Zinc Oxide Nanoparticle and its characterization in the LTO/ZnO composite for lithium-ion battery anode

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Abstract. One of the most popular active materials that are being used in lithium-ion batteries is lithium titanate/Li4Ti5O12 (LTO), as it exhibits zero strain properties as well as high resistance to volume change. Its disadvantages are low capacity and low electrical conductivity. In this experiment, the addition of zinc oxide nanoparticles into LTO as composite is aimed at increasing the capacity of LTO. LTO was synthesized from LiOH and anatase TiO2 using the solid-state method. The composite powders were prepared with 5, 8, and 11 wt.% composition of ZnO-NP. XRD and SEM were used to investigate the composition and microstructure of LTO/ZnO-NP composites. The electrochemical properties of the LTO/ZnO-NP electrode studied by electrochemical impedance spectroscopy, cyclic voltammetry, and charge-discharge. ZnO nanoparticles were uniformly distributed in LTO. The XRD showed a rutile TiO2 and dilithium titanate as a minor phase, while SEM showed particle distribution of LTO/ZnO-NP. LTO/ZnO-NP-11 exhibits excellent cycling performance and high capacity when used as anode with a specific capacity of 166.96 mAh/g at 0.1C, which is better than LTO pure.

1. Introduction
Lithium-ion batteries have been prevalent in acting as the power source for a host of modern consumer electronic devices, dating back to their commercial introduction in the early 1990s. Li-ion and other emerging technologies have also appealed as an option to be the power source of a variety of well-known electric and hybrid-electric vehicles. Acknowledging the popularity of these Lithium-Ion batteries, many of the research efforts today are focused on improving the performance and design of these LIBs [1].

Development of Li4Ti5O12 (LTO) as a lithium-ion battery anodic material has become a popular topic for use in electrochemical energy storage and electric vehicles. The disadvantages of LTO are low electronic conductivity and a low lithium-ion diffusion rate, which are two problems to improved performance from the LTO-based electrode [2]. The typical research conducted to improve electrochemical performance by conducting morphology optimization, doping, nano-structuring [3], and making composites [4]. The enhancement of capacity with adding components by metal oxide, such as SnO2, Fe3O4, MnO2, and ZnO [5]. Among them, zinc oxide nanoparticles (ZnO NPs) as a promising
anode for LiBs because of their high theoretical capacity (988 mAhg-1), good chemical stability [6], low cost, and minimal pollution [5].

This research will be focused on the fabrication of spinel LTO/ZnO-NP composite to be used as the material in a lithium-ion battery anode. The different concentrations of ZnO-NP will also be observed to determine which amount of ZnO-NP in the LTO would be most effective in the battery’s overall performance.

2. Methods

2.1. Synthesis of LTO and LTO/ZnO-NP Composite

Li$_4$Ti$_{12}$O$_{42}$ (LTO) was prepared by a solid-state method using lithium hydroxide (98% LiOH, Merck) and titanium dioxide (EMSURE® TiO$_2$, Merck) prepared with a high-energy ball milling machine (MSK-SFM-3, MTI) for 3 hours at a speed of 1500 rpm using 0.5 mm ZrO2 beads. Following this process, LiOH and TiO$_2$ powders were mixed at 4:5 Li: Ti ratio. An excess of 6% Li to prevent dissipation of Li in the subsequent high-temperature sintering. The reagent mixed with ethanol to favor the mixing process. Then, dried to form a dry powder. The dried powders were sintering at 800°C for 8 hours to obtain LTO samples.

LTO/ZnO-NP composite with a solid-state method is also applied. LTO powder milled with commercial ZnO nanoparticle (ZnO-NP) with differing percentages of ZnO-NP composition (0, 5, 8, and 11 wt.%). This composition was chosen based on the best result in other research with 6 wt.% ZnO [7]. The ball-milling process is done in 10-minute intervals with a 10-minute break using zirconium balls of 1.6 mm diameter.

2.2. Fabrication of electrode

The working electrode was prepared using a mixture of 80 wt.% active material (LTO, LTO/ZnO-NP-5, LTO, LTO/ZnO-NP-8, and LTO/ZnO-NP-5), 10 wt.% polyvinylidene fluoride (PVDF) as a binder, and 10 wt.% conductive acetylene black. The mixture was dispersed in N, N-dimethylacetamide solvent, and mixed until homogenous. Copper foils were coated with the resulting slurries and dried in an oven at 80°C. The coated foils were punched into 16 mm diameter to obtain the working electrode, lithium metal as the counter electrode, Celgard polypropylene as the separator (21 mm), and the electrolyte was 1 M LiPF$_6$ dissolved in a 1:1 mixture of EC/DMC. The electrode cells were assembled inside a glovebox in the argon atmosphere.

