Optimization of ZnO-nanorods addition toward Li$_4$Ti$_5$O$_{12}$ (LTO) performance using sol-gel solid state method as half-cell lithium-ion battery anode

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Abstract. Performance optimization for the anode of lithium-ion batteries (LIBs) can be conducted by adding ZnO through sol-gel solid-state reaction. In this research, the Li$_4$Ti$_5$O$_{12}$ (LTO) used was synthesized through the sol-gel solid-state process and added with ZnO-nanorods obtained ZnO synthesis after LTO synthesis done. LTO-ZnO obtained was characterized to determine the main phase and chemical composition by XRD and SEM-EDS respectively. Electrochemical performance of LTO-ZnO was tested by EIS, CV, and CD. ZnO-nanorods characterization with SEM-EDS results shows that the ZnO inside the LTO dispersed homogeneously. Characterization using XRD revealed that the ZnO successfully enter the LTO with the variation of the amount of 4, 7, and 10 wt% of ZnO. Electric conductivity test shows improvement at an optimum addition amount of ZnO at 4 wt%, although BET result shows at the optimum amount of surface area with 75.545 m$^2$/g. Electrochemical performance result shows optimum performance in ZnO at 4 wt% for its ability to withstand EIS test at 20C compared to 7 wt% and 10 wt%. Also, the capacity of 4 wt% added is 110.2 mAh/g compared to 7 wt% with 109.1 mAh/g and 10 wt% with 96.7 mAh/g.

1. Introduction
In this current era, energy is one principal concerning matters in current ages. With every appliance that helps human need energy. For this, lots of energy is necessary to maintain the equilibrium of supply and demand. Fossil fuel had been long occupying this section, with the line already oversaturated by this product, alternative energy came as the solution to this problem. Alternative energy came ranging from many natural inexhaustible forces, such as wind, solar, water, geothermal, and so on. For this to be used, there is a necessary vessel that able to store this energy so it could be harvested [1].

The battery is an electrochemical device, which converts electrochemical reaction into electrical energy by oxidation-reduction reaction, reversal process in recharging is used for the rechargeable battery system, involving reaction in the form of transfer of electrons, with an electrical circuit, the transfer of an electron from one material to another. The battery is a vital component in our life, our phone, laptops, and other devices mostly using the battery as their energy storage. Development of battery is very fast over the past decades; lithium-ion battery is one of the most promising prospects for the future [2].
In this research, the experiment was focused on synthesizing of Li$_4$Ti$_5$O$_{12}$ (LTO) with the addition of ZnO nanorods. Both of them is mixed before slurry made with a weight content of ZnO is 4, 7, and 10 wt%. Then, the slurry is coated to make an anode sheet and assembled into a Li-ion battery (LIB) half-cell with copper foil sheet and the Li chip is used as the counter electrode. The influence of ZnO nanorods content (in weight %) in the LTO slurry mixture was observed using Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Charge-Discharge (CD) testing. The EIS is conducted to measure the conductivity and CV is performed to measure the specific capacity and working voltage using LiPF$_6$ as an electrolyte. Then, the CD test is carried out to know the rate capability and coulombic efficiency, with 20 cycles to test the LTO/ZnO battery.

2. Experimental
2.1 Materials synthesis and electrode fabrication
Starting with TiO$_2$ synthesis from titanium (IV) butoxide reagent grade 97% from Sigma Aldrich using sol-gel method. Preparation of primary solution consisted of 40 ml ethanol pH 3 and 6.80 gr of titanium (IV) butoxide, followed by a secondary solution of made of 10 ml ethanol pH 3 and 1.26 gr of distilled water. Then secondary mixed with a primary solution while being stirred with a magnetic stirrer. The solution being stirrer until it becoming sol-gel for 60 minutes. Then, we hold sol-gel for 24 hours and open the beaker glass for a week. Next, we grind the powder until it finer in size. Next, we use tube furnace for calcination and put a sample inside alumina tube for 2 hours and 300°C with on hold time 15 minutes in the end with 300 °C and let the sample to cool to room temperature under slow cooling inside the furnace after turn the furnace off. Sample mixed with Lithium source LiOH along TiO$_2$ by ball mill both sample for 30 minutes and put back to a petri dish for next stage. In the sintering process, we put a sample that already mixed to alumina tube and heated inside a tube furnace with 750°C and 3 hours, along with on hold time in the end for 15 minutes. LTO spinel is obtained after finishing this synthesis [3].

