of Li$_4$Ti$_5$O$_{12}$ nanorod, it could be concluded that by using hydrothermal and solid-state methods, the synthesis of lithium titanate is not quite successful, in which the result of XRD showed the small amount of Li$_4$Ti$_5$O$_{12}$ in every samples. The impurities that appears such as Li$_2$TiO$_3$ and salt can lower the conductivity performance. The surface area obtained from the BET examination has shown relatively high surface area. The result for ZnO with 4% addition through 7% and 10% addition respectively 348.736 m$^2$/g, 98.786 m$^2$/g and 88.246 m$^2$/g.

Conductivity of each samples varied which could be compared from EIS examination. The highest conductivity was 4% of ZnO addition. The resistivity of LTO/C@ZnO-4 was 100.4 Ω. The agglomeration that happened in other samples make the conductivity decrease. The highest capacity that resulted from charge-discharge achieved by LTO/C@ZnO-4 was 32.84 mAh/g. As comparison, the sample that using commercial LTO (LTO-K/C@ZnO-10) has the capacity of 123.4 mAh/g.

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