



EFFECT OF CARBON COATING ON ELECTROCHEMICAL PERFORMANCES OF $\text{LiTi}_2(\text{PO}_4)_3$ AS ANODE FOR AQUEOUS ELECTROLYTE LITHIUM ION BATTERY

Lukman Noerochim, Zeddy Argasani and Diah Susanti

Department of Materials and Metallurgical Engineering, Faculty of Industrial Technology Sepuluh Nopember

Institute of Technology Surabaya, Indonesia

E-Mail: lukman@mat-eng.its.ac.id

ABSTRACT

One of the renewable energy storage systems that are widely used today is the rechargeable lithium-ion battery. There are four main components in the rechargeable lithium-ion battery, one of which is anode. In this research, $\text{LiTi}_2(\text{PO}_4)_3$ with nasicon-type crystal structure is introduced as a candidate for anode material for aqueous electrolyte lithium ion battery. Conductive coating process is applied to improve the conductivity of $\text{LiTi}_2(\text{PO}_4)_3$ by heating sucrose at 600°C for 3 hrs in an argon gas to form carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ ($\text{LiTi}_2(\text{PO}_4)_3/\text{C}$). The content of carbon in $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ is measured as much as 8%, 13%, and 17.2% wt. CV results show that the addition of carbon can improve the stability, electronic conductivity, and specific capacity $\text{LiTi}_2(\text{PO}_4)_3$. In the charge-discharge results, $\text{LiTi}_2(\text{PO}_4)_3$ with 8% of carbon enhance the intercalation lithium ion with the highest charge capacity of 45.9 mAh/g after 100 cyclic. Based on all the results, $\text{LiTi}_2(\text{PO}_4)_3$ could be the potential candidate as anode for aqueous electrolyte lithium ion batteries.

Keywords: carbon coating, $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$, anode, aqueous electrolyte, lithium ion battery.

INTRODUCTION

In this new era, clean and renewable energy storage devices have become high demand of both the power industry and research development. Fossil fuels have been and still are the major energy source, but society's current individual mobility behavior is creating a plethora of looming problems, such as fossil carbon intensity and the concomitant consequences regarding fossil resource supplies and emissions of pollutants such as nitrogen oxides (NO_x), sulphur dioxide (SO₂), and particulate matter [1]. One of the renewable energy storage system is rechargeable lithium-ion battery. Rechargeable lithium-ion battery involves the insertion/extraction of lithium ions back and forth from/to the host matrix (electrode material) during charge-discharge process. The process of insertion/ extraction of lithium occurs in the electrolyte which flows back and forth accompanied by oxidation-reduction reaction within the host matrix assisted with the flow of electrons through an external circuit [2].

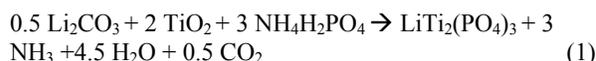
$\text{LiTi}_2(\text{PO}_4)_3$ is the most promising anode material in aqueous electrolyte lithium-ion battery. $\text{LiTi}_2(\text{PO}_4)_3$ with NASICON-type rhombohedral crystal structure has a good operating voltage in the aqueous electrolyte (2.5 V vs Li/Li⁺, -0.5 V vs NHE)[3] and high theoretical capacity (~138 mAh/g). However, one of shortcomings of $\text{LiTi}_2(\text{PO}_4)_3$ is low electric conductivity ($2-3 \cdot 10^{-3} \text{ Scm}^{-1}$) [4]. Moreover, in aqueous electrolyte, the operating voltage window of $\text{LiTi}_2(\text{PO}_4)_3$ is close the hydrogen evolution peaks (-0.7 V) [5]. The hydrogen evolution can block the process of intercalation and release of Li⁺ ions due to the potential spill over effects. In this research,

carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ with various compositions of carbon were synthesized by solid-state reaction process and all prepared samples were be studied systematically.