2.3. Characterization and electrochemical measurements

The morphology of the sample was observed with a scanning electron microscope (SEM) (Tescan Vega3). The particle size of the sample was measured with Image J software. Phase identification was examined by X-ray diffraction analysis (PANalytical X’Pert PRO, Cu Kα 1.5Å).

The electrochemical performance was tested with CR2032 coin cells between voltage ranges 1.0-3.0 V. Cyclic voltammetry (CV) by measured by an electrochemistry workstation (WonATech WBCS 2000) with a sweep scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy (EIS) test was performed to measure charge transfer resistance and electrolyte using HIOKI RM3544 with a frequency range of 0.1-20.000 Hz. The charge-discharge (CD) testing on the recycler battery system (WonATech WBCS 2000) was conducted to evaluate the cell electrochemical performance with a C-rate variation of 0.5C, 1C, 2C, 5C, 10C, and 15C.

3. Results and discussion

3.1 Structure and morphology analysis

The structure of the synthesized powder was characterization using x-ray diffraction (XRD). The XRD pattern of LTO and LTO/ZnO-NP composites powders are shown in figure 1. This indicated that four phases are Li$_4$Ti$_{12}$O$_{42}$, Li$_2$TiO$_3$, ZnO, and rutile TiO$_2$, where Li$_2$TiO$_3$ and rutile TiO$_2$ is the material that
doesn’t form the desired chemical formula during the solid-state and sintering processes. Phase peak of Li$_2$TiO$_3$ (23.89°), rutile TiO$_2$ (27.394°), and ZnO (30.255°) for LTO/ZnO-NP-5. No peaks of rutile TiO$_2$ are detected in the patterns of LTO/ZnO-NP-8 and LTO/ZnO-11, indicating the high purity samples. The existence of these impurities caused by the presence of lithium cation loss and upon mixing with insufficient homogeneity [8].

![Figure 1. XRD pattern of LTO and LTO/ZnO-NP composite powders.](image)

The morphology of the LTO and LTO/ZnO-NP in figure 2 was physically characterized by scanning electron microscopy (SEM). Figure 2(a) has a uniform distribution, and the particles are small and disperse, although there is also evidence of clump formations (agglomerations) that could be due to poor mixing that isn’t homogenous enough.

![Figure 2. SEM images of (a) Li$_4$Ti$_5$O$_{12}$, (b) LTO/ZnO-NP-5, (c) LTO/ZnO-NP-8 and (d) LTO/ZnO-NP-11.](image)

The method of compositing is through a solid-state ball milling process, and thus to reduce the particle size, the smaller diameter of zirconium balls should be utilized. Another method of preventing the
agglomerations from forming is by using ethanol as a medium to prevent agglomerations [9,10]. At it is shown in figure 2 (b) to (d), after adding ZnO, the agglomeration started to break down, and the particle was well distributed for the samples containing higher ZnO-NP content. Morphology enhancement via ZnO loading, where uniform morphology along with smaller particle size has been depicted in LTO/ZnO (11 wt.%) composite. This is based on reported less agglomeration after doping by metal/non-metal [11].

3.2. Electrochemical performance of LTO and LTO/ZnO-NP composite

The Electrochemical Impedance Spectroscopy (EIS) was conducted to investigate the charge transfer and transport process in a coin cell. Figure 3 shows the electrochemical impedance spectra of all samples with fitted with an equivalent circuit. An equivalent circuit consisting of three elements, i.e., two resistor elements, one constant phase element, and a Warburg diffusion element. R1/Re and R2/Rct are the solution resistance and charge transfer resistance, respectively.

![Electrochemical impedance spectra](image)

**Figure 3.** Electrochemical impedance spectra of the Li$_4$Ti$_5$O$_{12}$ materials with different content of ZnO nanoparticle (a) 0 wt.% (b) 5 wt.% (c) 8 wt.% and (d) 11 wt.%.

