

THE EFFECT OF NANO SN ADDITION TO $\text{Li}_4\text{Ti}_5\text{O}_{12}$ NANOROD ANODE PERFORMANCE IN LITHIUM ION BATTERY APPLICATION

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Abstract

Research has been conducted to study the synthesis of nanorod $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and the effect of Sn nanopowder and activated carbon addition to the battery performances. Firstly, Sol-gel process was conducted to synthesize TiO_2 powder which further subjected to hydrothermal process to obtain nanorod structure. Moreover, The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared through solid-state method. Activated carbon were prepared using NaOH 1M as activation agents while Sn nanopowder was added by 10 wt%, 15 wt%, and 20wt%. The powder then characterized by SEM-EDX, XRD, and BET, and the cell performance was tested using CV, CD, and EIS. The impurities such as Rutile TiO_2 , and Li_2TiO_3 present. The highest capacity was achieved by 20 wt% Sn addition which value is 192.1 mAh/g.

Keywords: Hydrothermal, composite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, sol-gel, activated carbon, Tin Nanopowder

Introduction

An LTO or Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anode has been developed, which has a voltage of 1.55 V vs. Li/Li + (Wang *et al.*, 2015). The anode's lithium insertion process occurs at a higher potential than the graphite anode, thereby reducing the decomposition of the solvent used to avoid the formation of the Solid Electrolyte Interface (SEI) and supported by height around 1.55 v vs. Li/Li + so that it can suppress lithium dendrite formation (Ni *et al.*, 2016), which can cause short-circuit. In addition, LTO is a material that does not experience a 0.2% change in too much cell unit volume, so it can be referred to as "zero-strain" when Li + ions are intercalated or de-intercalated (Sandhya *et al.*, 2014) and long operating lives in

the charge/discharge cycle. Moreover, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ may achieve a theoretical capacity of 175 mAh g⁻¹ (Borghols *et al.*, 2009; Yang *et al.*, 2016).

The deficiencies experienced by the LTO anode can be solved in various ways. The method adopted was the addition of metal dopants and carbon additive as a way to improve the performance of the LTO anode. The element Sn (tin) is one of the dopant elements that can increase theoretical capacity. The Sn element itself is fascinating to be used as a dopant because Sn's high theoretical capacity is 993.4 mAh g⁻¹ for $\text{Li}_4.4\text{Sn}$, a lot of availability, low operating voltage, and environmentally friendly (Molenda *et al.*, 2014). However, Sn can experience significant volumetric

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changes (300% expansion) (Aifantis *et al.*, 2012) when the process of combination and lithium separation can form significant internal stresses and cause deformation (Chao *et al.*, 2011). By embedding the Sn element into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ matrix, the volume expansion can be buffered (Cai *et al.*, 2010). The addition of Carbon additive is one of the methods to improve the performance of anodes, which is excellent due to process efficiency and economic aspects (Luo *et al.*, 2013; Zhang *et al.*, 2015). Activated carbon can increase the surface area formed by its porous structure. Another way to improve the performance of anodes is by utilizing LTO anode-sized engineering (Wang *et al.*, 2013). By controlling the size and structure of the particles, it will expand the contact area between the electrodes and electrolytes so that shortening the diffusion distance of Li^+ ions which causes the rate of charging/discharging increase. Also, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hydrothermal preparation has been reported to improve the performance of the anode. As reported by Wu *et al.* (2015), the hydrothermal method has successfully prepared the nanosheet LTO material, which can deliver a stable 175 mAh g^{-1} specific capacity at 0.1C to 20C (Wu *et al.*, 2015). The hydrothermal nanowire prepared by subsequent hydrothermal and the solid-state method exhibited a capacity of 198 mAh g^{-1} at 1C (Kim, and Yoon, 2013). However, the combination of such hydrothermal method with Sn and activated carbon addition have not been implemented yet. So, the recent study is aimed to investigate the effect of Sn and activated carbon addition into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod prepared from the hydrothermal method.

