



## **THE EFFECT OF FLUORINE DOPING AND CALCINATION TEMPERATURE ON $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ MATERIAL USING SOLID STATE METHOD**

ALVALO TOTO WIBOWO

*Department of Materials and Metallurgical Engineering  
Institut Teknologi Sepuluh Nopember,  
Jl. Teknik Kimia, Keputih, 60111, Surabaya, East Java, Indonesia  
[alvalototowibowo@gmail.com](mailto:alvalototowibowo@gmail.com)*

WIDYASTUTI

*Department of Materials and Metallurgical Engineering  
Institut Teknologi Sepuluh Nopember,  
Jl. Teknik Kimia, Keputih, 60111, Surabaya, East Java, Indonesia  
[wiwid@mat-eng.its.ac.id](mailto:wiwid@mat-eng.its.ac.id)*

LUKMAN NOEROCHEM\*

*Department of Materials and Metallurgical Engineering  
Institut Teknologi Sepuluh Nopember,  
Jl. Teknik Kimia, Keputih, 60111, Surabaya, East Java, Indonesia  
[lukman@mat-eng.its.ac.id](mailto:lukman@mat-eng.its.ac.id)*

\* Corresponding author

**Published** 31 January 2020

*Abstract* –  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  anode has advantage of stable operating voltage compared to graphite which cannot be used in high rate power conditions and the dimensions of graphite change when first charging. Addition of F to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode can improve electrochemical performance and influence the morphology of the anode  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . In this study a synthesis process was carried out and the addition of variations of F (0.1; 0.15; 0.2 moles) into  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode using the solid state reaction method. Then the calcination process was carried out with temperature variations of 700, 750 and 800°C. The reaction product is coated with carbon sourced from acetylene and argon gas. The XRD results show the highest peak at  $2\theta$  around 17-20°. The addition of F has been successfully carried out on LTO material. Ion F has been incorporated into the LTO crystal structure by substituting O ions without causing changes in the crystal structure characteristics. The presence of element F causes the XRD peak to change in a lower direction so that it becomes more crystalline, with the smaller lattice parameters and unit cells. SEM testing result was carried out to determine the morphology of anode  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  material. At calcination temperatures of 700 and 750°C the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  particles had irregular sphere shaped with nanometer size and homogeneous distribution. However, at a calcination temperature of 800°C agglomeration occurred, so that the particles adhere to each other and enlarge. This condition affects the electrochemical performance of the sample.

*Keywords:* anode  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ; ball mill; doping F; calcinations temperature

### **1. Introduction**

Lithium ion batteries are one source of energy that is widely used today. As we know, anode material often plays an important role in determining the safety and lifetime of lithium ion batteries (Babu,2018). Commercial batteries use graphite or carbonated material as an anode material. But carbonaceous materials have severe safety problems from dendritic lithium growth, due to their low operating voltage (Zhang,2013 ; Zhou,2015 ; Goodenough,2010 ; Etacheri,2011 ; Rui,2010 ; Winter,1999). Among all anode materials, LTO has been considered as an attractive anode substitute for graphite, because LTO has the ability to insert Li + ions rapidly, excellent cycle reversibility,

and good stability (Zhou,2015 ; Guo,2012; Zhang,2013 ; Yan,2014). But pure LTO has the disadvantages of electronic conductivity and a low diffusion coefficient of lithium, resulting in a decrease in the ability of lithium ion batteries (L.Zhao,2011 ; B.Li, 2012 ; G.-N Zhu, 2011 ; G.-N Zhu, 2011). One effective method to overcome this problem is to add (doping) with metal ions in the position of Li or Ti, or replace oxygen with nonmetal ions (Chen, 2018).

