Optimization of $Li_4Ti_5O_{12}$ (LTO) performance through the addition of ZnO-Nanorods using sol-gel solid-state method process as half-cell lithium-ion battery anode

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Abstract. Lithium-ion batteries have been a substantial power source for most electrical devices nowadays. Performance optimization for anode of lithium-ion batteries (LIBs) can be conducted by adding ZnO through sol-gel solid-state reaction. In this research, the $Li_4Ti_5O_{12}$ (LTO) used was synthesized through sol-gel solid-state process and directly added with ZnO-nanorods obtained from aging and annealing process. 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 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 96.459 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, capacity of 4 wt% added is 150.8 mAh/g compared to 7 wt% with 134.1 mAh/g and 10 wt% with 118.3 mAh/g.

1 Introduction

Fossil fuels, such as oil, coal, and natural gas, has been a major influence in the development of modern industry, economy, and society. Being the most used energy source also has its drawbacks. Fossil fuels usage is considered to have low-efficiency and abundant source, being it based on mainly combustion technology, has led to some major problem on the planet such as global warming and environmental pollution. In addition, fossil fuels are non-renewable energy sources that can lead to future generation running out of resources. Lithium-ion batteries (LIBs) has become an answer due to its high energy and power density to option for modern technology such as portable electronic devices to hybrid/full electric vehicle. While also recently being researched to have potential for electrical energy storage and as power sources due to their high voltage, lightweight, high power density, lack of memory effect, and environment-friendly [1].

Material development for Lithium-ion batteries has seen a bright future with LTO as base anodes such as $Li_4Ti_5O_{12}$ or Lithium titanate. LTO has been successful on the market because it can exhibit high rate and high cycle life despite the higher cost of Ti, the reduced cell voltage, and lower capacity. This leads to LTO having high stability during charging and discharging process. However, $Li_4Ti_5O_{12}$ exhibits low electronic conductivity which greatly limits its rate performance. Researches has been conducted to improve its capacity and rate capability by conducting morphological optimization, doping another element, and nanostructuring of $Li_4Ti_5O_{12}$ [2].

2 Experimental Procedure

An optimum addition amount of ZnO-nanorods is needed to make an optimal result of LTO/ZnO

anode material, which in this research is used difference in wt % addition. Variables of addition of ZnO in this research consist of 4 wt%, 7 wt%, and 10 wt%. Synthesis process of LTO/ZnO was using sol-gel solid-state method with the addition of ZnO-nanorods was added during sol-gel solid-state process.

ZnO-nanorods synthesis process is done by mixing together Zinc nitrate tetrahydrate ($(Zn(NO)_3.4H_2O$, Merck) and hexamethylenetetramine, HMTA ($C_6H_{12}N_4$, Merck) then dissolved in cold water in beaker glass. Then the beaker glasses are put inside a cooler box surrounded with crushed ice blocks inside it, then lock it for 1 hour. After cooling process, the beaker glasses will then move to the oven for heating process in 90^{o}C for three hours. Straining using filter paper is done after heating, then the ZnO-nanorods is obtained for drying process which could take up to 24 hours [3].

Synthesis process of LTO started with sol-gel method to obtain TiO_2 with titanium tetra-n butoxide and ethanol. Addition of ZnO-nanorods is done during this sol-gel solid-state process with the number of variables determined beforehand. Result of this process is amorph TiO_2 gel along with ZnO-nanorods dispersed inside the gel, then it continues to dry process until we obtain dried gel of TiO_2/ZnO. The obtained dried gel then crushed and pulverized into powder. Calcination then proceed to the powder TiO_2/ZnO in 300^{o}C for 2 hours inside the tube furnace to remove remaining water content and improving crystallinity [4].

Lithium source is required as a precursor to LTO. Lithium source that is used in this research is LiOH, which then mixed using mechanical process of ball milling for 30 minutes. Then mixed powder between TiO_2/ZnO powder and LiOH was obtained, it will then go to sintering process using tube furnace in 750^{o}C for 3 hours with 1 hour 45 minutes rising time and 15 minutes holding time to obtain spinel phase of LTO. Then LTO/ZnO powder is ready to use.

