ABSTRACT

Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ has been synthesized as anode material for lithium-ion batteries parallel with Li$_4$Ti$_5$O$_{12}$ anode material using solid state reaction method in an air atmosphere. LiOH.H$_2$O, TiO$_2$, and waste chicken eggshells in the form of CaCO$_3$ were chosen as sources of Li, Ti, and Ca respectively and prepared using stoichiometric. The phase structure, morphology, and electrochemical impedance of as-prepared samples were characterized using XRD, SEM, and EIS. The XRD characterization revealed that in Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample, all amount of dopant had entered the lattice structure of Li$_4$Ti$_5$O$_{12}$. The EDX image also detect the existence of Ca in the structure of Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$. The EIS characterization revealed that the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample had lower electrochemical impedance compared to the Li$_4$Ti$_5$O$_{12}$ sample. The diffusion coefficient were obtained by Faraday’s method, and exhibited that the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample (1.46986 x 10$^{-12}$ cm$^2$/s) had higher ionic conductivity than the Li$_4$Ti$_5$O$_{12}$ sample (4.40995 x 10$^{-16}$ cm$^2$/s). According to the cycle performance test, the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample also had higher charge-discharge capacity and stability compared to the Li$_4$Ti$_5$O$_{12}$ sample.

Keywords: Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$; Anode Material; Lithium-ion Batteries; Waste Chicken Eggshell; Ionic Conductivity;

1. INTRODUCTION

Nowadays, lithium-ion batteries have been widely used in several technology applications, such as Electric Vehicle (EV) and Hybrid Electric Vehicle (HEV) because of its advantages. In terms of life cycle and redox potential, LiB have excellency in both characteristics compared to another batteries such as NiCd and NiMH. [1] In fact, the development of Li-ion batteries in its power and energy density is the key of successful application. [2]

However, the characteristics of lithium-ion batteries depend on its material components, including the anode. [3] One of the most developed anode material for lithium ion batteries is lithium titanium oxide (LTO). The researches take place in improving specific capacity and ionic conductivity. Several researches have been done including carbon coating and doping with Mg,
Nd, Gd, and Al atoms. [4-15] These treatment is believed could improve the structure of LTO and enhance both specific capacity and ionic conductivity.

Lithium titanium oxide (LTO) is a material with cubic spinel structure and some spaces in the lattice which give possibility of lithium ion to intercalate as shown in figure 1. This material is also well known as zero strain material, as the change of lattice parameter in its structure is almost negligible when lithium ions intercalate. The unit cell of Li$_4$Ti$_5$O$_{12}$ is built of 8 unit formula of Li$_{8a}$[Li$_{1/3}$Ti$_{5/3}$]$_{16c}$O$_{4e}$ and the 16d sites is occupied by 1/6 Li atoms and 5/6 Ti atoms. [9] The only change is migration of lithium ion from 8a tetrahedral lattice into 16c octahedral lattice which forms Li$_7$Ti$_5$O$_{12}$. (Andreas Laumann, 2010) However, LTO has lower theoretical capacity, 175 mAh/g, and higher redox potential, 1.55 V Li$^+$/Li, compared to graphite anodes (372 mAh/g and ~100 mV Li$^+$/Li). This have been an advantage of the material compared to others. (Qianyu, 2015)

![Figure 1](image1.png)

**Figure 1** The cubic spinel structure of lithium titanium oxide [2]

However, chicken eggshells is known as the most unutilized kitchen waste which contain rich amount of CaCO$_3$. The CaCO$_3$ is believed could be a good Ca source for the dopant of LTO. The outer membrane of the eggshells can be taken and utilized for a natural CaCO$_3$ which is also believed having finer structure than the commercial one. [16]

2. EXPERIMENT

Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ were both synthesized by a simple solid state reaction method using stoichiometric calculation which the formula is shown in equation 1. LiOH.H$_2$O and TiO$_2$ were chosen as Li and Ti sources, respectively. In this experiment, eggshell powder in the form of CaCO$_3$ was utilized as Ca source. Waste eggshell was cleaned, ground, and dried at 100$^\circ$C for 12h to get nature-based CaCO$_3$. Raw materials were mixed and pounded in a bowl for 8 h at room temperature. Powders were calcined at 350$^\circ$C for 1 h, and 700$^\circ$C for 2 h, before it was sintered at 800$^\circ$C for 4 h, with temperature rate of 5$^\circ$C per minute. Both processes are done in a muffle furnace KSL-1700X.