In previous studies successfully synthesized LTO compounds doped with Br using a solid state reaction. Br which is doped to LTO compounds shows an excellent discharge capacity of 172 mAhg<sup>-1</sup> at 0.5 C, which is very close to its theoretical capacity (175 mAhg<sup>-1</sup>) (Y.Qi, 2009). Other researchers adopted a similar method for synthesizing Cl-doped LTO compounds (Y.Huang, 2012). Doping LTO with F<sup>-</sup> with a solid state reaction was successfully synthesized and showed an increase in electrochemical performance. However, the performance of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12-x</sub>F<sub>x</sub> rate is not satisfactory and its capacity is only 71.6 mAhg<sup>-1</sup> at the highest current density of 1.7 Ag<sup>-1</sup> (Z.Zhao, 2013).

In this research the synthesis of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> will be carried out with the addition (doping) of F<sup>-</sup>, then coated with carbon. The synthesis process of LTO doping F<sup>-</sup> by using the solid state reaction method. The carbon coating process is carried out by carbonization techniques using acetylene and argon gas. Variations used in this study are the addition (doping) of F<sup>-</sup> and calcination temperature. The variations used are expected to improve the performance of lithium ion batteries

## **2. Experimental**

### **2.1. Materials Preparation**

Li<sub>4</sub>Ti<sub>5</sub>O<sub>12-x</sub>, F<sub>x</sub>/C is made by mixing Li<sub>2</sub>CO<sub>3</sub> and TiO<sub>2</sub> precursors that have been calculated stoichiometry, then added with LiF. The first thing to do for synthesis is to clean all equipment that will be used for research so that it is not contaminated. The mass of each powder was weighed based on the variation used, namely 1 mole of LTO and mole variation of F doping (x = 0, 0.1, 0.15, 0.2). The weighed powder is then put into a ball mill and added alcohol (99%) as a solvent.

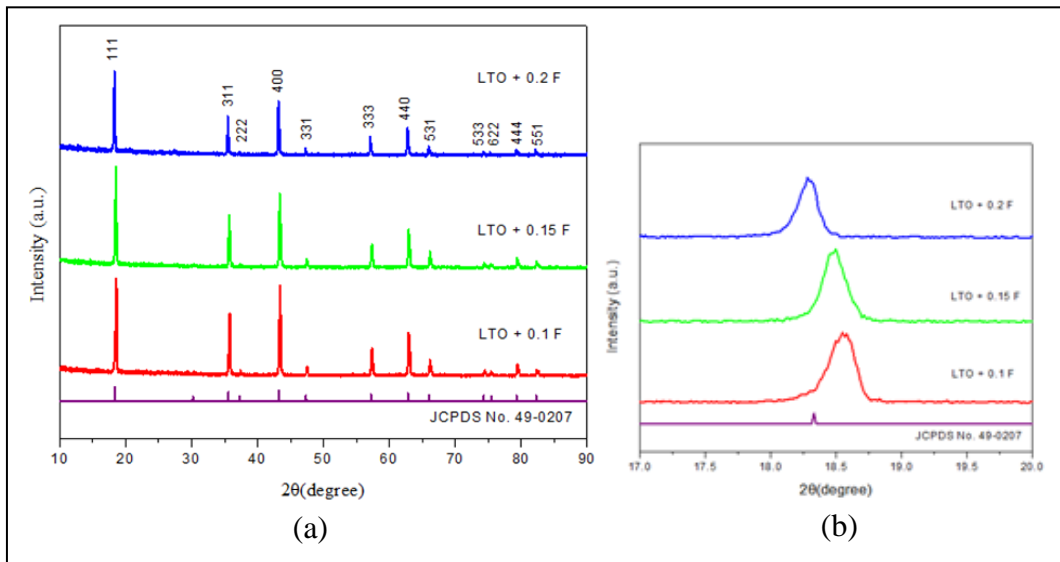
Samples were synthesized using the solid state reaction method using low temperature ball milling equipped with zirconia balls at a speed of 600 rpm for 6 hours. After the ball grinding process is carried out, the material is placed in an alumina glass and then calcined at 700°C, 750°C and 800°C for each doping variation. After the calcination process, the precursor material is coated with carbon. Material is placed in the furnace, then the furnace is flowed with acetylene and argon gas simultaneously under vacuum. Furnace settings for each calcination temperature variation, with a holding time of 1 hour so that the material is fully coated. Active ingredients are ready to use.

