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Effect of Sintering Temperature on Crystal Structure and Conductivity of the $CaCO_3$-Doped $Li_4Ti_5O_{12}$ Anodes from Blood Clam Shells (*Anadara granosa*)

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ABSTRACT

$CaCO_3$-doped $Li_4Ti_5O_{12}$ was synthesized by solid-state method with sintering temperatures at 750 °C, 800 °C, and 850 °C. The source of $CaCO_3$ was used from blood clam shells (*Anadara granosa*) with a content of 97.67%. The influence of sintering temperature on crystal structure and conductivity of $CaCO_3$-doped $Li_4Ti_5O_{12}$ are extensively studied. XRD results show there is no $CaCO_3$ phase found, which indicates that the doping of $Li_4Ti_5O_{12}$ with $CaCO_3$ has been successful. The smallest crystallite size was obtained at a sintering temperature of 800 °C, which is 46.49 nm, which is beneficial for shortening diffusion length and facilitating the electron and ion transport, causing an increase in anode conductivity. The most optimal conductivity was obtained in samples with a sintering temperature of 800 °C with a conductivity of 2.46 x 10^{-4} S/cm. When the sintering temperature is increased to 850 °C, the particles tend to agglomerate and deteriorate the electrochemical properties.

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I. Introduction

The development of lithium-ion (Li-ion) batteries is an interesting research focus as it is very useful in various applications such as mobile phones, computers, and other electronic devices [1]. Recently, many efforts have been made to improve its application to Hybrid Electric Vehicles (HEV) and effective energy storage systems [2]. The anode is one of the important components that play a role in creating the characteristics of Li-ion batteries [3].

$Li_4Ti_5O_{12}$ (Lithium Titanate Oxide) is a potential material as an anode for Li-ion batteries as it has several advantages over commonly used anode materials such as graphite, including during insertion/extraction of Li^+ ions does not change the structure (zero strain), high operating voltage (1.55 V) ensure safe operation of li-ion batteries and long lifetime [4][5]. However, the poor conductivity of $Li_4Ti_5O_{12}$ (< 10^{-13} S/cm) is a problem that can limit its rate performance [6].

Many methods have been developed to improve the performance of $Li_4Ti_5O_{12}$, including coating with a conductive material and atomic doping such as Ta, N, Br, Ag, Ca, Cu, Zr, and F [7]–[16]. Subhan et al. [3] synthesized Ca-doped $Li_4Ti_5O_{12}$ using chicken egg shells as Ca source by solid-state method, delivering $Li_{3.9}Ca_{0.1}Ti_5O_{12}$ had better electrochemical properties than the $Li_4Ti_5O_{12}$ sample. Priyono et al. also prepared Ca-doped $Li_4Ti_5O_{12}$ with various concentrations of dopant and explored the Ca^{2+} doping can significantly improve the electrochemical performance of $Li_4Ti_5O_{12}$ [17]. In this research, $CaCO_3$ from blood clam shells (*Anadara granosa*) was used as doping which had the same Ca content as chicken egg shells. It is known that the dominant content in blood clam shells is Ca [18].

The synthesis method and steps will affect the performance of the anode material, leading to various particle sizes and crystal structures [19]. Several methods can be used to synthesize $Li_4Ti_5O_{12}$ such as microwave, molten salt, hydrothermal, sol-gel, electrospinning, and solid-state method [20]–[29]. In this study, the solid-state method was chosen because the process is simple, lowcost, and does not require many precursors [1]. The formation of phase and crystal structure is strongly dependent on process parameters, especially sintering temperature and holding time. In the present study, $CaCO_3$-doped $Li_4Ti_5O_{12}$ was synthesized by a solid-state method with various sintering temperatures. The influence of sintering temperatures on crystal structure and conductivity of $CaCO_3$-doped $Li_4Ti_5O_{12}$ was investigated systematically.

II. Theory

Anadara granosa or known as blood clams are a type of shellfish in the family Mollusca and are commonly found in Asia, such as Indonesia [30]. This shellfish has a high level of productivity and can be processed into various products. In the province of the Bangka Belitung Islands, especially the West Bangka region, it is known that the total production of blood clams was 445.13 tons/year in 2015 [31]. The high consumption of blood clams produces a lot of shell wastes. Clam shells are useful in many applications such as adsorbent, catalyst, and hydroxyapatite [32]–[34]. In addition, blood clams are natural ingredients that are abundantly available and economical.