Methodology

Sol-gel Synthesis of TiO_2

Synthesis of TiO_2 was conducted by sol-gel synthesis method using Titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$, Sigma-Aldrich 97%) as titanium precursor. In the beginning, Ethanol (RCI-Labscan) was adjusted to pH 3 using 1M HCl (Merck). Then, This synthesis process was conducted by preparing the primary solution and secondary solution-the volume of 20 mL of prepared ethanol mixed with 3.4 g of Titanium tetrabutoxide compound. The secondary solution was prepared by adding 5 ml of ethanol mixed with 0.63 g of distilled water (Rw 3.5). The sol-gel method was conducted by adding the secondary solution drop-wisely to the primary solution. The solution was mixed using magnetic stirrer until the firm gel was formed. Furthermore, the gel was dried under ambient temperature. The dried crystals were ground using an agate mortar and further calcined in the tube

furnace at 300°C for 2 h in the ambient atmosphere. The calcination was conducted for 1 h with 15 rising times to the desired temperature and 45 min holding time at 300°C.

Nanorod TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) Powder Preparation

The as-obtained TiO_2 powder was used as precursors for nanorods synthesis through the hydrothermal method. TiO_2 powder was mixed into 10 M NaOH and stirred for 30 min then is put into the Teflon-lined autoclave. The hydrothermal method was carried out at 180°C for over 24 h. Furthermore, The hydrothermal solution was filtered and washed 0.1 M HCl until reaching pH 7-8 indicated by universal pH paper. The results of the washing are then filtered again and washed using aquadest until the pH becomes 7, and dried on a magnetic stirrer on a non-stirring petri dish for 1 h at 80°C.

The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared through the mechanochemical method wherein as obtained TiO_2 nanorod was mixed with LiOH using a ball-mill. The TiO_2 and LiOH (Merck) were mixed under the stoichiometric Li:Ti ratio of 4:5. The mixed powder was ball milled for 30 min, followed by a sintering process that was conducted at 750°C for 3 h. The detailed heating procedures were 2 h 30 min rising time and holding it for 30 min at the final temperature.

Carbon Activation Process

In this study, carbon is used as an increase in the surface area of the sample. Commercial Char was used as the primary precursor for the preparation of activated carbon. Particle size reduction was carried out using a coffee grinder followed by a sieving process at an 80-mesh size. The carbon powder was then put into the alumina tube and inserted into the tube furnace followed by heating at to 500°C for 2 h. The activation process was carried out by mixing the carbon with 1M NaOH followed by stirring for 2 h. Then, the powder was filtered and dried at 110°C for 4 h, further drying is carried out on the tube furnace while entering the reheating stage. The carbon was heated at 700°C under the protection of the nitrogen atmosphere. The as-obtained activated carbon was ground using agate mortar to reduce the particle size.

The Preparations of LTO/AC/Sn Composite

The LTO/AC/Sn composites were prepared by two subsequent steps. First, as obtained $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod was mixed by 3% wt. Of activated carbon. The powder was mixed using agate mortar. Furthermore, the mixed LTO/AC powder was added into Sn nanoparticles with compositions of 10%,

15%, and 20%wt. The samples were labeled as LCSn-X where X is the composition of Sn nanoparticles (10, 15, and 20). Moreover, each sample was assembled into anode to study its electrochemical properties.

The LTO/AC/Sn Composites Electrode Preparations and Electrochemical Characterizations

The active materials, LTO/AC/Sn composite, were mixed with *Acetylene Black* and *Polyvinylidene (PVDF)* with a ratio of 8:1:1. The powders were mixed into slurry by adding Dimethylacetamide (DMAC) as a solvent. The homogenous slurry was then coated onto Cu foil, followed by the drying process at 80°C for 1 h. To further characterize the sample's electrochemical properties, each electrode was assembled into half-cell coin battery using lithium metal as a counter electrode. The electrochemical characterizations were conducted using Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Battery analyzer (Charge-Discharge).

Result and Discussion

Powder and Electrode Microstructure Characterizations

Each LCSn sample was subjected to X-ray diffractometry (XRD, PANalytical, scanned from 20° to 90°) characterizations to reveal composite crystal structure. Moreover, surface area analysis for LCSn samples was conducted by Brunauer-Emmet-Teller (BET). The surface morphology analysis

of the electrode was characterized by Scanning Electron Microscopy (SEM) coupled with the EDX instrument.