### **2.2. Materials characterization**

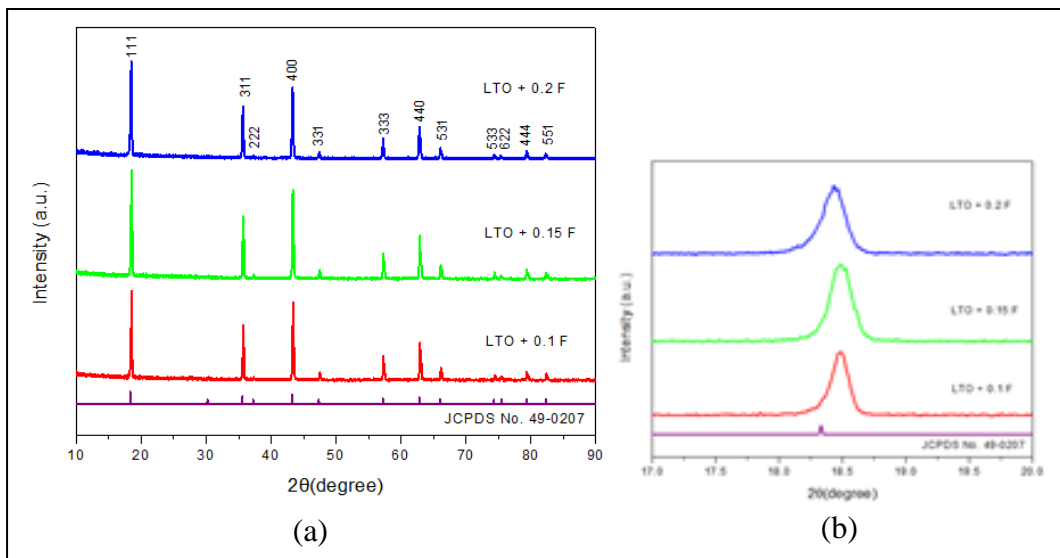
X-ray diffraction (XRD) measurements were carried out using PANalytical with Cu K $\alpha$  radiation ( $\lambda=15.4178$  nm) with a range of  $2\theta$  around 10° to 90° at room temperature. XRD testing was performed to determine the characteristics of the LTO crystal structure. Then a Scanning Electron Microscopy (SEM) test was performed using FEI INSPECT S50 to observe the morphology of the sample powder in the presence of variations in calcination temperature and doping Fluorine.

## **3. Result and Discussion**

Figure 1a and Figure 2a show the XRD pattern of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> with doping F variations of 0.1, 0.15 and 0.2 moles calcined at temperatures of 700°C and 750°C. The XRD pattern obtained shows that the diffraction peaks have formed at an angle position of  $2\theta$  around 18°, 35°, 43°, 47°, 57°, 63°, 66°, 74°, 75°, 79° and 82°. The fields formed at the  $2\theta$  corner position are (111), (311), (222), (400), (331), (333), (440), (531), (533), (622), (444) and (551). The XRD chart peaks are then matched with the JCPDS Card to determine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> compatibility. The graph on each variation shows the main peak of the cubic spinel LTO according to JCPDS card No.49-0207. Figure 1a and Figure 2a also show that no other impurities have formed in the LTO sample.



**Fig. 1.** (a) XRD LTO pattern with doping variation F and (b) Peak shift with variation in addition of doping F at 700°C.