Several methods prepared for ZnO synthesis, starting with Zn and Hexamethylenetetramine (HMTA) with 0.05 M concentration consist of Zn mass 1.3072 gram and HTMA mass of 0.70095 gram. Measure both of them and pour 100 ml of distilled water to sample. Next, we hold sample inside icebox for 1 hour; then we put a sample inside the furnace for 3 hours with temperature 90°C. Then we put the sample to filter out the residue and ZnO nanorods. The results are ZnO nanorods [4].

After both materials prepared, we mixed both materials with agate mortar with the composition of ZnO used is 4wt% and LTO is 96% respectively. Further information on LTO and ZnO grinding composition presented in Table 1. The results are LTO/4% ZnO nanorods, LTO/7% ZnO nanorods, LTO/10% ZnO nanorods.

| Material               | ZnO nanorods (gram) | LTO (gram) |
|------------------------|---------------------|------------|
| LTO-AC/4% ZnO nanorods | 0.08                | 1.92       |
| LTO-AC/7% ZnO nanorods | 0.14                | 1.86       |
| LTO-AC/10% ZnO nanorods| 0.20                | 1.80       |

Coin cells fabrication started with preparing active material which is LTO/ZnO nanorods, binder materials PVDF or polyvinylidene fluoride, and acetylene black for conductive agents. The ratio of the material of active material, binder, and conductive agents respectively 8:1:1. All material mixed along with dimethyl acetylamide (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 argon atmosphere [5].

2.2. Characterization and Testing
The LTO/ZnO characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) mappings to analyse the topography, microstructure and elements distributions. X-ray Powder Diffraction (XRD) test was used to identify the phase and content of each composite. Further, Brunauer-Emmett-Teller (BET) is used to measure the surface area of the samples.

The Cyclic voltammetry (CV) of coin cell was carried out at a scan rate of 100 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) tests were performed to show the impedance value. The charge and discharge (CD) testing were conducted to evaluate the cell electrochemical performance from low current (C/5) to high current (20C) discharge rate.

3. Results and discussion

3.1. The structure of LTO/ZnO
In this characterization, LTO/ZnO is observed to gain the microstructure and morphology of material by conducting SEM-EDS characterization. Figure 1 shows us all 3 parameters of LTO/ZnO of 4, 7, and 10 wt% with a magnification of 10,000 X.

Figure 1. SEM image of 10,000 X of LTO/ZnO with different variables (a)LTO/ZnO 4%, (b)LTO/ZnO 7%, (c)LTO/ZnO 10%.

We could see several rounded points of nanorods, showing that ZnO nanorods are successfully generated. Along with sample, there are several agglomerates that came from ununiform of the sample during the grinding process. Thus, the sample of LTO/ZnO 10% by increasing the ZnO content the agglomeration become massive and make the grain looks coarse and bigger than the grain of LTO/ZnO 7% and 4%.

3.2. The surface area LTO/ZnO
Brunauer–Emmett–Teller is conducted to know the surface area of LTO/ZnO nanorods. In this Table 2, we could see the effect of ZnO percentages on surface area with fluctuation between each part, with the highest surface area is LTO/ZnO 4%, followed by LTO/ZnO 10%, and LTO/ZnO 7%.