EXPERIMENTAL PROCEDURES

Synthesis of $\text{LiTi}_2(\text{PO}_4)_3$

In the process of synthesis of $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), stoichiometric amount of Li_2CO_3 , TiO_2 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed in distilled water and homogenized using a mortar and pestle at room temperature. The precursor was then calcined at a temperature of 900°C for 12 hour using a muffle furnace [6]. All process in this work using conventional solid state reaction method by mixing the three ingredients are based on stoichiometric calculations. These reactions can be explained by the following:



Coating Carbon Process

The coating process $\text{LiTi}_2(\text{PO}_4)_3$ using sucrose as a carbon source by using variations of grams of sucrose 5.25 g (LTP/C1), 10.5 g (LTP/C2), and 15.75 gr (LTP/C3), for 12.26 gr $\text{LiTi}_2(\text{PO}_4)_3$. Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) dissolved in distilled water first, then as-prepared $\text{LiTi}_2(\text{PO}_4)_3$ was mixed with sucrose solution using a hot plate and magnetic stirrer until homogeneous. After homogenization process, the mixture was heated using a horizontal furnace by flowing argon gas with temperatures of 600°C for 3 hours.



Structure Characterization and Electrochemical Measurement

The phase of the prepared sample was examined by X-ray diffraction (XRD Philips Xpert with a $\text{CuK}\alpha$ radiation), the morphology of particles were observed by scanning electron microscopy (SEM Philips FEI Inspect S-50), and the carbon content in the sample was measured with a LECO analyzer type IR-212.

To test the electrochemical performance, sample was respectively mixed with acetylene black (AB), polyvinylidene difluoride (PVDF) in agate mortar in a weight ratio of 85: 10: 5. Once homogeneous, the mixtures were added with N-Methyl-2-pyrrolidone (NMP) as a solvent to form slurry. The slurry was uniformly pasted onto pieces of stainless steel mesh foil with an area of 1 cm^2 . The prepared electrodes were dried with a temperature of 80°C for 12 hours and pressed under a pressure of approximately 3000 kg cm^{-2} for 10s. For the galvanostatic charge/discharge testing and cyclic voltammetry testing, Li_2SO_4 aqueous electrolyte was used with pH around 13. The electrolyte was mixture of 1 M Li_2SO_4 and 0.1 M LiOH dissolved in distilled water. CV test was performed in 1 M aqueous electrolyte Li_2SO_4 pH 13 with the platinum electrode as the counter electrode and SCE as reference electrode.

The galvanostatic charge-discharge experiment was conducted using a battery testing system (BTS 5V/1 mA, Neware technology limited corporation, China) from 0.1 to 1.6 V at room temperature. Cyclic voltammetry (CV) was performed at scan rates of $0.05\text{-}0.5 \text{ mV s}^{-1}$ from -1.0 to 1 V on a Metrohm AutoLab PGSTAT type 302N with SCE as reference electrode and platinum as the counter electrode.

RESULT AND DISCUSSIONS

The carbon content of carbon coated $\text{LiTi}_2(\text{PO}_4)_3$ was obtained 8% for LTP/C1, 13% for LTP/C2 and 17.2% for LTP/C3, respectively. Figure-1 shows the XRD pattern of $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) and $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$. All the reflection peaks in all samples could be indexed on the basis of a rhombohedral $\text{LiTi}_2(\text{PO}_4)_3$ structure with a space group of R3c (JCPDS 35-0754) without any detectable impurity phases. Nevertheless, no detectable reflections corresponding to carbon could be seen in the XRD pattern of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ composite due to its low content and amorphous structure.

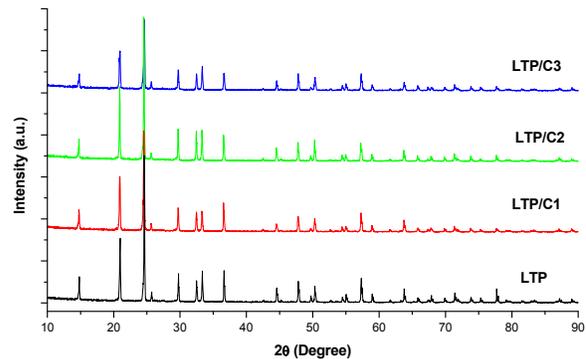


Figure-1. XRD patterns of $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), LTP/C1, LTP/C2 and LTP/C3, respectively.

XRD patterns shown in Figure 5 show the highest peaks be found at an angle $2\theta = 20.97^\circ$, 24.6° , and 29.76° which indicates the direction of the field (1 0 4), (1 1 3) and (0 2 4). The XRD pattern showed that the crystal structure $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ did not change after calcined at 600°C for 3 hours for carbon coating process. However, all the peaks of carbon-coated LTP show slightly low intensity than the pristine of LTP. It could be the carbon coated of LTP hindered the reflection of XRD.