$$3.9\text{LiOH.H}_2\text{O} + \text{TiO}_2 + 0.1\text{CaCO}_3 \rightarrow \text{Li}_{3.9}\text{Ca}_{0.1}\text{Ti}_5\text{O}_{12}$$ (1)

X-ray Diffractometer(XRD) was used in characterizing powders crystalline phase and structure of waste eggshells, Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ powders with CuK$\alpha$ radiation. The XRD
identified the phase with scan rate of 8.00 deg/min and scan range of 10.00 - 90.00 deg. Besides, SEM-EDX was used in characterizing morphology of Li_{3.9}Ca_{0.1}Ti_{5}O_{12} and detecting the particle distribution of Ca in its structure.

Battery samples were prepared by mixing active materials with Acetylene Black (AB) as conductive material, and Polyvinylidene Flouride (PVDF) as binder in 80 : 10 : 10 weight ratio in DMAC solution. The mixtures were spread onto Cu-foil in Automatic Thick Film Coating and dried at 81°C in a drying box for 3 hours. Battery cells were prepared by assembling coin-type samples (d = 16mm) as working electrodes and coin-type Li-metal (d = 16mm) as reference electrode, while Celgard polymers were used as separator in a glove box which both moisture and oxygen content were at least condition and Ar gas was used as inert gas.

Electrochemical Impedance Spectroscopy was used in characterizing the electrochemical impedance of the anodes. The output of characterization was used to calculate Warburg coefficient and Diffusion coefficient of the anodes, which could determine the ionic conductivity.

Warburg coefficient was calculated with the following equation,

$$Z_{re} = R_e + R_{ct} + \sigma_w \omega^{-1/2}$$

(2)

Where, $Z_{re}$ is total impedance, $R_e$ is electrolyte resistance, $R_{ct}$ is charge transfer resistance, $\sigma_w$ is Warburg coefficient, and $\omega$ is angular frequency.

Diffusion coefficient which determine the ionic conductivity of anodes was calculated with the following equation,

$$D = \frac{R^2T^2}{2n^4A^2F^2\sigma^2C^2}$$

(3)

where, $R$ is gass constant, 8.314 J/mol.K, $T$ is absolute temperature, 298.15 K, $F$ is Faraday constant, 96500 C/mol, $A$ is area of samples, 0.000201 m², $C$ is lithium ion concentration, 4370 mol/m³, $n$ is the number of electron transfered during lithium ion intercalation, 3 for Li_{4}Ti_{5}O_{12}, and $\sigma$ Warburg coefficient (Ω.m².s⁻¹/²).

### 3. RESULT AND DISCUSSION

The XRD patterns of waste eggshell is shown by figure 2 in the form of CaCO₃ in accordance with the standard diffraction pattern of CaCO₃ which [104] peak appeared as primary peak. [104] peak revealed that waste eggshell contains high amount of CaCO₃, indicates that waste eggshells as nature-based CaCO₃ can be used as source of Ca.
Figure 2 The XRD pattern of waste eggshell in the form of CaCO$_3$

The XRD patterns of Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ is shown by figure 3. In accordance with the standard diffraction pattern of LTO, both samples can be indexed to a cubic spinel structure with the space group of Fd-3m. The XRD peak also revealed that CaCO$_3$ phase was not detected in Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$, indicates that Ca$^{2+}$ ions have successfully entered into the 8a lattice structure of LTO and substitutes the amount Li ion which can be noted as Li$_{0.13}$Ca$_{0.03}(8a)[Li_{1/3}Ti_{5/3}]_{16c}O_{4(32e)}$. The morphology of Ca distribution was also detected in SEM-EDX images which is shown in figure 4. This evidence has proven that nature-based CaCO$_3$ is efficient to be used as a source of Ca as the dopant of LTO.
Figure 3 XRD pattern of Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample

Figure 4 EDX mappings of Calcium (atomic % = 0.2) in the structure of Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$
The lattice parameter and composition of both samples are shown in table 1 which can be seen that there is no significant difference between Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$. This result indicates that small Ca doping will not effect on the lattice parameter of LTO.

Table 1. Lattice parameter and composition of Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample

| Sample           | a (Å)     | % LTO  | % TiO$_2$ rutil |
|------------------|-----------|--------|-----------------|
| Li$_4$Ti$_5$O$_{12}$ | 8.3596(8) | 97.2(16) | 2.8(4)         |
| Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ | 8.3573(9) | 95.1(16) | 4.9(6)         |

Figure 5: Electrochemical impedance of Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$
Figure 6 shows the plot of $\omega^{-1/2}$ and $Z'$. Figure 5 shows the electrochemical impedance of Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$. It can be seen that Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ has lower electrochemical impedance, indicating that it will have higher ionic conductivity. The slope of the graph is called as Warburg coefficient. The diffusion coefficient was then calculated after knowing the Warburg coefficient.

