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# Manufacture of Lithium Lanthanum Titanate Active Material as a Lithium-Ion Capacitor Anode Using Solid-State Reaction Methods

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**ABSTRACT**

Lithium lanthanum titanate, $Li_{0.2}La_{0.6}TiO_3$ (LLTO) was synthesized for the manufacture of lithium-ion capacitors using the solid-state reaction method. in this study, the active ingredients were synthesized using variations of lithium and lanthanum as raw materials. The raw materials used are $Li_2CO_3$, $La_2O_3$, and $TiO_2$. The three raw materials were mixed according to the stoichiometric calculations then added 13 ml of Ethanol solution so that the raw materials were mixed evenly during the milling process for 5 hours. Sintering was carried out for 8 hours at 800$^o$C and then at 1150$^o$C for 12 hours. The sintered powder was ground using a mortar and pastel and then sieved on a 400 mesh sieve. The anode sheet was made by mixing the active ingredients: PVDF: Super-P with a composition of 85:10:5 by adding 3 ml of DMAC solvents. The characterization test was carried out using XRD while the electrochemical test used CV and EIS. The XRD result shows the formation of the main phase and the impurity phase with the main phase percent of 96.4%. From the results of electrochemical testing, the percentage of capacity is 73%.

**Keyword:** Anode Materials, Lithium Ion Capacitors, Solid-State Reaction Method, Variations of Lithium Lanthanum

**ABSTRAK**

Litium lantanum titanat, $Li_{0.2}La_{0.6}TiO_3$ (LLTO) disintesis untuk pembuatan kapasitor ion lithium menggunakan metode reaksi solid state. Dalam penelitian ini, bahan aktif disintesis menggunakan variasi lithium dan lantanum sebagai bahan baku. Bahan baku yang digunakan adalah $Li_2CO_3$, $La_2O_3$, dan $TiO_2$. Ketiga bahan baku tersebut dicampur sesuai perhitungan stoikiometri kemudian ditambahkan larutan Etanol sebanyak 13 ml sehingga bahan baku dicampur secara merata proses penggilingan selama 5 jam. Sintering dilakukan selama 8 jam pada suhu 800 $^o$C kemudian pada suhu 1150 $^o$C selama 12 jam. Bubuk sinter digiling menggunakan mortar dan pastel dan kemudian disaring pada saringan 400 mesh. Lembar anoda dibuat dengan mencampur bahan aktif: PVDF: Super-P dengan komposisi 85:10:5 dengan menambahkan 3 ml pelarut DMAC. Uji karakterisasi dilakukan dengan menggunakan XRD sedangkan untuk uji elektrokimia menggunakan CV dan EIS. Hasil xrd menunjukkan pembentukan fase utama dan fase pengotor dengan persen fase utama sebesar 96,4%. Dari hasil pengujian elektrokimia, persentase kapasitasnya adalah 73%.

**Kata Kunci:** Bahan anoda, kapasitor ion lithium, metode reaksi keadaan padat, variasi lithium lantanum

## 1. Introduction

Lithium-ion capacitors were first produced in 2001 and are considered to be one of the most effective devices for energy storage. LIC can provide high power density (>10 kW/Kg) and long lifetimes (typically > 5000 cycles) [1] – [4]. However, to meet the need for greater electrical energy, an efficient lithium-ion supercapacitor (LIC) was developed further. Lithium- Ion Capacitors are rechargeable energy storage systems, which belong to the class of hybrid capacitors or asymmetric capacitors and can b classified between lithium-ion batteries and electric double-layer capacitors (EDLC) where the positive electrode uses activated carbon as in conventional EDLC [5] – [8]. Lithium Ion Supercapacitor (LIC) is an ideal choice which has a higher energy density than electric double-layer capacitors and has a better rate capacity than lithium-ion batteries [9]. Supercapacitors have several advantages, namely higher power density, Faster charging, and longer cycle life and shelf life. This shows that the supercapacitor has a much greater energy density than conventional capacitors and a much greater power density than the battery.