Figure-2 shows the SEM images of $\text{LiTi}_2(\text{PO}_4)_3$ and carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$. SEM image of LTP shows relative small size of particles with dimension range $3\text{-}9 \mu\text{m}$ and low agglomeration.

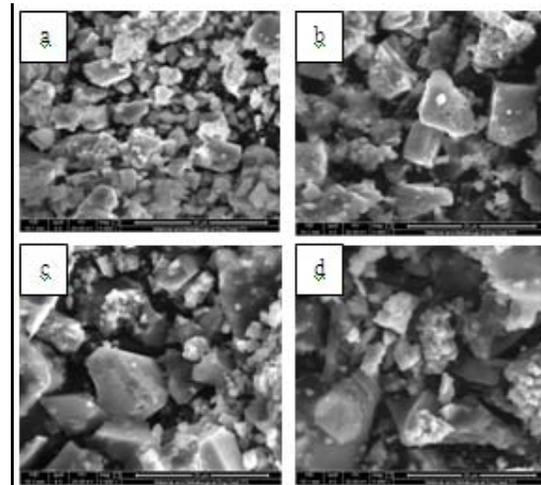


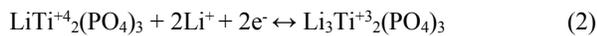
Figure-2. SEM images of (a) LTP, (b) LTP/C1, (c) LTP/C2, and (d) LTP/C3.

SEM images of carbon-coated LTP were observed that the particles $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ tends to form big agglomeration with large particle size in the range of $5\text{-}15 \mu\text{m}$ due to the effect of temperature 600°C for 3 hours when the process of carbon coating. Agglomeration and

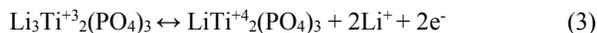


increasing particle size could lead to decreased ionic conductivity.

The CV curves of LTP and carbon-coated LTP in aqueous electrolyte for initial cycle are given in Figure-3. A pair of redox peaks in Figure-3 (a) is observed at 0.22 and 0.48 V (versus SCE) for LTP, indicating only one step of lithium intercalation/de-intercalation into Nasicon structure, in agreement with that previously observed in organic electrolyte. By applying the empirical formula, this rhombohedral Nasicon type crystal structure can accommodate up to 2 mol Li atoms to form $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$ upon discharge. This reduction is reversible and upon charging, the material is oxidized back to $\text{LiTi}_2(\text{PO}_4)_3$. Equation 1 and 2 illustrates the reduction and oxidation (redox) reactions. At the time of discharging process, occur reduction reaction at the $\text{LiTi}_2(\text{PO}_4)_3$, namely:



While charging, occurs the oxidation reaction at the $\text{LiTi}_2(\text{PO}_4)_3$ is:



Storage charge (charging) conducted by the reduction reaction of the Ti values ranging from +4 to be +3, while the discharge (discharging) is performed with the Ti oxidation reactions ranging from +3 to be +4 value [7]. In aqueous electrolyte, must be considered will be the evolution of hydrogen and oxygen evolution at the negative electrode of lithium ion after the entered into and exit from the host during the charging-discharging process due to take place over a potential that exceeds the limits of the ability of aqueous electrolyte itself.