The crystal structure of the LCSn samples was characterized by X-ray Diffraction analysis, which results were shown in Figure 1. The XRD pattern mainly consists of two-phase, which are Sn and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. The Sn shows pronounced peaks at 2θ of 30.6°, 32.1°, 43.7°, 44.9°, 55.4°, 62.6°, 64.6°, 72.2°, 73.24°, 79.5° indicating (200), (101), (220), (211), (301), (112), (321), (420), (411), and (312) Sn planes. The Sn pattern is in good agreement with JCPDS 4-0673 (Sivashanmugam *et al.*, 2011). The existence of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is indicated by some peaks at 2θ 18.6° and 35.9° which corresponds to (111) and (113) plane of Lithium Titanate (JCPDS 49-0207) (Tocoglu *et al.*, 2016). However, the low intensity and broadened peak of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ correspond to the low crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the samples (Shen *et al.*, 2013). According to Figure 1, the carbon peaks can not be observed due

to the amorphous nature of activated carbon and a small amount of addition (Liu *et al.*, 2018).

The average crystallite size of LTO from each sample was calculated using the Scherrer equation, considering the (111) peak of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The result is included in Table 1. It is shown that the crystallite size of LCSn-10, LCSn-15, and LCSn-20 are 10.4 nm, 11.8 nm, and 10.2 nm, respectively.

SEM and EDX tests are carried out to determine the morphology of the LTO powder formed through the Backscattered electron method, to find out the elements contained in the LTO powder with EDS, and to see if there is an agglomerate that occurs in the sample tested. Figure 2 shows the morphology of a sample of LCSn at 10000x magnification size.

The depiction of SEM in the structure of the nanorod shown in Figure 2(a-c) shows that the synthesis process succeeded in forming a nanorod structure. In Figure 2(c), there is an agglomeration which is one of the weaknesses of Nanomaterial synthesis. On the results of the depiction, however, there is still a nanorod structure which can later be seen when the magnification becomes 20,000 and 50,000 times. In the three pictures, it can be seen that the structure of Sn and carbon has been mixed with LTO nanorod, causing agglomeration at some point from the addition. Figure 2(d-f) is the result of an enlargement of 20,000 times in 3 different nano LCSn samples. At this magnification, the structure of the nanorod begins in the three images, where the

Table 1. Crystallite size of the LCSn samples derived from the Debye-Scherrer equation

Sample	Peak (2θ)	FWHM	Crystallite size (nm)
LCSn-10	18.61	0.7655	10.40
LCSn-15	18.67	0.6749	11.79
LCSn-20	18.60	0.7829	10.16