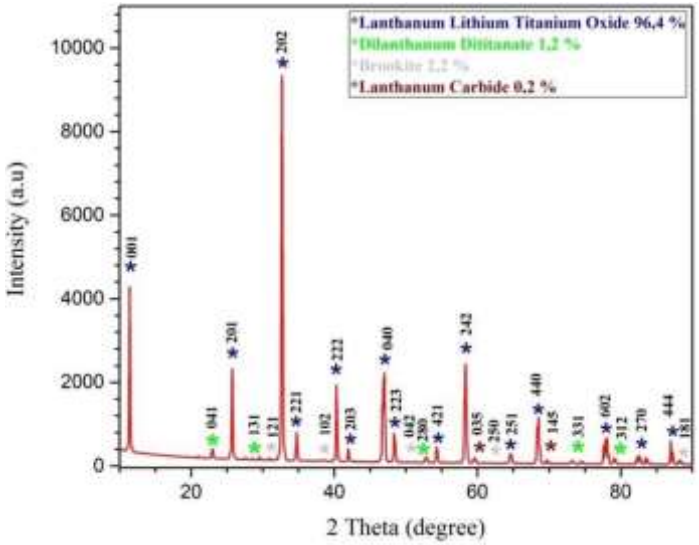
The most important criterion for selecting anode material is the potential of the electrode. $Li_4Ti_5O_{12}$ material is known as a high-grade anode material, while its drawbacks, such as low capacity and too high working potential can severely limit the output energy density of a full cell. So, there is still a big challenge to find suitable host material for $Li^+$ with multiple functions of high capacity and safe potency. therefore, the material $Li_{3x}La_{2x}TiO_3$ a group of beneficial anode materials was developed as seen this anode shows a high specific capacity of 225 $mA.h.g^{-1}$ and supports 3000 cycles involving a reversible phase transition. Without reducing the particle size from micro to nanoscale, its speed performance has surpassed that of nanostructured $Li_4Ti_5O_{12}$. further characterization and calculations revealed that pseudocapacitance determines the lithium and ion storage processes that are favorable for electronic transport such as electric cars and are responsible for the advancement of the technology [10].

## 2. Method

In this study, the synthesis of lithium lanthanum titanate with a solid-state reaction method. the research includes raw material preparations, synthesis process, drying process, calcination process, and characterization. anode material $Li_{0.2}La_{0.6}TiO_3$ (LLTO) was synthesized for the manufacture of lithium-ion capacitors using the solid-state reaction method. in this study, the active ingredients were synthesized using variations of lithium and lanthanum as raw materials. the raw materials used are $Li_2CO_3$, $La_2O_3$, and $TiO_2$. The three raw materials were mixed according to the stoichiometric calculations then added 13 ml of Ethanol solution so that the raw materials were mixed evenly in the milling process for 5 hours. After milling using a planetary ball miller, the sample will be dried at 70$^o$C to remove the remaining ethanol in the sample. Sintering was carried out for 8 hours at 800$^o$C and then at 1150$^o$C for 12 hours. The sintered powder was ground using a mortar and pastel and then sieve on a 400 mesh sieve. The anode sheet was made by mixing the active ingredients: PVDF: Super-P with a composition of 85:10:5 by adding 3 ml of DMAC solvents. The characterization test was carried out using XRD while the electrochemical test used Electrochemical impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV).