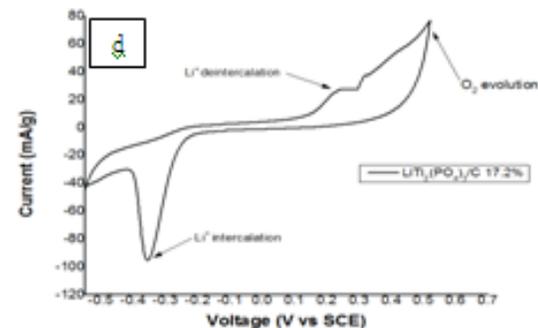
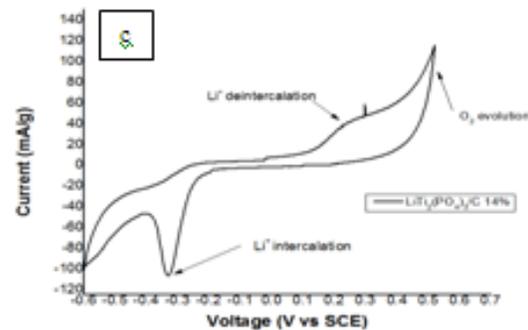
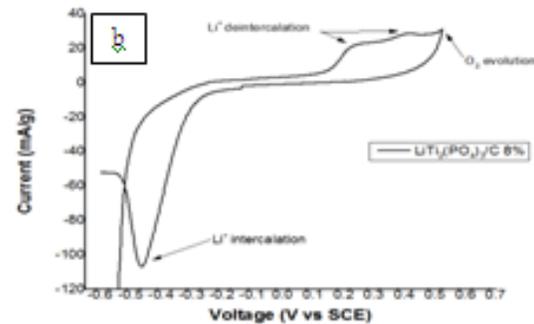
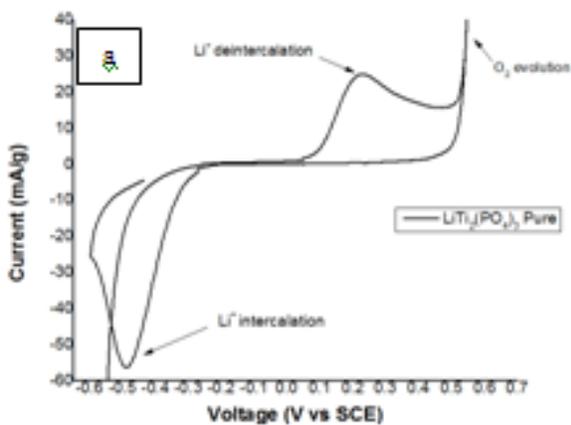


Figure-3. A typical CV curves of LTP and LTP/C at a scan rate 1 mV/s in the Li_2SO_4 pH 13 electrolyte solution (a) LTP), (b) LTP/C1, (c) LTP/C2 and (d) LTP/C3, respectively.

From CV result of LTP in Figure-3 shows two pairs of redox peaks at potential 0.22 and 0.48 V (versus SCE) which indicates that the lithium ions intercalation and de-intercalation occurs in NASICON structure before the occurrence of oxygen evolution at locations above 0.6 V and hydrogen evolution under -1 V. The potential separation between the anodic and cathodic peak (ΔV) of LTP is 0.7 V which indicates that the slow process of electron transfer in the electrolyte solution Li_2SO_4 pH 13. CV curves of carbon-coated $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ in Figure-3 show there are also two oxidation peaks with the potential separation between the anodic and cathodic peak (ΔV) of LTP/C1, LTP/C2 and LTP/C3 are 0.69, 0.58, and 0.57 V



respectively. This indicating that the increasing of carbon content decrease the potential separation between the anodic and cathodic peak that it will improve the ionic conductivity of the material and the rate stability $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ [8].

The electrochemical performance of LTP and carbon-coated of LTP have been evaluated as anode materials by galvanostatic charge/discharge test in full cell battery system using LiFePO_4/C (LFP/C) as cathode and 1 M Li_2SO_4 pH 13 as electrolyte. The initial charge-discharge performances of the cells with current density of 0.5 C and a potential range of 0-1.4 V are compared as shown in Figure-4. The specific capacity is obtained for LTP exhibiting a discharge capacity of 12.32 mAh/g as shown in Figure-4 (a) while LTP/C samples show higher discharge capacity of 45.9 mAh/g, 31.81 mAh/g, and 17.72 mAh/g, respectively. The high performance of LTP/C samples could be a sufficient carbon coating that enhanced the electronic conductivity of LTP.

