Synthesis and Characterization of Ca-doped Li$_4$Ti$_5$O$_{12}$ Using CaCO$_3$ from Chicken Eggshell as a Dopant for Lithium-Ion Battery Anode Material

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Abstract. In order to improve the performance of Li$_4$Ti$_5$O$_{12}$ (LTO) anode, this research was focused on Ca$^{2+}$ ion doping as a substitute to Li$^{+}$ ion to form Li$_{4-x}$Ca$_x$Ti$_5$O$_{12}$ with values of $x=0$, 0.05, 0.075, and 0.125 using solid-state reaction. The Ca$^{2+}$ ion source was CaCO$_3$ which synthesized from the chicken eggshell. The LTO was prepared by a solid-state method using TiO$_2$ Degussa. The pristine LTO and Ca-doped LTO sample powder was characterized by XRD, SEM, and were also tested its electrochemical performance by EIS, CV and CD. The CaCO$_3$ dopant characterization results showed CaCO$_3$ in calcite polymorph as the main phase, with agglomerated fine particulate morphology and high purity. Characterization of LTO sample powder with XRD revealed that dopant Ca successfully enter the structure of LTO spinel, with maximum addition level $x=0.05$, which excessive addition led to CaTiO$_3$ impurity forming. SEM result showed all Ca-doped LTO have almost similar morphology, which was agglomerated particulate. Ca-doped LTO samples have smaller particle size compared to pristine LTO. Electronic conductivity improvement was spotted at all of Ca-doped LTO sample, with Li$_{1.75}$Ca$_{0.125}$Ti$_5$O$_{12}$ (LCaTO-3) showed the lowest charge transfer resistance of 29.5 $\Omega$. Li$_{1.35}$Ca$_{0.125}$Ti$_5$O$_{12}$ (LCaTO-3) also had the highest initial discharge capacity of 168.2 mAh/g. Nevertheless, in high rate application, the best performance was showed by Li$_{1.125}$Ca$_{0.075}$Ti$_5$O$_{12}$ (LCAO-2) with the discharge capacity of 30.2 mAh/g at 12 C, which capacity retention percentage of 21.43% compared to its discharge capacity at 0.2 C.

Keywords: Li$_4$Ti$_5$O$_{12}$ anode, solid-state, Ca-doped, dopant CaCO$_3$, chicken eggshell waste

1. Introduction

Lithium-ion (Li-ion) battery is one of the most commonly used in today's technology. Increased demand for lithium batteries has increased over time, coupled with a decrease in the cost of manufacturing. The conventional LiB currently are generally made with graphite as anode material. Graphite has advantages include relatively low fabrication costs and large capacity (372 mAh/g) [1]. However, the safety level is still low in the use of graphite, and it is still the primary concern. This issue is due to the voltage operations close to 0 V (vs. Li/Li$^+$) at a time when the process of Li$^+$ insertion, so the metal lithium deposits formed on the surface of the carbon electrode is dendritic, commonly referred to as solid-electrolyte interface (SEI). SEI formed at potential under 0.8 V (vs. Li/Li$^+$) this will reduce the amount of lithium in the electrolyte, so that cause a decrease in the specific capacity [2].

Along with the rapid advancement of technology, other materials were developed to accommodate the shortcomings of graphite anodes, one of which is the titanate of lithium
The anode of lithium titanate (LTO) spinel has the specific smaller capacity (175 mAh/g) compared to graphite, but have higher operating potential (1.55 V vs. Li/ Li+) so it is safer to operate [3]. In addition to the above characteristics, LTO has other advantages, such as the nature of zero strain material LTO in the lithiation-delithiation process which have an impact on the results of the stability of cycles and good reversibility [4]. However, anode LTO has some disadvantages in addition to specific capacity is low, i.e. the coefficient of electronic conductivity is low \((10^{-13} \text{ S/cm})\) and the coefficient of diffusion of ions \(\text{Li}^+\) which is also low \((10^{-8} \text{ cm}^2/\text{s})\) that affect the rate of performance [5].

Based on the above conditions, improved performance anode LTO can be done in several ways, ranging from lower particle size, coat the surface of the particles with conductive materials such as carbon and silver, as well as doping by using ion metal and non-metal [3]. Increased performance and capacity can also be made by combining LTO with anode material combines with a higher value of the specific capacity.