Table 2. The Warburg coefficient and the diffusion coefficient of Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$

| Sample               | $\sigma$ (Ω.m$^2$.s$^{-1/2}$) | $D$ (cm$^2$/s) |
|----------------------|--------------------------------|----------------|
| Li$_4$Ti$_5$O$_{12}$  | 113.300                        | 4.40995 $\times$ 10$^{-16}$ |
| Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ | 16.529                       | 2.07205 $\times$ 10$^{-14}$ |

From table 2, it can be seen that Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ has a higher diffusion coefficient than Li$_4$Ti$_5$O$_{12}$ sample, with the value of 2.07205 $\times$ 10$^{-14}$ cm$^2$/s and 4.40995 $\times$ 10$^{-16}$ cm$^2$/s respectively. It indicates that Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material has an optimum structure to have high ionic conductivity. The higher ionic conductivity indicates the easier lithium ion to intercalate.

A charge-discharge characterization also had been done to determine the electrochemical performance of both samples, cycle rates at 0.2C. Figure 7 shows that the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material has higher charge-discharge capacity, with the value of 158.3 mAh/g and 150 mAh/g respectively, than the Li$_4$Ti$_5$O$_{12}$ anode material, with the value of 142.7 mAh/g and 127 mAh/g respectively. This has proven that the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material has also more optimum structure to receive charges than the Li$_4$Ti$_5$O$_{12}$ anode material.
Figure 7 Charge-discharge (at 0.2C) characterization shows the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material has higher charge-discharge capacity than the Li$_4$Ti$_5$O$_{12}$ anode material.

In addition to that, figure 8 shows cycle performance of both anode material with cycle rate of 2C for 60 cycles, which LTO represents the Li$_4$Ti$_5$O$_{12}$ anode material, while LCaTO represents the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material. An outstanding performance has been exhibited by the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material which still has charge-discharge capacity of 104.1 mAh/g and 49.3mAh/g respectively after 61 cycle. These values are still higher than the Li$_4$Ti$_5$O$_{12}$ anode material charge-discharge capacity drop, with the value of 76.2 mAh/g and 30.3 mAh/g. The Coloumbic efficiency stabilizes at 100% after 61 cycle, which is due to the excellency of Li$^+$ intercalation during charge-discharge process. This stability of cycle can be donated to the enhancement of ionic conductivity of the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material.
4. CONCLUSION

Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ had been synthesized parallel with Li$_4$Ti$_5$O$_{12}$ using simple solid state method. Waste chicken eggshell was chosen to be utilized as Ca source. XRD pattern shows that waste chicken eggshells is in the form of CaCO$_3$ and can be utilized as Ca source for the dopant of LTO. XRD and SEM-EDX characterization on Li$_4$Ti$_5$O$_{12}$ and Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ powder shows that both samples match with the standard peak of LTO and Ca had been successfully entered to the structure of LTO and substitutes the amount Li ion which can be noted as Li$_{0.13}$Ca$_{0.03}$[(Li$_{1/3}$Ti$_{5/3}$)$_{16c}$O$_{32e}$] in Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample. EIS characterization shows that Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ has higher diffusion coefficient than Li$_4$Ti$_5$O$_{12}$ sample, with the value of 2.07205 x 10$^{-14}$ cm$^2$/s and 4.40995 x 10$^{-16}$ cm$^2$/s respectively. The charge-discharge test exhibits that Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample (158.3 mAh/g and 150 mAh/g) has higher charge-discharge capacity and stability than Li$_4$Ti$_5$O$_{12}$ sample (142.7 mAh/g and 127 mAh/g). According to the cycle performance test, the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ sample also has good stability with charge-discharge capacity of 104.1 mAh/g and 49.3 mAh/g, still higher than Li$_4$Ti$_5$O$_{12}$ sample with charge-discharge capacity of 76.2 mAh/g and 30.3 mAh/g after 61 cycle, indicates that the Li$_{3.9}$Ca$_{0.1}$Ti$_5$O$_{12}$ anode material has high ionic conductivity and good for anode material candidate of lithium-ion battery.

5. ACKNOWLEDGEMENT

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