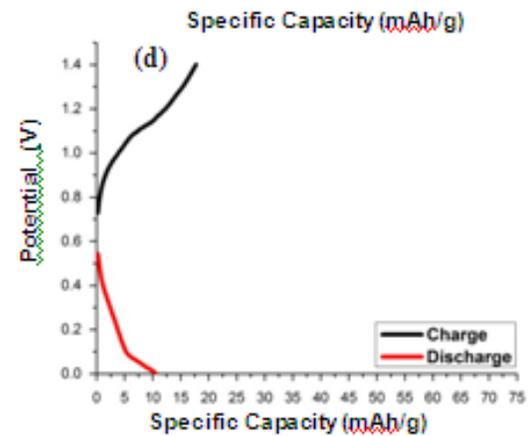
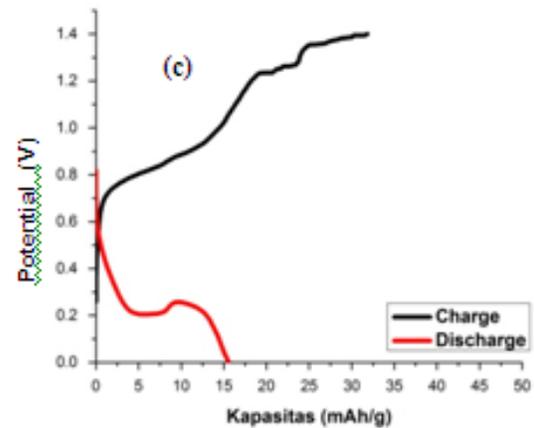
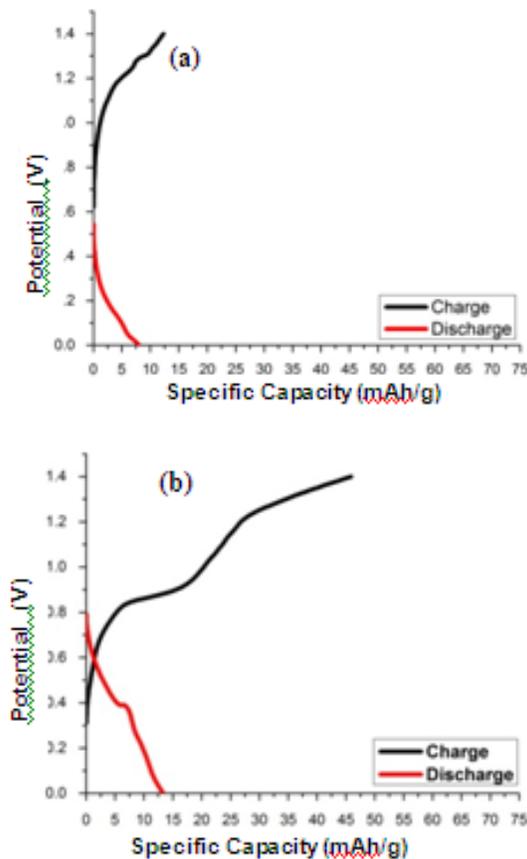


Figure-4. Typical initial curves charge/discharge cell of LTP in aqueous electrolyte 1 M Li_2SO_4 with pH 13 at 0.5 C: (a) LTP, (b) LTP/C1, (c) LTP/C2, and (d) LTP/C3.

The charge-discharge results indicated that the discharge capacity of LTP and LTP/C samples is highly influenced not only on the content of carbon, but also the particle size, and the occurrence of agglomeration. The more the carbon content, the ionic conductivity decreases due to enlarged grain size particles and agglomeration which consequently blocked a way intercalation/de-intercalation Li ion. But with increasing addition carbon content also increase ionic conductivity and increase capacity compared to that without carbon coating. In the charge-discharge test, capacity results obtained are closely related to the results of CV, morphology, structure, and chemical composition of the material $\text{LiTi}_2(\text{PO}_4)_3$.

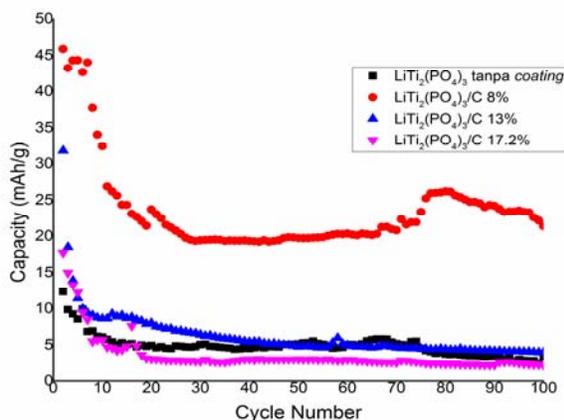


Figure-5. Cycling performance of LTP and LTP/C samples in aqueous electrolyte 1 M Li_2SO_4 with pH 13 at at 0.5 C with range 0-1.4 V.