$Li_4Ti_5O_{12}$ or Lithium Titanate Oxide (LTO) in an anode is known as “zero strain material” because it has negligible structure change during lithium-ion intercalation/deintercalation [35]. The structure of $Li_4Ti_5O_{12}$ is Face-Centered Cubic (FCC) spinel with lattice parameter sizes ranging from 8.352 to 8.370 Å [36]. The performance of $Li_4Ti_5O_{12}$ is known to have a good specific capacity and density of 175 mAh/g and 3.5 g/cm^3, respectively. In addition, it also has a long life cycle of more than 10000 cycles [37].

III. Method

Materials

The precursors used in the synthesis of Li_4Ti5O_{12} were $LiOH.H_2O$ and TiO_2. Blood clam shells or *Anadara granosa* (see Figure 1) were used as $CaCO_3$ sources for doping. As a binder, the material used was Polyvinylidene Fluoride (PVDF), N-Methyl-2-Pyrrolidone (NMP) was applied as the solvent, and Acetylene Black (AB) was used as the conductive carbon.

Preparation of $CaCO_3$ Powder

First of all, the blood clam shells are cleaned with water and then dried in the sun. After that, clam shells were ground and sieved through a 200 mesh sieve. To ensure that the sample is completely dry, the white powders were heated in an oven at 100 °C for 12 hours. Finally, the $CaCO_3$ powders were obtained and characterized using X-Ray Fluorescence (XRF) analysis to determine the chemical composition of materials and X-Ray Diffraction (XRD) analysis for phase identification.

Synthesis of $CaCO_3$ Powder

$CaCO_3$-doped $Li_4Ti_5O_{12}$ were synthesized via the solid-state method. 0.1 mol of $CaCO_3$ was used for doping. Firstly, the precursors material which includes $LiOH.H_2O$ and TiO_2 were grounded to pass through 200 mesh. A mixture of $LiOH.H_2O$, TiO_2, and $CaCO_3$ was mixed by mortar until homogeneous. The mixture was calcined at 700 °C with a holding time of 2 hours. Afterward, sintering was performed at temperature variations of 750 °C, 800 °C, and 850 °C with the same holding time for 4 hours. As a result, the $CaCO_3$-doped $Li_4Ti_5O_{12}$ was obtained and then characterized using XRD for crystal structure analysis (see Table 1)

Fabrication of $CaCO_3$-doped $Li_4Ti_5O_{12}$ Anodes

To fabricate the anodes, $CaCO_3$-doped $Li_4Ti_5O_{12}$ powder, PVDF, and AB (80%: 10%: 10%) were uniformly mixed in NMP solvent. The resulting mixture is put into a mold container and heated in an oven at 50 °C until dry. For the EIS measurements, the anode samples were made into squares with a side length of 1.5 cm. Electrochemical Impedance Spectroscopy (EIS) analysis was used to determine the conductivity value of $CaCO_3$-doped $Li_4Ti_5O_{12}$.

IV. Results and Discussion

Characterization of $CaCO_3$ from Blood Clam Shells

XRF and XRD analyses were used to show the characteristics of $CaCO_3$ from blood clam shells. The elemental compositions of prepared $CaCO_3$ from blood clam shells were evaluated using XRF as shown in Table 2.

Figure 1. Blood clams or *Anadara granosa*

Table 1. Sample code of $CaCO_3$-doped $Li_4Ti_5O_{12}$

Formulation	Sintering Temperature (°C)	Sample Code
$Li_{3,9}Ca_{0,1}Ti_5O_{12}$	750	L-1
	800	L-2
	850	L-3

Table 2. Elemental composition of $CaCO_3$ powders

Chemical element	Concentration (%)
Ca	97.67
Ag	0.91
Sr	0.35
Al	0.34
Other elements	0.73