Active material (LTO/ZnO) obtained from the process will then proceed to fabrication process that starts with slurry making. Slurry making process involves mixing between the active material, PVDF as binder, acetylene black as conductive agent with the ratio of 8:1:1 between the three of the material, and 5 grams of DMAC as solvent in the slurry making process. This process was conducted on a hot plate using magnetic stirrer to obtain homogenous slurry, the process can take up to 3 hours. Slurry obtained from the process will then proceed to coating process on Cu foil using doctor blade, followed by drying for 30 minutes in the oven of 80^{o}C. Then the coated anode material is ready to use.

Table 1. LTO/ZnO composite composition.

Material	Mass (gram)			
	Active Material	Total Active Material	Acetylene Black	PVDF
LTO/ZnO 4%	1.6	2	0.25	0.25
LTO/ZnO 7%	1.6	2	0.25	0.25
LTO/ZnO 10%	1.6	2	0.25	0.25

Characterization of the material is conducted after synthesis process. Characterization process in this research involves XRD to analyze compounds and substance produced from the LTO synthesis process. SEM-EDS to detect element exists in the material along with the morphology and physical structure of the material itself. BET is also conducted to determine the surface area of the material. Performance test conducted in this research are EIS (electrochemical impedance spectroscopy) to find out the resistivity of the material, CV (cyclic voltammetry) to find out the capacity and potential, and CD (charge-discharge) to find out the retained capacity performed by the material at different C-rates.

3 Results and discussion

XRD peak result in figure 1 shows the presence of LTO, ZnO, and rutile phase of LTO exists in sample LTO/ZnO 4%, LTO/ZnO 7%, and LTO/ZnO 10% respectively. Angle applied in finding the compound existed was 20^o up to 80^o using Xpert HighScore program to conduct the XRD analysis. From all the samples with different variables can be seen that $Li_4Ti_5O_{12}$ exists in all samples which is synthesized LTO powder. Not only the LTO exists, added ZnO-nanorods also detected in the analysis along with the remaining of rutile phase of TiO_2 due to synthesis process that may be conducted not very properly that may leave some impurities behind [5].

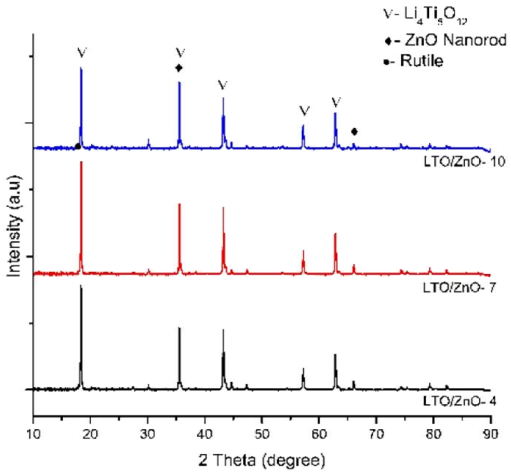

Fig 1. XRD Result of LTO/ZnO 4%, LTO/ZnO 7%, and LTO/ZnO 10%

Observation of microstructure morphology of synthesized LTO was done by using SEM-EDS and compared between variables of samples. Figure 2 shows that morphology comparison between LTO/ZnO 4% and LTO/ZnO 7% and 10% is that there are still chunks of particles exists in the material which resulted from ununiform pulverizing process, this shows that the particle size is not homogenous. ZnO-nanorods is also not visible in the SEM images due to orientation of the nanorods itself that makes them not appear in the image, although the ZnO-nanorods are successfully formed using the method used can be seen in figure 3.

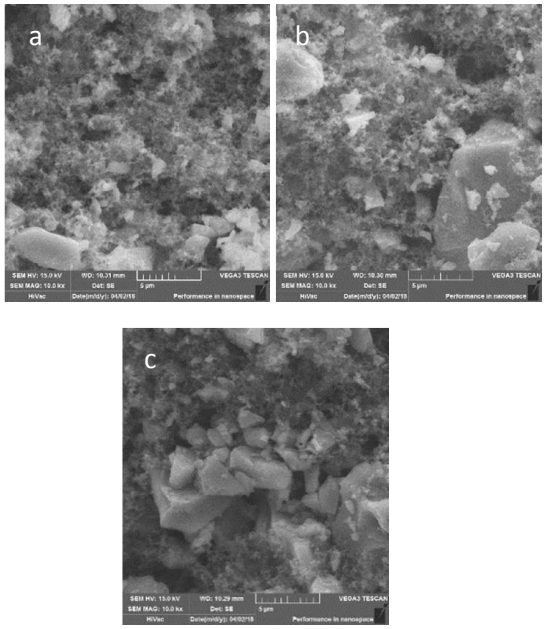

Fig 2. SEM Images of (a) LTO/ZnO 4%, (b) LTO/ZnO 7%, (c) LTO/ZnO 10% with 10,000X magnification