The increase in conductivity is also one of the ways to improve the performance of LTO. Conductive phase such as carbon or FRS is usually added in the matrix so that the conductivity of LTO increases. Also, the treatment of doping can also be done, such as using metal ions (Ag+, Mg2+, Zn2+, Sr2+, Sn2+, etc.) and other non-metallic ions (F-, Br-, etc.). Doping on LTO is proven to increase the electronic conductivity effectively [6]. One of the interesting research is doping LTO using the atom of calcium. Generally, the source of dopant atoms in calcium derived from CaO or CaCO3.

On the other hand, the CaCO3 turns out to be is a constituent component of natural materials such as shells and egg shells [7]. The said two ingredients can be processed and used as CaCO3 from a natural source to serve as the dopant of the LTO.

2. Materials and Methods

Calcium carbonate was used in this research is prepared with the same method as the previous research [8]. Preparation process begins with obtained ingredients of chicken eggshells are then cleaned of debris physically using the water until clean. Once cleaned, chicken egg shells are then crushed and pounded until fine powder-shaped. Then, the powder obtained is dried at a temperature 100°C for 12 hours. The results obtained are calcium carbonate derived from nature.

The main ingredients needed are a titanium oxide TiO2 as a source of titanium, lithium carbonate (Li2CO3) as a source of lithium, and CaCO3 prepared from chicken eggshells as a dopant source. The calculation was made so that the final result was obtained by the stoichiometry of \(\text{Li}_4\text{Ca}_x\text{Ti}_5\text{O}_{12}\) with variable values \(x\) of 0, 0.05, 0.075, and 0.125. The TiO2 used is TiO2 nano-sized Degussa P25 commercial size ~ 20-30 nm, while Li2CO3 was Merck Sigma Aldrich. The composition of reactants used customized with stoichiometric forming \(\text{Li}_4\text{Ti}_5\text{O}_{12}\), except of \(\text{Li}_2\text{CO}_3\) where added in-excess of 4% to accommodate the loss of the \(\text{Li}^+\) during the high sintering temperature. The addition of dopant is then carried-out by mixing CaCO3 from eggshells along with Li2CO3 and TiO2.

Table 1 shows the composition used in this research, in which the amount of dopant CaCO3 adapted to the variable substitution for lithium ion doping \(\text{Li}_4\text{Ca}_x\text{Ti}_5\text{O}_{12}\).

| Table 1. Formulation and sample code |
|-------------------------------------|
| Formulation | Moles of Ca doping (x) | Moles of Li | Material | Sample Code |
|--------------|------------------------|-------------|----------|-------------|
| \(\text{Li}_4\text{Ca}_x\text{Ti}_5\text{O}_{12}\) | 0 | 4 | \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) | LTO |
| 0.05 | 3.90 | \(\text{Li}_3.90\text{Ca}_{0.05}\text{Ti}_5\text{O}_{12}\) | L\text{CaTO}-1 |
| 0.075 | 3.85 | \(\text{Li}_3.85\text{Ca}_{0.075}\text{Ti}_5\text{O}_{12}\) | L\text{CaTO}-2 |
| 0.125 | 3.75 | \(\text{Li}_3.75\text{Ca}_{0.125}\text{Ti}_5\text{O}_{12}\) | L\text{CaTO}-3 |
Once weighed, all reactants are introduced into the chamber of the High Energy Vibrating Ball Mill (MSKK-SFM-3 High-Speed Vibrating Ball Mill-1200 rpm) for mixing so that the mixture is homogeneous. Milling was done during the 45-minute pauses every 10-15 minutes stopped to avoid overheating in the chamber because of the process of high-energy, rotation and release particles that stick to the wall of the chamber. Powder milling result is then ejected from the chamber to be calcined at a temperature of 800°C for 6 hours.

The process of manufacturing the batteries begins with the preparation of materials active. The active material is crushed with a mortar until smooth then sifted with a 140 mesh sieve. Active material already sifted is then weighed to measure that is specified by the stoichiometric. Next up is the mixing of the slurry, i.e. by dissolving active anode materials of Li$_4$Ti$_5$O$_12$, PVDF, and acetylene black in comparison with 8:1:1 in a solution of NMP. Further mixing with magnetic stirrer sized for 2 hours until homogenized slurry is formed.

The slurry then coated on a sheet of a current collector of Cu foil. This coating process used a special tool that is doctor-blade. After slurry exposed on a certain thickness, with results of the coating is heated in the appliance at a temperature of 80°C. The results of coating is then transferred to the oven at a temperature of 120°C and kept for 24 hours.