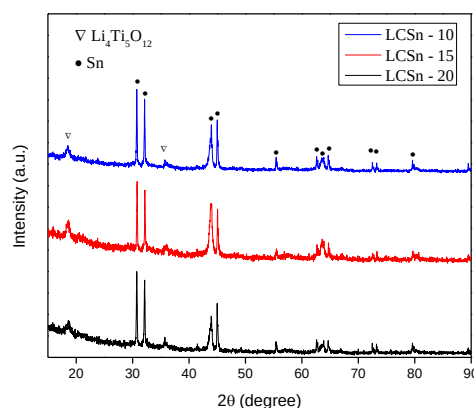


Figure 1. XRD pattern of the LCSn Samples

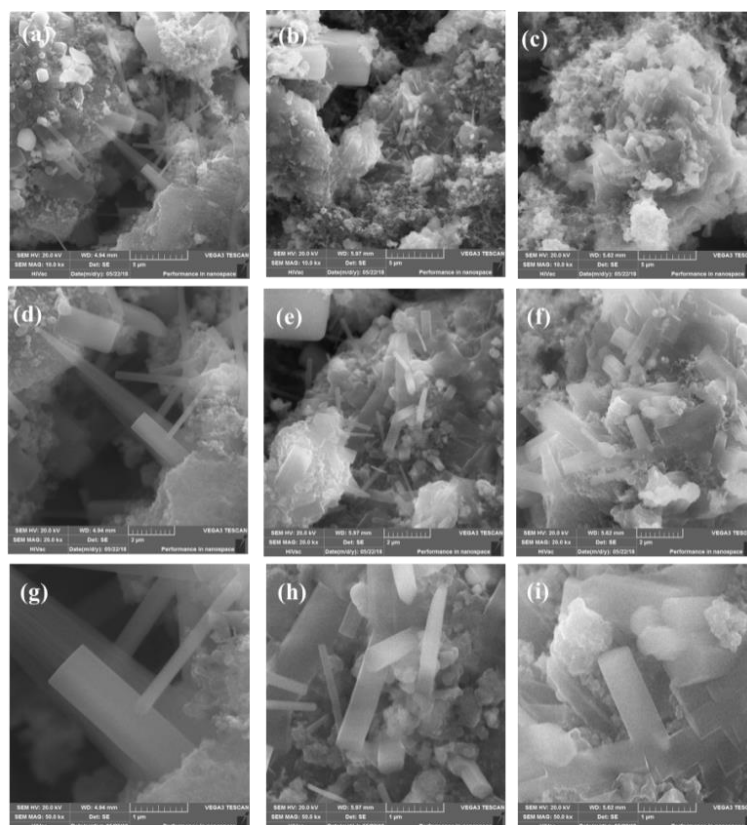


Figure 2. SEM Magnification of 10.000x (a) LCSn-10, (b) LCSn-15, (c) LCSn-20, 20.000x, (D) LCSn-10%, (e) LCSn-15, (f) LCSn-20, 50.000x, (g) LCSn-10, (h) LCSn-15, and (i) LCSn-20

10% sample and 15% sample presents the structure of the nanorod formation (Priyono *et al.*, 2019). Figure 2(g-i) is an enlargement of a sample of 50,000 times. At this magnification, the nanorod structure can be seen independently, from which all three samples show a similar shape.

The EDX test was conducted to determine the elemental distribution added to the electrode. It is shown in Figure 3 that each sample shows a relatively homogenous carbon atom distribution. The increase of carbon atom content in the EDX mapping result is contributed from the addition of acetylene black during electrode preparation. The Sn atom distribution in LCSn-10 shown in Figure 3(a) is relatively dispersed on the electrode surface. Meanwhile, the LCSn-15 and LCSn-20 show an agglomeration. Regarding the result, the increasing Sn addition will increase the tendency of agglomeration. This was due to the nanoparticle's nature that exhibits high surface energy (Cheng *et al.*, 2017). The surface area of the electrode was analyzed using BET which results were shown in Table 2. The value is representative of the surface area of the sample. It was observed that LCSn-10 exhibiting the highest surface area which value is

75,618 m^2/g . On the other hand, the LCSn-15 sample shows a slightly lower surface area, 60.938 m^2/g , compared to that of LCSn-20, 70.287 m^2/g . The result is possibly due to the larger crystallite size of LCSn-15 compared to that of LCSn-20 (Shen *et al.*, 2013). Besides that, the agglomerated microstructure of LCSn-15 and LCSn-20 shown by SEM data confirm the increasing surface area values.

Electrochemical Characterization Results

The Cyclic voltammetry test was conducted to the coin half-cell to characterize its electrochemical reaction during applied voltage from 0 to 3 V. The Cyclic voltammograms of LCSn-10, LCSn-15, LCSn-20 were shown in Figure 4. In general, Cyclic voltammogram shows similar peaks for all LCSn samples. During a positive scan, it was observed that three peaks occur at a voltage value of ~ 6.8 V to

Table 2. Brunauer-Emmett-Teller Test Results

Sample	Surface area (m^2/g)
LCSn-10	75.618 m^2/g
LCSn-15	60.938 m^2/g
LCSn-20	70.278 m^2/g