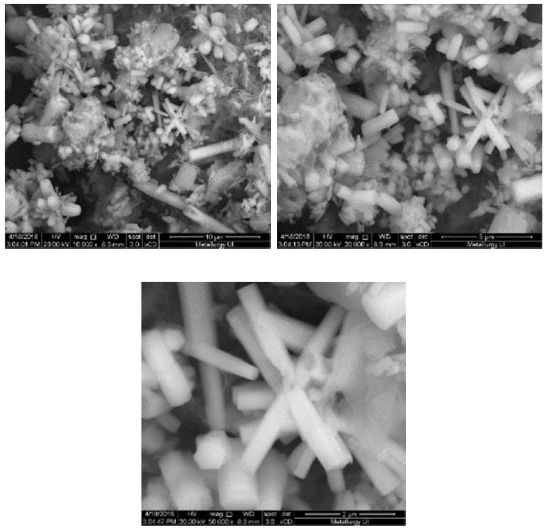

Fig 3. FESEM result for ZnO-nanorods with 10,000X, 20,000X, and 50,000X magnification

EIS result shows conductivity of each sample. The result shows the highest resistance to the lowest resistance being LTO/ZnO 7%, LTO/ZnO 10%, and LTO/ZnO 4% respectively. Table 2 also shows the conductivity value from each sample, shows that LTO/ZnO 4% have lower R_{ct} value which means it can provide good conductivity compared to the other two samples.

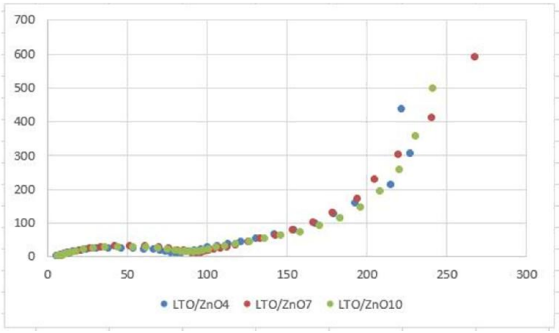

Figure 4. EIS graph of LTO/ZnO samples

Table 2. Rct values from all samples.

Sample	Rct (Ω)
LTO/ZnO 4%	76.05
LTO/ZnO 7%	87.94
LTO/ZnO 10%	83.85

Working potential is measured for every sample using cyclic voltammetry test. Figure 7 shows results of LTO/ZnO 4%, 7%, and 10% after the test, revealed that there is almost no difference in cathodic and anodic peaks from one another but there are two additional peaks exists in LTO/ZnO

7% and 10%. Additional peak present in the CV results indicates ZnO, which is given at an excessive amount. LTO/ZnO 4% does not really show the presence of additional peak. ZnO-nanorods tested in cyclic voltammetry shows the voltage peak is around 1.4V-1.6V, which is almost similar to Lithium [6].

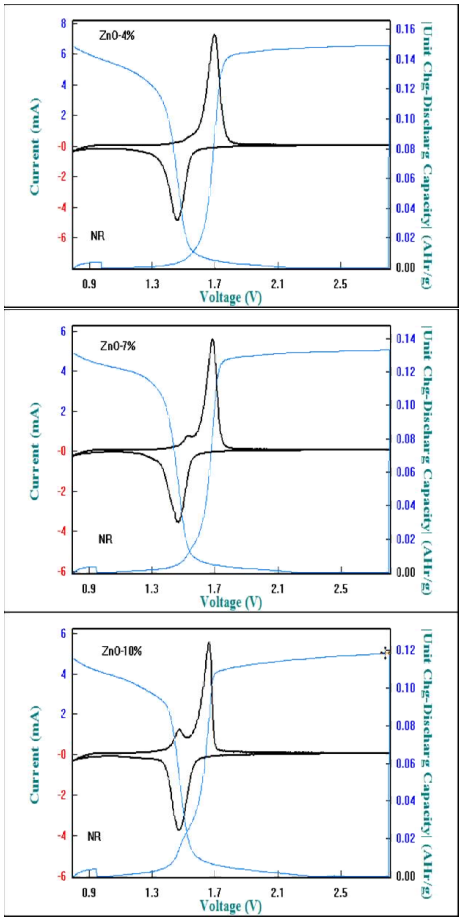

Fig 5. Cyclic voltammetry curve for LTO/ZnO 4% (top left), LTO/ZnO 7% (top right), and LTO/ZnO10% (bottom).