Further cutting of sheet forming a circle with dimensions that match the size of the coin battery half-cell. Other cell components also prepared as a counter electrode (lithium foil), LiPF$_6$ as an electrolyte, and 2300 Celgard as a separator. Everything is placed in the glove box with argon gas atmosphere and moisture content of less than 10 ppm. Coin cell battery components assembled in the glove box.

A pressure of 10 MPa was applied for compacting of the battery arrangement. Next, the battery left for 24 hours to be ready to do the testing and performance.

### 3. Results and Discussion

#### XRD Analysis

Figure 1 shows the XRD diffractogram of the samples. The XRD characterization results were processed using the program Plus HighScore X’Pert refers to ICDD PDF2 database. The diffraction peak of recording range trail from 10° up to 80° (2θ). Diffraction XRD peak data charts of each sample can be seen in Figure 1. The phase Component tries to found through matching with the reference code is Li$_4$Ti$_5$O$_12$ (00-049-0207), TiO$_2$ rutile (01-072-1148), and CaTiO$_3$ (01-072-1192). It also seen how the influence of addition of doping ions of Ca$^{2+}$ on the characteristics of the diffraction patterns of a sample.

![XRD diffractogram](image_url)
Figure 1. Diffraction patterns LTO, LCaTO-1, LCaTO-2 and LCaTO-3.

All of the four samples are characterized, the majority of the main peak is the diffraction patterns from Li4TiO12 spinel. Diffraction peak (2θ) appear at the angle 18.45°, 37.29°, 43.47°, 47.43°, 57.45°, 63.08°, 66.14°, 74.42° and 79.41° which is the main constituent of diffraction peak patterns of phase LTO spinel. Through matching with reference code JCPDS no: 00-049-0207 on a sample LTO without doping, the sample LCaTO-1, LCaTO-2 and LCaTO-3 gained a score of 89, 91, 83, 78, respectively. Thus, it indicates that compound of lithium titanate (LTO) was successfully synthesized using methods of the synthesis of solid-state doping, and the addition of Ca2+ into LTO does not change the structure of the host of the LTO.

The peak of CaTiO3 shows at the 33.21° from the sample of LCaTO-2 and LCaTO-3. The peak matches with JCPDS no: 01-072-1192 with common name calcium titanate. The formation of calcium titanate is due to the calcium ion doping has exceeded the maximum doping amount. Further, from XRD test results above, it is found that the amount of TiO2 rutile which is very few in the four samples, the samples are either doped or without doping. Matching for the phase2 rutile TiO2 use the JCPDS reference code: 01-072-1148 on LTO without doping, LCaTO-1, LCaTO-2, and LCaTO-3 row obtained a score of 4, 0, 3, and 4. The existence of this phase of TiO2 rutile is not significant when compared to the phase of the LTO. So, it shows that the amount of TiO2 powder rutile in very little. Some factors that become the cause is the use of calcined TiO2 nano-sized and the temperature high enough. The use of TiO2 nano-sized lead to spread of the material that is more equitable and homogeneous. Also, the high surface area of the use of TiO2 nano-sized has the advantages of increasing the probability of contact between the titanium source with a lithium source, and with the spread evenly so the amount of TiO2 reacting become more massive.

The size of the crystallites averages obtained through approach using Scherer’s equation. The average value of the smallest size of crystallites is variable with a value of LTO 38.12 nm, followed by LCaTO-2, LCaTO-1 and LCaTO-3 consecutive 47.32, 52.78, and 59.66 nm. Thus, this LTO preparation using TiO2 Degussa obtained a nanocrystalline particle.

SEM Analysis
Figure 2 shows the morphology of the LTO sample. It can be seen that the particles experience the agglomeration with various size distribution. Agglomeration occurs starting from the process of mixing using HEBM that is too long. Particle LTO mutually connects between each other occur because of high sintering temperature. Agglomerate in the picture also big. It is possible to occur because of the snapping and hardening powder on the wall of the chamber HEBM during the process of mixing. Characteristics of morphology sample are also porous. The calculation of the average particle size of the sample LTO using software image-J shows the value of 0.809 μm with a standard deviation of 0.155 μm.
Figure 2. The SEM result of LTO.