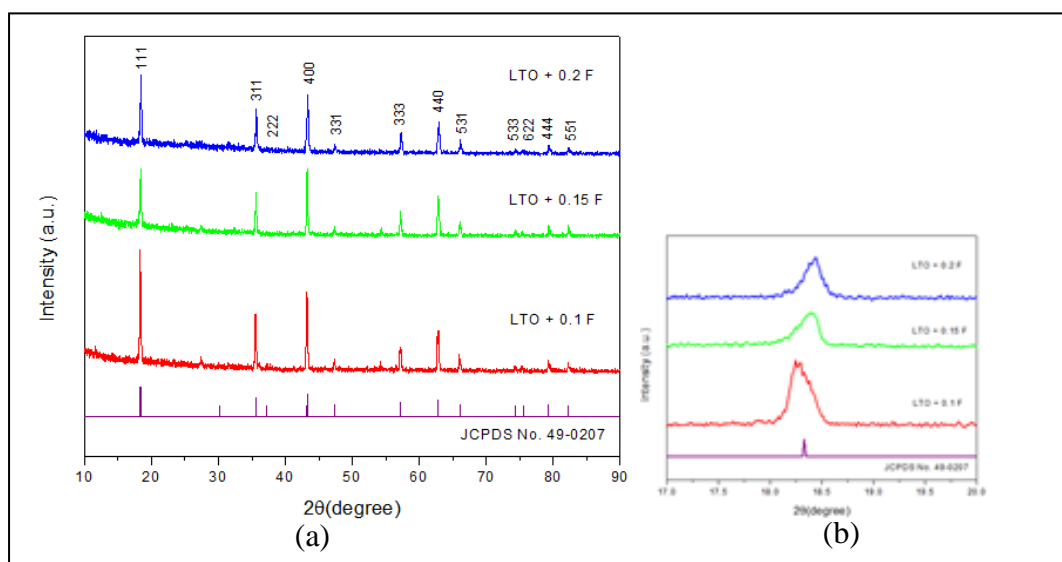


**Fig. 2.** (a) XRD LTO pattern with doping variation F and (b) Peak shift with variations in addition of doping F at temperatures of 750°C.

Figure 1b and Figure 2b are observations on plane (111) which is one of the highest peaks of LTO with an angle position of  $2\theta$  spanning 17-20°. The addition of F has been successfully done substitutionally on LTO material. Fluorine has been inserted into the LTO crystal structure without causing changes in the characteristics of the crystal structure. The substitutional doping is the process of entering foreign elements into a host material, and then the dopant element replaces some parts/sites of the previous host material. In substitutional doping can maintain the shape of the crystal structure. So that the compounds are doped by substitution, the exact position of the atom is in the crystal lattice. Fluorine successfully diffuses well replacing the existing O position on the LTO. The addition of

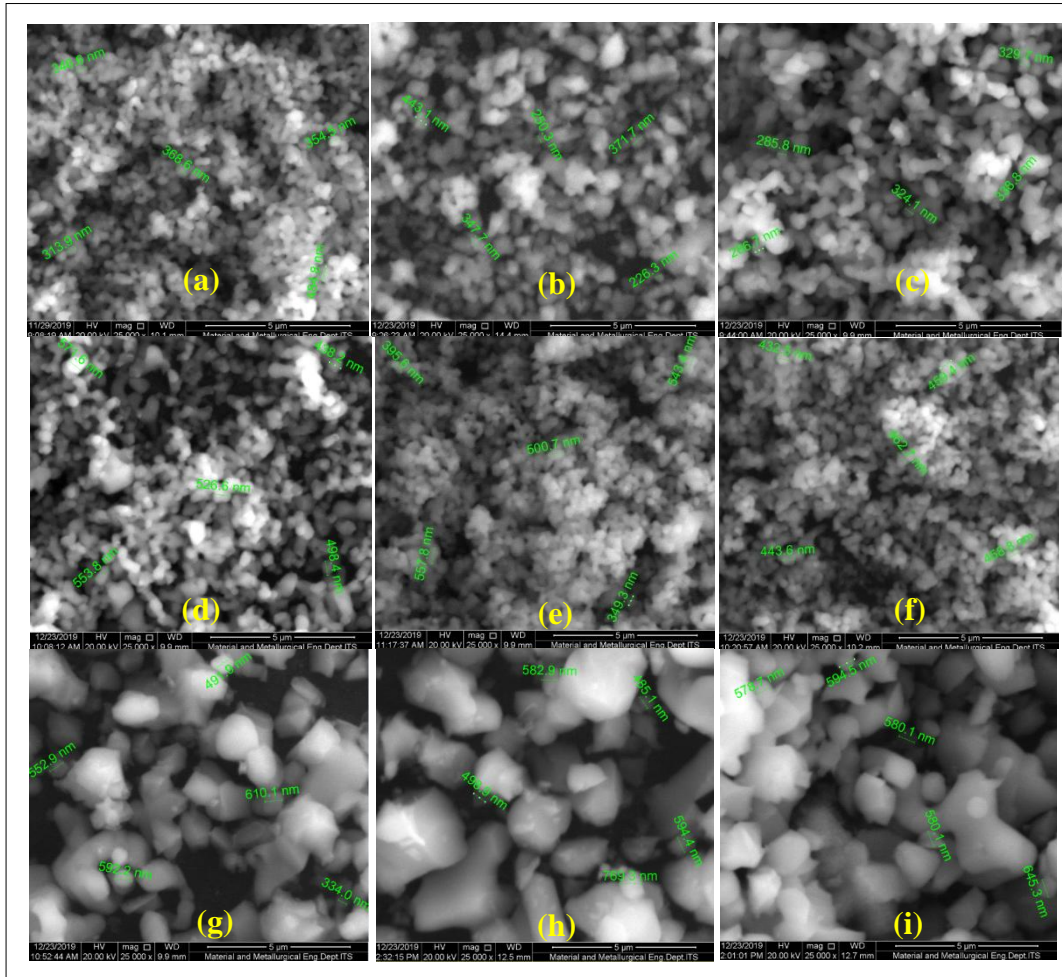
F does not affect the LTO spinel structure that has been synthesized it's just that the addition of the element F is doped through LiF to make the XRD peak change sample shifts towards a lower degree so that it becomes more crystalline (Kamarlzaman, 2012).