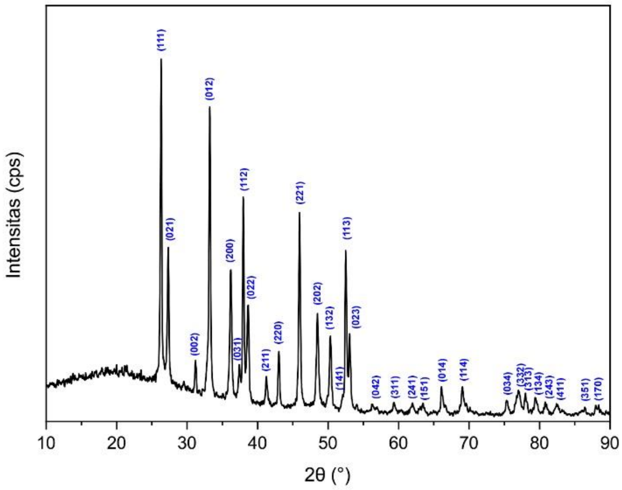

Figure 2. XRD patterns of $CaCO_3$ from blood clam shells

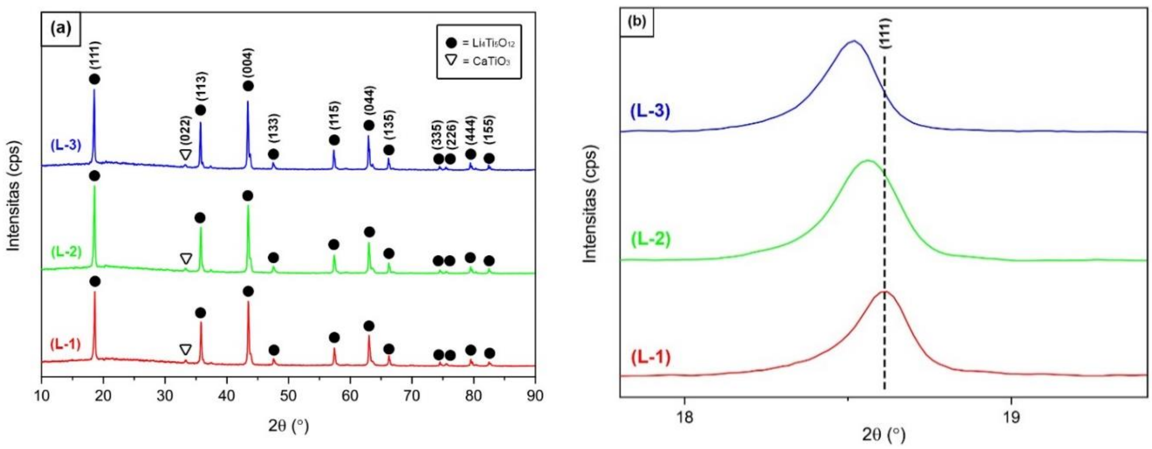

Figure 3. (a) XRD patterns of $CaCO_3$-doped $Li_4Ti_5O_{12}$ at different sintering temperatures. (b) Enlarged (111) plane of samples

XRF analysis showed the main component of blood clam shells is Ca, with a percentage content of 97.67%. The amount of impurities (Ag, Sr, Al, and other elements) is very low when compared to the Ca content, which proves that the blood clam shells have high purity. The results of this study were also proven by several studies that showed Ca content of blood clam shells in the range ≥ 90% [38]–[40].

The XRD pattern of $CaCO_3$ from blood clam shells is shown in Figure 2, the analysis using software Match 2! results show that the phase obtained from the sample is aragonite ($CaCO_3$). The major diffraction peaks are observed at 2θ values such as 26.31°, 33.21°, 37.98°, 45.95°, and 52.51° with miller index of (111), (012), (112), (221), and (113), respectively. All of the diffraction peaks are well agreed with the reference patterns of $CaCO_3$ (COD No. 4001361). In addition, the highest peaks of 26.31° correspond with the previous study showing the highest peaks at 2θ of 26.22° [18], and 26.10° [41]

Crystal Structure Analysis of $CaCO_3$-doped $Li_4Ti_5O_{12}$

Figure 3(a) shows the XRD patterns of $CaCO_3$-doped $Li_4Ti_5O_{12}$ with sintering temperatures at 750 °C, 800 °C, and 850 °C. The results of analysis using Match 2 software shows that the dominant phase in the sample is $Li_{1.33}Ti_{1.67}O_4$ (or spinel of $Li_4Ti_5O_{12}$). The planes at (111), (113), and (004) confirmed that $Li_4Ti_5O_{12}$ has a cubic structure and perfect accordance with corresponding COD No. 10111098. There is no $CaCO_3$ phase found, which indicates that the doping of $Li_4Ti_5O_{12}$ with $CaCO_3$ has been successful. However, there was $CaTiO_3$ phase formation in the samples marked at 2θ values of 33.35° for L-1, 33.33° for L-2, and 33.35° for L-3. The presence of the $CaTiO_3$ phase is caused by Ca^{2+} ions that exceed the maximum

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doping amount, following the previous study by Priyono et al. (2019) also has a $CaTiO_3$ peak at 2θ of 33.21° [17].

Figure 3(b) shows an enlarged (111) plane at different sintering temperatures. It can be observed that the (111) peak shifted to a lower angle with increasing the sintering temperatures, which is indicating an increase in lattice parameters [42]. To analyze the effect of sintering temperature on the crystal structure, several crystal parameters were calculated including average crystallite size, lattice strain, lattice parameters, and unit cell volume. The average crystallite size of $CaCO_3$-doped $Li_4Ti_5O_{12}$ is calculated by using Debye-Scherrer's equation:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (1)$$

Where β is Full Width at Half Maximum (FWHM) and λ is the wavelength of CuKα.