Figure 4 shows the morphology of the samples (a) LCaTO-1 (b) LCaTO-2, and (c) LCaTO-3. Similar to the morphology at the sample of LTO, LCaTO-1 also shows the agglomeration particles and porous microstructures as seen in Figure 3 previously. However, the agglomerate formed not as big as that of the sample LTO without doping. Calculation of particle size using software image-J produces average particle size worth 0.548 µm with a standard deviation of 0.125 µm. The results of SEM samples LCaTO-2 shows the characteristics of agglomerate particles and porous as seen in the results of SEM other variables. Calculation of average particle size produces an average of 0.347 µm with standard deviation 0.052 µm, where this value is the average value of the smallest compared to other variables. On a scale of 5 µm particle size that looks smooth and pores that much formed. The results of SEM samples LCaTO-3 still shows the morphology of agglomerate particles and porous. If viewed on a scale of 20 µm, the agglomerate formed to have the shape and size of a fairly homogeneous. Meanwhile, the size of the particles a bit more rounded than the other samples. The average particle size is obtained through measurements using image-J software is 0.622 µm with standard deviation 0.124 µm. From this finding, the Ca-doping could reduce the agglomeration size in general.
Figure 3. The results of SEM of samples (a) LCaTO-1 (b) LCaTO-2 (c) LCaTO-3.

EIS Analysis
The test results of the EIS can be seen in Figure 4. The value of $R_{ct}$ smallest displayed by LCaTO-3 with a value of 29.5 $\Omega$, followed by LCaTO-1 with a value of 68.8 $\Omega$, and LCaTO-2 with 84.4 $\Omega$. Sample LTO without doping results $R_{ct}$ highest, i.e.: 86.7 $\Omega$.

With reverse relations as already described above, then the information can be drawn that the LTO without doping have the lowest conductivity among other samples. In general, it can be inferred that the ion doping treatment of $Ca^{2+}$ in the LTO can lower the resistivity, which means it also increases the value of conductivity.

Figure 4. The combined Graph EIS for each sample.

Table 2. The value of the charge transfer resistivity of each sample

| Sample    | $R_{e}$ (\(\Omega\)) | $R_{ct}$ (\(\Omega\)) |
|-----------|-----------------------|-----------------------|
| LTO       | 14.3                  | 86.7                  |
| LCaTO-1   | 20.1                  | 68.8                  |
| LCaTO-2   | 8.6                   | 84.4                  |
| LCaTO-3   | 12.9                  | 29.5                  |

EIS test results can be seen in Figure 5. In general, it could be concluded that the treatment of $Ca^{2+}$ ion doping on LTO can lower the resistivity, which is about increasing the value of conductivity. Referring to the XRD diffraction data of test results, the shift of the diffraction peaks on doped samples showed $Ca^{2+}$ influx into the LTO structure replaces multiple $Li^{+}$ ion sites. $Ca^{2+}$ influx into the host structure LTO to replace $Li^{+}$ ions will contribute more electrons. Compensation charge of substitutions cause a transition from $Ti^{4+}$ to $Ti^{3+}$, where the presence of additional electron donation will increase the electrical conductivity due to the increased
concentration of electrons. Ti$^{3+}$ ions play a role more effectively in the increase and decrease in polarization electrode conductivity\cite{11}\cite{12}.

The presence of impurities in the form of CaTiO$_3$ also possible to affect the electronic conductivity doped samples. Their impurity dopant showed that the number of atoms that made it into the lattice structure of the LTO had passed the optimum limit. In several studies such as doping atom doping Gd and Ce on the structure of LTO, the impurity phase will create barriers charge transfer becomes larger so that the lower the value of conductivity\cite{13}\cite{14}, But in this study, a decrease in conductivity does not occur. One indication of the cause of the high levels of conductivity is CaTiO$_3$ characteristics that have perovskite crystal structure and an n-type semiconductor \cite{15}. In a study on the characterization of CaTiO$_3$ perovskite ceramics found variations in the electronic conductivity of $1.4 \times 10^{-9}$ to $4.2 \times 10^{-11}$ S / cm, where the value is still higher than the value of the electronic conductivity LTO ($10^{-13}$ S / cm) \cite{16}.

Cyclic Voltammetry Analysis

The Figure 5 shows CV graph in the peak results of cathodic and anodic generated by each sample is not much different from each other. Cathodic peak and anodic from the sample LTO are at 1.785 and 1.405 volts, respectively. The working voltage is obtained from average voltage of oxidation and reduction on LTO sample at 1.595 V.