Figure 3 LTO with variations of 0.1F, 0.15F and 0.2F calcined at 800°C, there is a new phase in the form of TiO<sub>2</sub> phase where at an angle of 2θ around 28° there is a new peak formed even though the intensity value is small. This peak results from the small amount of rutile TiO<sub>2</sub> present in the lattice that is converted from an unreacted anatase due to lithium evaporation during the calcination process. The rutile phase is a stable TiO<sub>2</sub> phase while the anatase TiO<sub>2</sub> phase is metastable. This phase is an impurity that can arise due to the influence of too high calcination temperature. Temperature can also cause phases that are initially balanced to become unbalanced (Yuan, 2010). Temperature can also cause a decrease in the XRD peak, where at 800°C the peak XRD decreases causing the material not to be too crystalline.



**Fig. 3.** (a) XRD LTO pattern with doping variation F and (b) Peak shift with variation in addition of doping F at 800°C.

Figure 4 shows the SEM results of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel calcined at 700°C, 750°C and 800°C, doping F variations and carbon coated using acetylene, with a magnification of 25.000x. It can be clearly seen that the sample shows block-shaped particles with uniform particle size distribution. Many nanometer-sized grains and in general look homogeneous. This is shown in Figure 4.a through Figure 4.f. Particle size also tends to increase little by little with increasing calcination temperature used. This is seen in Figure 4.g, Figure 4.h and Figure 4.i. With the temperature increased from 700 to 800°C, the particles change to become larger (Zhang, 2013). High temperatures above 800°C cause agglomerated grains to become solid. The solid granules can make the insertion/extraction of Li<sup>+</sup> ions in LTO grains homogeneous. This solid particle is inactive especially during cycles of high current density due to an increase in the diffusion distance of Li<sup>+</sup> ions. Conversely the small and uniform LTO grain size can contribute to improving the electrochemical performance of lithium ion batteries (in cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge) (Babu,2018).



**Fig. 4.** Results of SEM LTO 25,000x magnification for each variation (a) LTO + 0.1F at a temperature of 700°C, (b) LTO + 0.15F at 700°C, (c) LTO + 0.2F at 700°C, (d) LTO + 0.1F at 750°C, (e) LTO + 0.15F at 750°C, (f) LTO + 0.2F at 750°C, (g) LTO + 0.1F at 800°C, (h) LTO + 0.15F at 800°C and (i) LTO + 0.2F at 800°C.