The results can be seen in Table 1 shows electrolyte resistance (R1/Re) and resistance charge transfer (R2/Rct) to determine the resistance or impedance at the half cell batteries.

| Samples          | R1/Re (Ω) | R2/Rct (Ω) |
|------------------|-----------|------------|
| LTO (0 wt.% )    | 7.59      | 47.40      |
| LTO/ZnO-NP-5     | 7.28      | 78.18      |
| LTO/ZnO-NP-8     | 9.39      | 99.92      |
| LTO/ZnO-NP-11    | 16.50     | 105.5      |

Based on Table 1, it is visible that the LTO/ZnO-NP composite samples with the concentration of LTO/ZnO-NP-5 (5 wt.%) have the lowest Rct value, which means that it exhibits the best charge resistivity properties. This sample has the most optimum ZnO-NP content compared to the other.
Figure 4 shows the cyclic voltammetry curve of all samples in anodic and cathodic scanning from 0.4 – 2.8 V at 10 mV/s scan rate. All the samples conducted both oxidation and reduction peaks. LTO pure has oxidation peak located at 1.709 V, while the reduction peak in 1.471 V. For composite samples, LTO/ZnO-NP samples has oxidation peak located around 1.6 V, whereas the reduction peak around 1.4 V. LTO peak with an average potential of 1.55 V which correlated to two phases that is \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and \( \text{Li}_7\text{Ti}_3\text{O}_{12} \) phases in the intercalation and de-intercalation process [8]. The ZnO peak appears at the peak located at 0.597 V (5 wt.%), 0.74 V (8 wt.%), and 0.719 V (11 wt.%). This indicated that ZnO peak increases along with ZnO addition. The discharge capacity for all samples was LTO (125 mAh g\(^{-1}\)), LTO/ZnO-5 (159.63 mAh g\(^{-1}\)), LTO/ZnO-8 (159.43 mAh g\(^{-1}\)), and LTO/ZnO-11 (166.96 mAh g\(^{-1}\)). The addition of zinc oxide nanoparticle, increasing the discharging capacity of LTO with an added optimum of 11 wt.% ZnO.

![Cyclic voltammetry curves](image)

**Figure 4.** Cyclic voltammetry curves of (a) LTO, (b) LTO/ZnO-NP-5, (c) LTO/ZnO-NP-8 and (d) LTO/ZnO-NP-11.

Figure 5 shows charge-discharge curve for all samples with 0.5C, 1C, 2C, 5C, 10C and 15C in a potential range from 0.4 to 2.8 V. LTO/ZnO-NP-11 has the highest overall charge and discharge capacity followed by LTO/ZnO-NP-5, then LTO/ZnO-NP-8. Correlation from CV test, LTO/ZnO-NP-11 (0.5C: 146.05 mAh g\(^{-1}\), 1C: 128.23 mAh g\(^{-1}\), 2C: 110.58 mAh g\(^{-1}\), 5C: 93.91 mAh g\(^{-1}\), 10C: 80.36 mAh g\(^{-1}\), 15C: 47.25 mAh g\(^{-1}\)) demonstrates higher capacity than LTO (0.5C: 114.02 mAh g\(^{-1}\), 1C: 97.75 mAh g\(^{-1}\), 2C: 85.72 mAh g\(^{-1}\), 5C: 59.804 mAh g\(^{-1}\), 10C: 27.76 mAh g\(^{-1}\), 15C: 22.06 mAh g\(^{-1}\)). The addition of zinc oxide to the sample will correlate proportionally to the battery’s charging and discharging capacity. Therefore, the higher the amount of ZnO added, the higher the overall charge and discharge capacity of the sample than pure LTO [7].
4. Conclusion
In this work, Li_{4}Ti_{5}O_{12} and LTO/ZnO-NP composites were successfully prepared by the solid-state method from commercial LiOH and TiO_{2}. The addition of zinc oxide nanoparticle at different concentrations to lithium titanate effects the performance of the lithium anode half-cell samples. ZnO nanoparticles were uniformly distributed in LTO. The phases identified in this experiment are Li_{4}Ti_{5}O_{12}, Li_{2}TiO_{3}, ZnO, and rutile TiO_{2}, while SEM showed particle distribution of LTO/ZnO-NP. Based on the CV results, the working potential of all the samples is higher compared to the theoretical LTO. This is visible from the CD results where the capacity is higher with increasing amounts of Zinc Oxide compositions compared to the pure LTO.

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