The LCaTO-1 sample Cathodic voltage value and anodic of 1.759 V and 1.434 V, with a working voltage of 1.5965 V. On sample LCaTO-2, cathodic and anodic voltage value of 1.424 V and 1.776 V consecutively, with working voltage 1.6 V, while at the doping with the highest concentration of Ca i.e., sample LCaTO-3, anodic and cathodic voltage value of 1.739 V and 1.453 V, with 1.596 V working voltage.

![Graph of cyclic voltammetry sample LTO, LCaTO-1, LCaTO-2 and LCaTO-3.](image)

All samples show the voltage value is not much different from each other, either cathodic voltage, anodic or working voltage cells. Working voltage on all samples show the value that almost approaches the working voltage theoretical LTO, which is 1.55 V. This shows that the phase is the phase of the primary constituent of the LTO from the powder of the active material.
View from the perspective of polarization, there was a decrease in the level of polarization on the atomic addition of Ca doping in the process. Difference of cathodic voltage and anodic is one of the parameters of the polarization level electrode electrochemical cell. The lowest level of polarization is owned by LCaTO-3 sample, with a value of voltage difference 0.286 V. then followed by LCaTO-1, LCaTO-2, and LTO with consecutive values 0.325 V, 0.352 V, and 0.38 V. Decrease in the level of polarization is closely related with the electronic conductivity factor, where the polarization of the lowest represented by the sample with the highest electronic conductivity, i.e. LCaTO-3. The trend of his descent is also the same with the existing trend of increased electronic conductivity in the analysis of the test results of the EIS in advance. It is aligned with the findings stating that the Ca atom doping into the structure polarization levels decline supports LTO electrode so that the kinetics reaction better [17].

**Charge and discharge Analysis**

Figure 6 shows the curve of the charge/discharge in C-rate. Almost all samples show the plateau in the form of a straight line in ~ 1.6 volts, which is by the characteristics of charge and discharge materials spinel LTO [2]. On any increase in C-rate decline in capacity. This phenomenon could be explained that the greater the flow rate causes a reaction that occurs is not comprehensive to all parts of the active material. On high C-rates, a lithiation reaction happens more on the surface. From this downturn, it will be seen how the retention capacity of the sample, i.e. the percentage of the sample capacity at a certain rate if compared to the capacity at the smallest C-rate (0.2 C).

**Figure 6.** Charge/discharge curve of the sample (a) LTO (b) LCaTO-1 (c) LCaTO-2 (d) LCaTO-3.

Figure 7 shows the initial capacity rate obtained at the C-rate 0.2. Generally, Ca-doping is proven to increase the specific capacity value of LTO. The highest capacity at 168.2 maH/g obtained at doping of 0.125 mol Ca – 3.75 mol Li (LCaTO-3). This result corresponds to the charge-transfer resistivity ($R_{ct}$) value obtained from the EIS testing result. The Ca-doping will decrease the charge-transfer resistivity ($R_{ct}$) value and thus, increasing the specific capacity of the sample [18].
Figure 7. Initial Discharge capacity rate

Figure 8 shows the graph of C-rates of performance in each sample. It can be seen a reduced rate of specific capacity with the increasing rate is used. Sample LCaTO-1 and LCaTO-3 have the highest specific capacity value is indeterminate at rate of 0.2 C, i.e. 166.6 mAh/g. Sample with specific capacity under them is LCaTO-2 value of 140.9 mAh/g, and the last is a sample LTO with capacities the lowest specific i.e. 123.7 mAh/g. With the increase in the rate of current use, the specific capacity gradually decreases. On the higher rate, the performance of the samples is best shown by the LCaTO-2 with capacity discharge 30.2 mAh/g at 12 C, and 39.2 mAh/g at 10 C. Sample LCaTO-3 has a capacity at the C-rate is high under LCaTO-2, i.e. worth 16.25 mAh/g at 12 C and 24.6 mAh/g at 10 C. Under LCaTO3, there is LCaTO-1 sample with a discharge capacity of 11.75 mAh/g at 12 C and 12.5 mAh/g at 10 C.