This BET results of each sample correlate with the SEM photomicrograph result. The addition of 7% ZnO leads to lowering the surface area compare to the 4% ZnO. It could be predicted that the some of ZnO particle may block the pore of LTO particle. Nevertheless, as a result of some agglomeration of ZnO particle at the composition of 10% ZnO, at the certain level the agglomeration of ZnO may reduce the particle that blocking the LTO pore. That would be the possible cause why the sample of 10% ZnO possesses the higher surface area than that of 7% ZnO.
Table 2. The surface area of LTO/ZnO nanorods sample.

| Samples       | Surface Area   |
|---------------|----------------|
| LTO/ZnO with 4% | 75.545 m²/g   |
| LTO/ZnO with 7% | 40.103 m²/g   |
| LTO/ZnO with 10% | 63.158 m²/g  |

3.3. Phase analysis of the LTO/ZnO

The structure of the synthesized powder was characterized using X-ray diffraction (XRD). The data is processed using XRD results X’Pert High Score Plus and Based on the data we could see several parameters that are Li₄Ti₅O₁₂ (LTO), ZnO, and rutile phase. LTO/ZnO parameter consists of LTO/ZnO in 4, 7, and 10 wt%, with angle that been taken within 20° and 80° by conducting with Xpert High score analysis program, with LTO along with ZnO found in all parameter and rutile phase in this process occurs because it could not construct LTO/Li₄Ti₅O₁₂ and in this case it becoming impurities inside LTO/ZnO nanorods [6]. The peak at 2θ for LTO with JCPDS no. 00-049-0207 [7], with peak number 18.33°, 43.24°, 62.84°, 66.08°. Next is ZnO with JCPDS no. 00-036-1451 [8], with peak number 34.42°, 36.25°, 56.60°, 62.86°, 66.38°.

![Figure 2. X-ray diffraction patterns of LTO/ZnO powder.]

3.4. EIS characterization of LTO electrodes

Half-cell measurement of LTO and a lithium counter electrode using electrochemical impedance spectroscopy (EIS) using the frequency of 0.1 – 2.000 Hz. In this characterization, we conduct this method by taking semi-circle graph from sample LTO/ZnO with various compositions.
The electrode-polarization resistance increased of ZnO, the resistance also increasing along with it, that we can be seen in table 3 shows resistance to charge transfer (Rct) to determine the resistance or impedance at the half-cell batteries.

In this EIS data, there is Randles circuit that works as equivalent circuit. Within Randles circuit there is several parameter, such as Re as solution resistance, CDL as capacity double layer and RCT resistivity charge transfer is representing the impedance in the porous electrode, and then W for warburg is constant for semi-infinite diffusion condition. The fitting was conducted using EISSA software. The value of each element is shown in Table 3.

![Complex impedance plots of the half-cell with LTO/ZnO anode with its equivalent circuit.](image)

**Figure 3.** Complex impedance plots of the half-cell with LTO/ZnO anode with its equivalent circuit.

| Sample      | $R_s$ (ohm) | $R_{ct}$ (ohm) | $C_{dl}$ (F)   | $W$            |
|-------------|-------------|----------------|----------------|----------------|
| LTO/ZnO 4%  | 11.44       | 87.70          | 1.210 E-06     | 221.24         |
| LTO/ZnO 7%  | 19.58       | 129.36         | 1.234 E-06     | 285.08         |
| LTO/ZnO 10% | 16.69       | 131.77         | 1.145 E-06     | 388.66         |

Based on Table 3 we could see with increasing ZnO content, it affects sample conductivity, with the highest conductivity is LTO/ZnO 4%, while the lowest conductivity is LTO/ZnO 10%.

### 3.5 Cyclic Voltammetry of LTO/ZnO electrodes

Cyclic Voltammetry is used to gain work potential and specific capacity of the sample, where every sample is tested, it shows us differences between each of them are insignificant, with sample LTO/ZnO 4, 7, and 10 wt% is 1.594 V, 1.589 V, and 1.593 V, respectively.