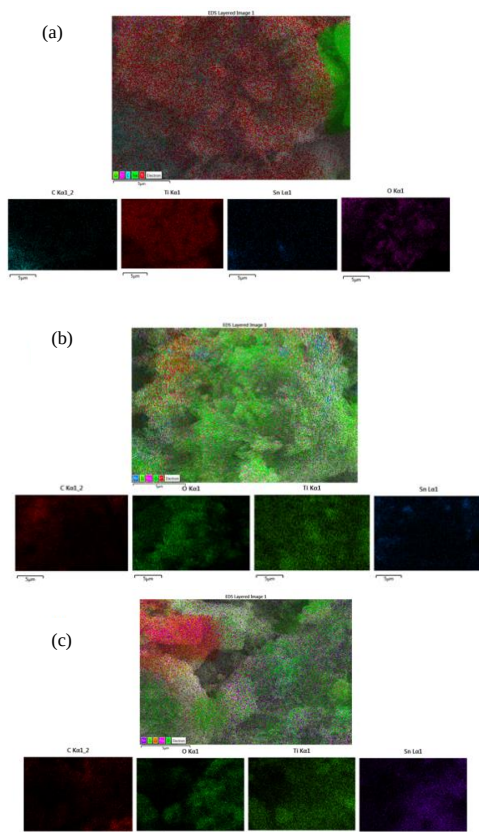


Figure 3. SEM EDX mapping result of (a) LCSn-10, (b) LCSn-15, and (c) LCSn-20

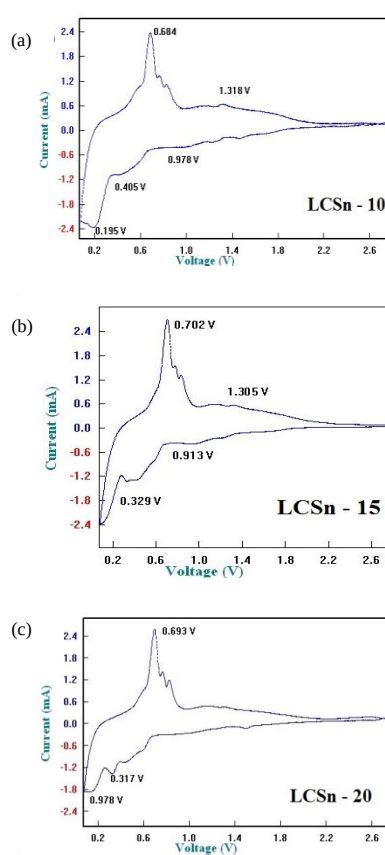


Figure 4. Cyclic voltammetry results on (a) LCSn-10, (b) LCSn-15, and (c) LCSn-20

nearly 0.9 V which indicates the conversion Li-Sn alloy to Sn (Sivashanmugam *et al.*, 2011; Huang *et al.*, 2015; Cheng *et al.*, 2017). While the reduction peaks at the voltage of 0.401 V, 0.329 V, and 0.317 V on LCSn-10, LCSn-15, and LCSn-20 are mainly contributed from Li-Sn alloying phenomena (Li_xSn ; $x \leq 4.4$) (Zhong *et al.*, 2015). Furthermore, the reduction and oxidation peak occurred at $\sim 0.19\text{V}$ and 1.3V indicates the Li^+ insertion and extraction into the disordered layer of carbon confirming the activated carbon existence within the LCSn sample (Huang *et al.*, 2015; Yang *et al.*, 2015). However, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can not be observed in the overall voltammogram. It was reported that lower crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ would distort the anodic/cathodic peaks and diminish the peaks intensity (Yue *et al.*, 2018). Hence, the absence of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ CV peaks is possibly due to the low crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the LCSn samples.

Considering the CV data, the LCSn-10 shows a discharge capacity of 139 mAh/g while LCSn-15 and LCSn-20 are delivering 150 mAh/g and 192 mAh/g, respectively. The charge-discharge result shows that the higher capacity is achieved by LCSn-20. It can be said that the higher Sn addition will

lead to a higher specific capacity (Sivashanmugam *et al.*, 2011).

The electrode prepared from each sample was characterized using a battery analyzer to reveal its electrochemical responses during different C-rate. The charge-discharge profiles were shown in Figure 5. In general, the LCSn samples exhibit a gradual slope with a multi-staged Li^+ extraction plateau, which occurs at the voltage of 0.4-1.1 V. The plateaus agreed with the cyclic voltammetry result that the Li^+ is intercalated into the Sn particles resulting in different Li-Sn alloy compound (Sivashanmugam *et al.*, 2011; Zeng *et al.*, 2016). The absence of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ voltage plateau may be due to the low crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Shen *et al.*, 2013).