Table 3. Percentage of capacity retention on different C-rate vs. capacity at the rate of 0.2 C

| C-Rate | Percentage of capacity retention |
|--------|--------------------------------|
| LTO    | LCaTO-1 | LCaTO-2 | LCaTO-3 |
| 100    | 167.4    |          |          |
| 150    |          | 135.4    |          |
| 200    |          |          | 168.2    |
Discharge capacity retention percentage is highest at the rate implied by the high flow samples LCaTO-2. Initially at a rate of flow is low (0.5 C and 1 C), LCaTO-3 still show retention capacity with the highest percentage (93.34% vs. capacity at 0.2 C). However, starting in the current rate of 2 C to 12 C, LCaTO-2 shows the performance of the most high capacity retention among all samples. In the 12 C, sample LCaTO-2 shows the discharge capacity of 30.2 mAh/g, 21.43% of capacity at 0.2 C. This value is far greater than the sample LTO without doping which saw capacity 8.19 mAh/g, only 6.62% of the capacity of 0.2 C. This finding shows that the rate capability performance also increased with Ca-doping [18].

In addition to retention capacity at the C-rate is high, coulombic efficiency data is also included in the test data processing charge-discharge. Figure 9 shows the graph of the coulombic efficiency of each sample in C-rate. The value of this coulombic obtained from the efficiency percentage of capacity discharge divided by the capacity charge on each C-rate. All samples showed high efficiency values almost reaching ~ 99%, with the lowest efficiency 98.80%. There are anomalies where the value of the efficiency that exceeds 100% on one sample. This happens because the application of cut-off voltage at 0.80 V, so it is possible there are still some lithium ion that is left on the previous cycle and migrating the next cycle so that the resulting value of the efficiency exceeding 100% because the discharge capacity. In general, high coulombic efficiency on all samples showed that doping does not influence negatively to coulombic efficiency LTO obtained due to the characteristic zero strain when the lithiation/delithiation process.

| C/2 | 81.33 | 89.44 | 92.19 | 93.34 |
|-----|-------|-------|-------|-------|
| 1C  | 61.28 | 72.33 | 78.85 | 77.37 |
| 2C  | 49.80 | 53.72 | 63.31 | 57.02 |
| 4C  | 27.49 | 37.88 | 52.56 | 39.50 |
| 6C  | 19.32 | 24.61 | 42.87 | 29.77 |
| 8C  | 13.66 | 17.53 | 34.40 | 21.97 |
| 10C | 10.19 | 11.52 | 27.75 | 14.77 |
| 12C | 6.62  | 7.05  | 21.43 | 9.75  |

![Figure 9](image_url) **Figure 9.** The graph of the coulombic efficiency vs. C-rates.

### 4. Conclusions

1. Synthesis of active anode material Li$_4$Ti$_5$O$_{12}$ doped using dopant Ca$^{2+}$ from CaCO$_3$ of chicken eggshell successfully carried out using the method of solid-state.
2. Characterization via XRD testing indicates doping ion $\text{Ca}^{2+}$ does not change the host structure of LTO spinel. Optimum doping levels ion $\text{Ca}^{2+}$ can enter the structure of LTO shown by $\text{Li}_{3.96}\text{Ca}_{0.03}\text{Ti}_5\text{O}_{12}$, with the addition of doping impurities produce exceeds the value in the form of $\text{CaTiO}_3$. There is a difference in the size of the crystallites on average on a significant sample of LTO and $\text{Li}_{3.85}\text{Ca}_{0.075}\text{Ti}_5\text{O}_{12}$ probably caused by less evenly temperature distribution on a furnace that used.

3. SEM Results showed material synthesis through the method of solid-state using High Energy Ball Mill (HEBM) produces the characteristic morphology of the agglomerate particles and porous on all samples. The addition of doping on LTO exerts influence in the form of a decrease in the size of the particles, with $\text{Li}_{3.85}\text{Ca}_{0.075}\text{Ti}_5\text{O}_{12}$ as the smallest particles with the size of the sample.

4. Calcium Doping LTO using dopant $\text{CaCO}_3$ chicken eggshells enhance electronic conductivity in general. The highest conductivity indicated by $\text{Li}_{3.75}\text{Ca}_{0.125}\text{Ti}_5\text{O}_{12}$ charge transfer barriers with the lowest i.e. 39.5 $\Omega$.

5. The CV test results showed that doping calcium ions on the LTO using dopant $\text{CaCO}_3$ chicken egg-shells exert influence on the decline in the level of polarization of electrodes that deliver impact reaction kinetics.

6. Calcium doping improves performance on high C-rates. The best performance is indicated by $\text{Li}_{3.85}\text{Ca}_{0.075}\text{Ti}_5\text{O}_{12}$ with discharge capacity totalling 30.2 mAh/g at 12 C along with the increase in electronic conductivity and decrease of particle size so that shortening the diffusion distance.

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