To find out the particle size values from the SEM results above are shown in the following Table 1. Table 1 show the particle size of each variation of LTO/C. Determination of particle size is done at five points from SEM results of magnification of 25,000x, then averaged to get a particle size value with a standard deviation value. This is done in order to know the size and distribution of the particles in one interpretation, homogeneous or not. At a temperature of 700°C with a doping of 0.1 F obtained an average particle size value of 369.68 nm. Then the F level added 0.15 moles, obtained a particle size of 327.82 nm. Element F is added to 0.2 moles obtained with a particle size of 313.02 nm. At this temperature with the addition moles of F, the greater the doped F element, the smaller the particle size. The same thing happened at temperatures of 750°C. At a temperature of 750°C with the addition of 0.1 F obtained an average particle size of 517.72 nm. 0.15 F doping obtained a particle size of 469.36 nm, and doping 0.2F with a particle size of 451.4 nm. There is no significant difference in particle size from temperatures of 700 and 750°C. However, at a temperature of 800°C, the particle size is getting bigger along with the increase in the amount of doping F used, starting from 0.1F doping with an average particle size value of 514.22 nm, doping 0.15F with a particle size of 586.12 nm and doping 0.2F with a particle size of 595.74 nm. With the tolerance values listed in the

table shows that the smaller the tolerance value, the more accurate. At this temperature variation agglomeration occurs so as to make the particle size not homogeneous.

**Table 1.** Particle size of each LTO/C variation

<b>Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/C</b>	<b>Average Particle Size (nm)</b>	<b>Standard Deviation (nm)</b>
Doping 0.1F; 700°C	369.68	56.84
Doping 0.15F; 700°C	327.82	89.34
Doping 0.2F; 700°C	313.02	25
Doping 0.1F; 750°C	517.72	52.39
Doping 0.15F; 750°C	469.36	92.39
Doping 0.2F; 750°C	451.4	12.89
Doping 0.1F; 800°C	514.22	112.13
Doping 0.15F; 800°C	586.12	113.41
Doping 0.2F; 800°C	595.74	28.45

Factors that cause agglomeration during solid state reaction and calcination temperature difference are due to the very small and irregular particle size (aggregate) so that it has high surface tension and roughness. To reduce these surface stresses, the particles are physically fused together (agglomeration) and interlocking. Due to the heat generated by the calcination temperature, a diffusion surface occurs between the particles causing a sintering effect. Sintering causes an increase in particle size. According to Wang (2009) a higher synthesis temperature of 750°C will produce undesirable (large) particle growth, which is not favorable for electrochemical performance.

#### 4. Conclusions

LTO has been successfully created. LTO with the addition of mole F variations and carbon coating has been successfully synthesized using the solid state method. The results and XRD analysis showed that the addition of F was successfully inserted and did not change the LTO crystal structure. Ion F replaces Ion O by substitution because the size of F ion is slightly smaller than Ion O, resulting in a shift in the XRD peak. The peak of the LTO sample has shifted towards a lower degree, making it more crystalline. SEM test results show that with variations in calcination temperature, LTO which were initially in the form of blocks were homogeneously distributed at temperatures of 700 and 750°C, changing in size to be slightly larger and not homogeneous at 800°C. This happens because LTO has agglomerated so that the particle size is getting bigger.

#### Acknowledgments

This writer would like to thank several parties who have provided support, guidance, and opportunities to the author so that this research can be completed.

#### References

- B. Li, C. Han, Y.-B. He, (2012), 'Facile synthesis of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/C Composite with Super Rate Performance', *Energy Environ Sci*, 5 9595–9602.
- Babu. B. Vikram, Babu. K. Vijaya, Aregai. G. Tewodros, Devi. L. Seeta, Latha. B. Madhavi, Reddi. M. Sushma, Samantha. K. Veeraiah. V, (2018), "Structural and Electrical Properties of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> Anode Material for Lithium-Ion Batteries", *Result in Physics*, Vol. 9, hal. 284 - 289.
- Chen. Yuan, Qian. Chen, Zhang. Pengfei, Zhao. Rongfang, Lu. Junjie, Chen. Ming, (2018), 'Fluoride Doping Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> Nanosheets as Anode Materials for Enhanced Rate Performance of Lithium-Ion Batteries', *Journal of Electroanalytical Chemistry*, Vol. 815, hal. 123-129
- Etacheri V, Marom R, Elazari R, Salitra G, Aurbach D. (2011), *Energy Environ Sci*,4:3243–62.