Battery half-cells assembled from each sample was subjected to the charge-discharge test at different current density. The result is shown in Figure 5. It can be observed that at 0.2C LCSn-20 deliver the highest capacity of 161 mAh/g. Meanwhile, LCSn-10 and LCSn-15 achieve a specific capacity of 128 mAh/g and 152 mAh/g, subsequently. Moreover, starting at 8C current density and higher, LCSn-10 shows better capacity

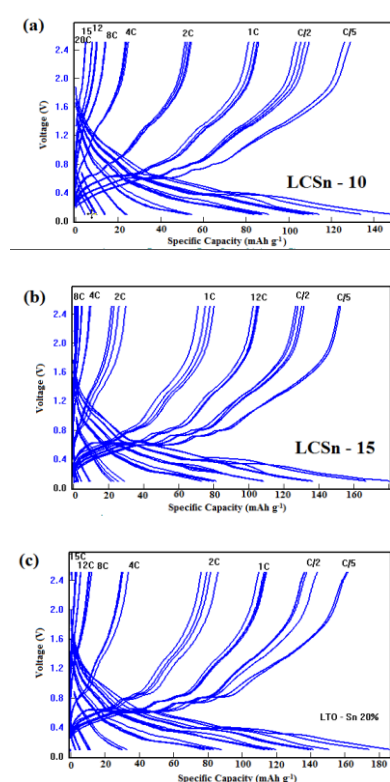


Figure 5. The charge - Discharge profile of (a) LCSn-10, (b) LCSn-15, and (c) LCSn-20 half cells cycled from various current rates

retaining ability. The LCSn-10 samples can retain 11% of capacity at 8C relative to its value at 0.2C. Meanwhile, the LCSn-15 and LCSn-20 samples exhibit only 6% and 7% of capacity from 0.2C. Moreover, LCSn-10 can deliver a capacity of 4.78 mAh/g at 20C while LCSn-15 and LCSn-20 can barely deliver 0.76 mAh/g and 0.51 mAh/g. It shows that LCSn-10 has a better rate capability. In addition, the nanocrystallite-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can effectively buffer the anode's volume expansion for LCSn-10. The higher amount of Sn addition will lead to the agglomeration that will make the anode more susceptible to pulverization (Cai *et al.*, 2010).

The Electrochemical impedance responses were conducted, which result is shown in Figure 6. The Nyquist plot was fitted to the Randles circuit shown in inset. The equivalent circuit is composed of R_{el} , which corresponds to the impedance contributed from electrolyte resistance in the half-cell. The R_{ct} represents the charge transfer resistance of the material, while CPE indicates the charge transfer capacitance, both of which representing the semicircle in the middle frequency. On the other hand. The low-frequency region shows a straight line which corresponds to the lithium-ion diffusion in the solids. According to Figure 6, the

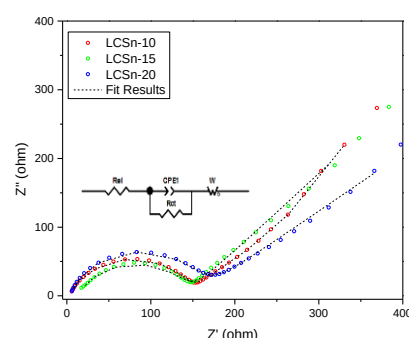


Figure 6. Cole Cole Plot of LCSn Sample and the corresponding equivalent Randles circuit

LCSn-15 exhibits the lowest R_{ct} value at 132 ohm which comparable to that of LCSn-10 at 147 ohm. The highest R_{ct} value is shown by LCSn-20, 160 ohm. It can be inferred that LCSn-15 shows the lowest electrical resistance. Nevertheless, the LCSn-15 sample shows the lowest capacity retention value according to the charge/discharge test. Chauque *et al.* informed that the high crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ would favor the electrochemical performance. However, the increase in crystallite size would be related to the larger particle size which deteriorate the rate capability of the battery (Chauque *et al.*, 2017). Hence, the lower LCSn-15 impedance may be contributed from its' bigger crystallite size. Furthermore, the LCSn-15 is possibly experiencing a more sinterization effect which leads to lower capacity retention than that of LCSn-10 and LCSn-20. Nevertheless, further research needs to be conducted to confirm this anomaly in R_{ct} .