The specific capacity of sample LTO/ZnO could be obtained by cyclic voltammetry test. Sample capacities of sample LTO/ZnO 4% are 110.2 mAh/g, LTO/ZnO 7% are 109.1 mAh/g, and LTO/ZnO 10% are 96.7 mAh/g. Based on the data, there is decreasing specific capacity, and also ZnO content didn’t improve specific capacity, that could be proof by the content, with LTO/ZnO 4% is the highest specific capacity with 110.2 mAh/g, while LTO/ZnO 7 wt% and 10 wt% is lower than that.
Figure 4. Cyclic Voltammetry curve for LTO/ZnO 4% (a), LTO/ZnO 7% (b), and LTO/ZnO 10% (c).

3.6. Charge-Discharge (CD) characterization of LTO/ZnO electrodes
Charge-Discharge (CD) is done to gain an understanding of battery performance by conducting charges discharges from 0.2 C to 20 C, with 1C means the charges and discharges current that occur for 1 hour for battery performance reaching top performance.

Figure 5. Charge Discharges for LTO/ZnO 4% (a), LTO/ZnO 7% (b), LTO/ZnO 10% (c) of half-cell with current rate 0.2C to 20C.
Based on Figure 5 it shows that with increasing C-rate, there is degradation of sample durability of LTO/ZnO with different results. For LTO/ZnO 4% it started with 0.2 C and end with 20 C, charges from 103.1 mAh/g to 24.87 mAh/g and discharges from 102.7 mAh/g to 24.8 mAh/g. LTO/ZnO 7% started with 0.2 C to 20 C with charges from 95.6 mAh/g to 8.6 mAh/g and discharges from 99.5 mAh/g to 8.4 mAh/g. LTO/ZnO 10% started with 0.2 C to 20 C, with charges from 91.8 mAh/g to 20.76 mAh/g and discharges from 91.6 mAh/g to 20.6 mAh/g. In the previous experiment, specific capacity at a high C-rate of 10C [9], while with the addition of ZnO our C-rate achieves charge-discharge until 20C. 

Based on Figure 6, we could see the highest capacity within 0.2 C is LTO/ZnO 4%, followed by LTO/ZnO 7% and LTO/ZnO 10%. While at this point, there is a declining rate with increasing current rate, that toward 20C it becoming lowered down, while it could also be seen in Figure 6.

![Figure 6. Capacity discharge vs current rate of LTO/ZnO.](image)

Within the graph, above we could observe that the current rate within 20C LTO/ZnO 4% still the highest capacity followed by LTO/ZnO 10% and LTO/ZnO 7%, where 7 wt% had steep decline within 15C becoming the lowest capacity. From here we could see with lesser ZnO component in LTO/ZnO, the higher capacity of battery material that we could see at LTO/ZnO 4%. Although all the sample unable to reach the theoretical capacity of LTO itself at 175 mAh/g [10], but the addition of nanorods increasing the discharge capability of the LTO/ZnO until 20 C.

4. Conclusion

Li$_4$Ti$_5$O$_{12}$ (LTO)/ZnO synthesis occurs successfully, with mixing of xerogel TiO$_2$ and LiOH in milling process becoming LTO, and mixing with ZnO, becoming LTO/ZnO in slurry preparation. Based on battery fabrication of LTO/ZnO with each composition of them are 4, 7, 10 wt% of mass within battery, with the highest capacity is LTO/ZnO 4% with 110.2 mAh/g, followed by LTO/ZnO 7% with 109.1 mAh/g, and finally LTO/ZnO 10% with 96.7 mAh/g. Coin cell battery conductivity of LTO/ZnO has different value of resistivity, with LTO/ZnO 4% is the lowest of resistance value, while it implies that it has the highest conductivity value, as LTO/ZnO 4% is 103 Ω, while LTO/ZnO 7% and 10% is 160 Ω and 163 Ω respectively. It is shown that increasing ZnO content influence the conductivity of the material, with ZnO mass content affect the capability of battery conductivity.

References

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