## MATERIALS RESEARCH COMMUNICATIONS 1(1) (2020) 1-7

Alvalo et. al.

- G.-N. Zhu, H.-J. Liu, J.-H. Zhuang, (2011), 'Carbon-Coated Nano-Sized  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Nanoporous Micro-Sphere as Anode Material for High-Rate Lithium Ion Batteries', *Energy Environ Sci*, 4 4016–4022.
- G.-N. Zhu, Y.-G. Wang, Y.-Y. Xia, (2012), 'Ti-Based Compounds as Anode Materials for Li-Ion Batteries', *Energy Environ. Sci*, 5 6652–6667.
- Goodenough JB, Kim Y. *Chem Mater* 2010; 22:587–603.
- Guo XF, Wang CY, Chen MM, Wang JZ, Zheng JM. J, (2012), *Power Sources*, 214:107.
- Kamarlzaman, N dan Jaafar M, (2012), *Synthesis and Stoichiometric Analysis of a Li-Ion Battery Cathode Material*, Book Chapter, Stoichiometry and Material Science, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia
- L. Zhao, Y.-S. Hu, H. Li, (2011), 'Porous  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  Coated with N-doped Carbon from Ionic Liquids for Li-ion Batteries', *Adv. Mater*, 23 1385–1388.
- Rui XH, Ding N, Liu J, Li C, Chen CH, (2010), *Electrochim Acta*, 55:2384–90.
- Wang, L, Liang, G.C, Ou, X.Q, Zhi, X.K, Zhang, J.P., dan Cui, J.Y, (2009), "Effect of Synthesis Temperature on The Properties of  $\text{LiFePO}_4/\text{C}$  Composites Prepared by Carbothermal Reduction", *Journal of Power Sources* 189, pp 423–428
- Winter M, Besenhard JO, (1999), *Electrochim Acta*, 45: 31–50.
- Y. Huang, Y. Qi, D. Jia, (2012), 'Synthesis and Electrochemical Properties of Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Cl}_x$  Anode Materials for Lithium-Ion Batteries', *J. Solid State Electrochem*, 16, 2011–2016.
- Y. Qi, Y. Huang, D. Jia, (2009), 'Preparation and Characterization of Novel Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$  Anode Materials', *Electrochim. Acta*, 54, 4772–4776.
- Yan Q, Zhao H, Wang J, Wang J, Wang C, Hou X, (2014), *Mater Renew Sustain Energy*, 3:24.
- Yuan. Tao, Yu. Xing, Cai. Rui, Zhou. Yingke, Shao. Zhongping, (2010), 'Synthesis of pristine and carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and their low temperature electrochemical performance', *Power Sources* 195.49997-5004
- Z. Zhao, Y. Xu, M. Ji, H. Zhang, (2013), "Synthesis and electrochemical performance of F doped  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  for lithium-ion batteries", *Electrochim. Acta* 109 645–650.
- Zhang Q, Zhang C, Li B, Jiang D, Kang S, Li X, Wang Y, (2013), *Electrochim Acta*, 107:139–46.
- Zhang QY, Zhang CL, Li B, Kang SF, Li X, Wang YG, (2013), *Electrochim Acta*, 98:146.
- Zhang. Zhenwei, Cao. Liyun, Huang. Jianfeng, Wang. Dunqiang, Meng. Yan, Cai. Yingjun, (2013), 'Temperature Effect on Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as Anode Materials for Lithium Ion Batteries', *Electrochimica Acta* 88, 443-446
- Zhou TP, Feng XY, Guo X, Wu WW, Cheng S, Xiang HF, (2015), *Electrochim Acta*, 174:369–75.