Table 3 shows the increase in sintering temperature will affect the enlargement of the lattice parameters and unit cell volume. This is because, during the sintering process, some ions are converted, leading to an increase in lattice parameters as the sintering temperature increases [43]. Furthermore, an increase in the sintering temperatures also leads to a decrease in crystallite size. The sintering temperature is proportional to the amount of energy the atoms receive which affects the crystallite size and atomic bonding [44]. At higher temperatures (850 °C), this facilitates diffusion and agglomeration, causing the crystallite size of L-3 samples to become larger than those of L-1 and L-2. The size of crystals gives space for the atoms in the crystal [45]. At larger crystallite size, the atoms are close together, so the lattice strain becomes smaller, as shown in Table 3.

Conductivity Analysis of $CaCO_3$-doped $Li_4Ti_5O_{12}$

Further analysis of electrochemical properties of $CaCO_3$-doped $Li_4Ti_5O_{12}$ was performed by EIS. The EIS measurement aims to determine the conductivity of the anode. In the EIS measurement, using an AC voltage source of 1 V and test range frequency of 4 Hz to 5 MHz. Figure 4 represents the Nyquist plot of the samples and equivalent circuits used for EIS data analysis. The value of charge transfer resistance (R_{ct}) was obtained by fitting the Nyquist plot with the Simplified Randless Cell model using Zview software.

In the Nyquist plot, it can be observed that the spectrum consists of semicircle patterns. The radius of the semicircle indicates the R_{ct} of $CaCO_3$-doped $Li_4Ti_5O_{12}$. The smaller the diameter of the semicircle, representing lower R_{ct}, the better the conductivity of samples [46]. Figure 4 shows the order of semicircle patterns from smallest to largest for L-2, L-1, and L-3, respectively. This indicates that L-2 has the highest conductivity among the others, which is approved by the conductivity data obtained from the fitting Nyquist plot shown in Table 4.

According to Table 4, the sintering temperature can affect the conductivity of the $CaCO_3$-doped $Li_4Ti_5O_{12}$, in samples L-1 and L-2 the conductivity value increases, while in sample L-3 the conductivity value decreases. For higher temperatures (850 °C), agglomeration occurs in the sample so that crystallite size increases. The enlarged size of the crystallite increases the diffusion length and decreases the conductivity value [47].

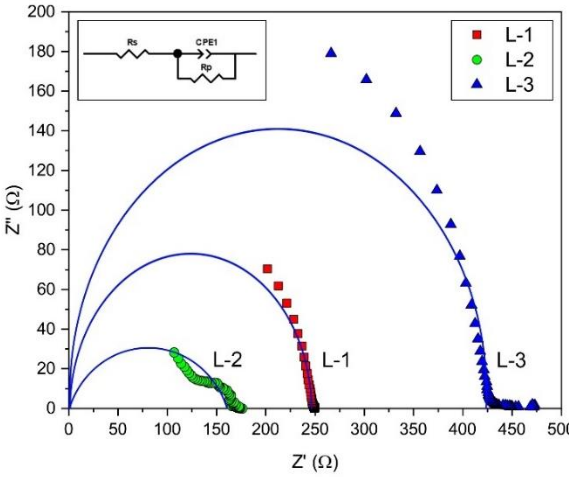

Figure 4. Nyquist plot of $CaCO_3$-doped $Li_4Ti_5O_{12}$

Table 3. Crystal parameters of $CaCO_3$-doped $Li_4Ti_5O_{12}$

Sample Code	2θ (°)	Lattice Parameter (Å)	Unit Cell Volume (Å^3)	Lattice Strain (10^{-3})	Average Crystallite Size (nm)
L-1	18.58	8.26	563.73	0.39	46.49
L-2	18.56	8.27	566.11	0.41	41.25
L-3	18.49	8.30	572.75	0.31	55.14

Table 4. The conductivity of $CaCO_3$-doped $Li_4Ti_5O_{12}$

Sample Code	R_{ct} (Ω)	Conductivity (S/cm)
L-1	289	2.20×10^{-4}
L-2	269.7	2.46×10^{-4}
L-3	481.4	1.06×10^{-4}

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V. Conclusion

The effect of sintering temperature on crystal structure and conductivity of $CaCO_3$-doped $Li_4Ti_5O_{12}$ from blood clam shells was investigated. The smallest crystallite size was obtained at a sintering temperature of 800 °C, which is 46.49 nm, which is beneficial for shortening diffusion length and facilitating the electron and ion transport, causing an increase in anode conductivity. The most optimal conductivity was obtained in samples with a sintering temperature of 800 °C with a value of 2.46 x 10^{-4} S/cm. When the sintering temperature is increased to 850 °C, the particles tend to agglomerate and deteriorate the electrochemical properties.

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Declarations

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