The LCSn-20 sample was characterized by Transmission electron microscopy characterization and the results are represented in Figure 7. According to Figure 7(a), the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanorod surface is embedded with some particles. The particles were characterized by HRTEM to measure the corresponding d-spacing. The lattice fringe shown in Figure 7(b) showed the d-spacing value of 4.844 Å which corresponds to the (111) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in short order arrangement (Yue *et al.*, 2018). The result supports the XRD result that (111) plane was present in the sample. Furthermore, Figure 7(c) depicts a particle that having a d-spacing of 3.38 Å, which nearly similar to the graphite lattice at 3.36 Å (Hayes *et al.*, 2014). Since activated carbon is not identified in XRD due to its amorphous nature, the TEM results confirm that activated carbon was embedded on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface. Moreover, it was observed from Figure 7(d) that agglomerated Sn particles existed on the surface of the nanorod as well. It was confirmed by the particles with

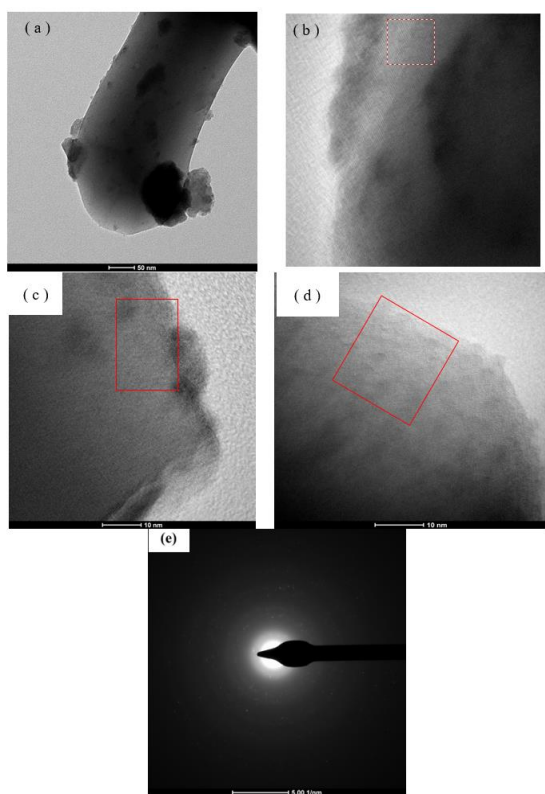


Figure 7. Transmission Electron Microscope characterization result depicting (a) LTO nanorod, (b) LTO lattice fringe on (110) plane (c) activated carbon lattice fringe on nanorods surface (d) agglomerated Sn nanoparticles (e) acquired SAED pattern of LCSn-20

a d-spacing value of 2.1 Å which corresponds to the (220) of Sn nano. The agglomerated particles occurred due to the high surface energy of Sn nano (Cheng *et al.*, 2017).

The Selected Area Diffraction (SAED) was conducted on the LCSn-20 powder which results showed on Figure 7(e). It was observed from the pattern that the presence of spot and ring were correlated to the polycrystalline nature of LCSn-20 sample (Luo, 2016).

The result of SEM-EDX, TEM, and electrochemical characterization are confirming each other that the addition of Sn will increase the specific capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It is observed that the LCSn-20 exhibits a higher specific capacity at 0.2C. However, the LCSn-10 shows higher capacity retention relative to the 0.2C at higher current density charge-discharge (8C and 20C). On the other hand, the presence of nanocrystallite sized of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ will help to alleviate the Sn pulverization effect by buffering the volume expansion of Sn.

Meanwhile, excessive Sn addition ~20% will lead to more severe pulverization of anode (Cai *et al.*, 2010).

Conclusions

The nanorod $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been successfully prepared through the hydrothermal method. The LCSn samples mainly consist of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Sn phase. At the same time, the activated carbon is undetected in XRD due to its amorphous nature. The low crystallinity of nanorod $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a favorable effect in buffering the volume expansion of Sn. According to the electrochemical analysis, The higher the Sn addition would lead to the increasing capacity of the anode. However, it would give a more severe pulverization effect which can be shown by lower capacity retention of LCSn-20. The addition of 10wt% Sn, denoted as LCSn-10, into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - carbon material shows higher capacity retention at a high current density which capable of delivering 14 mAh/g at 8C while LCSn-15 and LCSn-20 barely delivered a capacity of 9 mAh/g and 11 mAh/g. The capacity retentions of LCSn-10, LCSn-15, and LCSn-20 are 11%, 6%, and 7% relative to the capacity at 0.2C. In Summary, The 10 wt% Sn addition gives an optimum result for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for high current density application.

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