The cycling performance $\text{LiTi}_2(\text{PO}_4)_3$ and $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ in the 1M Li_2SO_4 pH 13 aqueous electrolyte at 0.5 C with a range of 0-1.4 V is shown in Figure-5. Figure-5 shows an initial capacity of LTP is 12.32 mAh/g and decrease drastically of 3.3 mAh/g after 100 cycles, with the capacity lost 73.13%. LTP/C1 shows an initial capacity of 45.9 mAh/g and the capacity when at 100 cycle is 21.39 mAh/g, indicating 53.4% capacity loss. LTP/C2 shows an initial capacity of 31.8 mAh/g and the capacity when at 100 cycle is 3.99 mAh/g, indicating the capacity lost 87.45%. And LTP/C3 shows an initial capacity of 17.72 mAh/g and the capacity when at 100 cycle is 2.19 mAh/g, indicating the capacity lost 87.61%.

Figure-5 shows typical curve of LTP/C with 8% carbon coating has the highest capacity as compared to $\text{LiTi}_2(\text{PO}_4)_3$ without coating, $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ 13%, and $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ 17.2% indicating the percentage of carbon-coating has enhanced ionic conductivity and improved the lithium ion during intercalation / de-intercalation process. While $\text{LiTi}_2(\text{PO}_4)_3$ without the coating has a low capacity due to the low ionic conductivity properties of LTP. Therefore, the appropriate amount of carbon coating increases the capacity and stability of LTP due to the enhancement of the ionic conductivity.

CONCLUSIONS

$\text{LiTi}_2(\text{PO}_4)_3$ powder can be synthesized by solid-state method. $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ was prepared by carbon coating using sucrose as a carbon source which is calcined at a temperature of 600°C for 3 hrs in argon atmosphere. The as-prepared LTP/C obtained the amount of carbon of 8%, 13%, and 17.2%. XRD results of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ material show that the addition of carbon does not affect the crystal structure of LTP. SEM results show that the addition of carbon increases the grain size of particles and leads to agglomeration. The CV test depicted that the addition of carbon increases the ionic conductivity, and

stability. Galvanostatic charge-discharge results show that LTP/C1 in the 1M Li_2SO_4 pH 13 aqueous electrolytes has the highest specific discharge capacity of 45.9 mAh/g with 53.4% capacity loss after 100 cyclic.

REFERENCES

- [1] Liu, D., dan Cao, G. 2010. Energy Environ. Sci., 3, 1218.
- [2] Nazri, G.A., and Pisoia, G. 2009. Lithium Batteries: Science and Technology, Springer, Miami.
- [3] Luo, Jia-Yan and Xia, Yong-Yao. 2007. "Aqueous Lithium-Ion Battery $\text{LiTi}_2(\text{PO}_4)_3/\text{LiMn}_2\text{O}_4$ with High Power and Densities as well as Superior Cycling Stability". Advanced Functional Materials. (17): 3877-3884.
- [4] Kosova, N.V., Osintsev, D.I., Uvarov, N.F., and Devyatkina, E.T. 2005. "Lithium Titanium Phosphate as Cathode, Anode.
- [5] Shivashankaraiah, R.B., Manjunatha, H., Mahesh, K.C., 2012. "Electrochemical Characterization of $\text{LiTi}_2(\text{PO}_4)_3$ as Anode Material for Aqueous Rechargeable Lithium Battery". Journal of the Electrochemical Society. (159): A1074-A1082.
- [6] Cui, Yongli., Hao, Yuwan., Bao, Wenjing., Shi, Yueli., Zhuang, Quanchao., and Qiang, Yinghui. 2013. "Synthesis and Electrochemical Behavior of $\text{LiTi}_2(\text{PO}_4)_3$ as Anode Materials for Aqueous Rechargeable Lithium Batteries". Journal of the Electrochemical Society. 160: A53-A59.
- [7] Arun, N., Aravindan, V., Ling, W., and Madhavi, S. 2014. "Carbon coated $\text{LiTi}_2(\text{PO}_4)_3$ as new insertion anode for aqueous Na-ion batteries". Journal of Alloys and Compound. 603: 48-51.
- [8] Liu, Li., Zhou, Meng., Wang, Guo., Guo, Haipeng., Tian, Fanghua., and Wang, X. 2012. "Synthesis and Characterization of $\text{LiTi}_2(\text{PO}_4)_3/\text{C}$ nanocomposite as lithium intercalation electrode materials ". Electrochimica Acta, 7: 136-141.