Performance test on battery can also be used to examine the capacity of the material tested that is obtained from cyclic voltammetry test. Capacities for the samples LTO/ZnO 4%, LTO/ZnO 7%, and LTO/ZnO 10% are 150.8 mAh/g, 134.1 mAh/g, and 118.3 mAh/g respectively. Theoretical capacity for LTO is around 175 mAh/g [7] which is higher even from the highest capacity that this research material is tested. Effect of ZnO addition can be seen from the result where higher ZnO-nanorods content will decrease the capacity of the material, the optimum addition of ZnO-nanorods is 4% from these 3 variables. Capacity decrease after the addition in this research was found to be 13.6% from the theoretical capacity. Also, ZnO-nanorods addition does not seem to change the value of cathodic and anodic capacity in any material, it only adds a hint of ZnO-nanorods presence during cyclic voltammetry test.

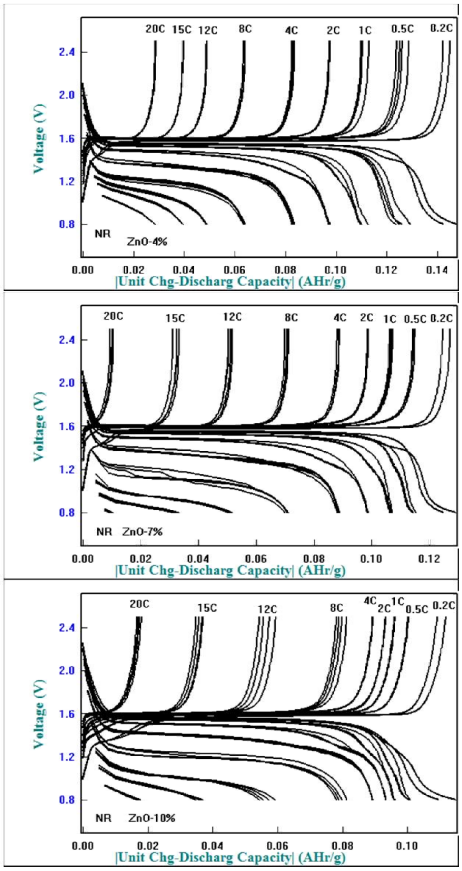

Fig 6. Charge-Discharge curve for every sample.

Charge-discharge test is done to find out the capacity of the battery under a certain C-rate, which the result of discharge can be seen form the figure 9. below. Figure 8 shows the charge-discharge curve for every sample. It shows that the higher C-rate will result in lower capacity produced caused by the battery and process not allowing for chemical reaction to take place. The result shows that with increasing C-rate, the capacity of each material will degrade. But LTO/ZnO 4% shows the best result by being able to retain 20C compared to LTO/ZnO 7% and 10%. This shows that the LTO/ZnO 4% will have better durability compared to LTO/ZnO 7% and 10%. ZnO-nanorods content added to the sample can improve the rate charge and discharge capability but with proper amount without harming the reaction kinetics [8].

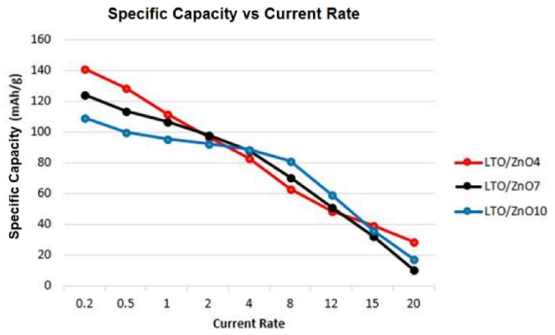

Fig 7. Specific capacity at particular C-rate.

4 Conclusion

Addition of ZnO-nanorods during synthesizing LTO has been done using sol-gel solid state process. Then it proceeds to slurry making process to be coated to Cu foil then tested. Material characterization and testing results in LTO/ZnO 4% being the best in performance and durability compared to LTO/ZnO 7% and 10%. Although with the addition of ZnO-nanorods will result in decrease of specific capacity from pure LTO. Then, it is an effective method to enhance durability as an application in lithium ion power battery.

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