## 3. Results and Discussion

*3.1 XRD Analysis*




Figures 1. Diffraction patterns of $Li_{0.2}La_{0.6}TiO_3$

Figure 1 shows the result of the XRD pattern of $Li_{0.2}La_{0.6}TiO_3$ which has been matched with the databases (ICSD 98-005-9647) there are 4 peaks of the highest intensity indicating that the Li phase $Li_{0.2}La_{0.6}TiO_3$ formed at angles of 32.5°, 11.3°, 40.2°, 46.8° has an Orthorhombic structure with a space group of C mmm and contains several impurities such US Dilanthanum Dititanate $La_2O_7Ti_2$ (ICSD 98-003-2537) with 4 highest intensity peaks at angles 29.7°, 27.7°, 32.7°, 20.8° has an Orthorhombic structure with Space group C mc21, Brookite element $TiO_2$ (ICSD 98- 015- 4606) with 4 peaks of highest intensity 25.5°, 31°, 25.8°, 48.4° having an Orthorhombic structure with Space group P bca, and Lanthanum Carbide $La_2C_3$ (ICSD 01-082-0622) with the 4 highest intensity peaks at angles 32.2°, 28.7°, 53°, 38.2° have a Cubic structure with Space group I-43d.

*3.2 CV Analysis*

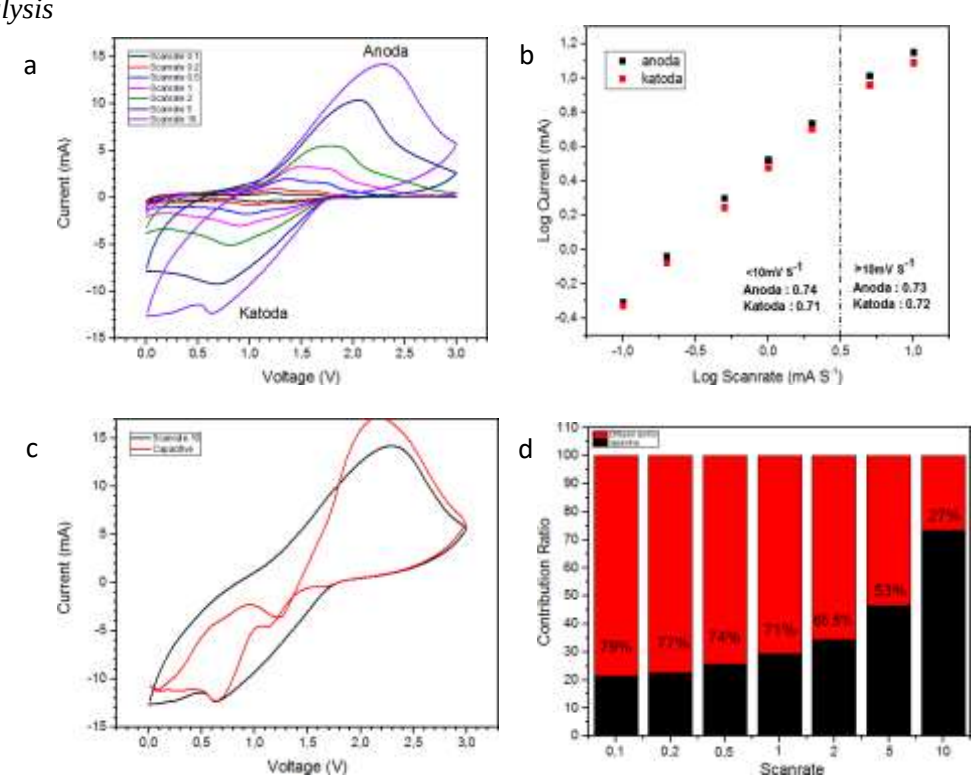



Figure 2. Cyclic Voltammetry Analysis of $Li_{0.2}La_{0.6}TiO_3$; a) CV curves at different Scanrate; b) Peak Current vs Scan rate logs; c) Capacitive and Diffusion Area at a Scanrate of 10 $mV.S^{-1}$; d) Pseudocapacitive Percentage at Different Scanrate

At different velocities of 0.1 $mV/s^{-1}$-10 $mV/s^{-1}$ shows broad anode and cathode peaks with a quasi-rectangular shape that extends across all scanning speeds indicating the contribution of pseudocapacitive during the intercalation and deintercalation process of the relationship between currents at A certain potential with a scan rate can determine the b-value determined by the ion storage mechanism and can be calculated by plotting slope (slope) log(*I*) log(*V*). To be more specific, an *ab* value of 0.5 means the process is completely diffusion controlled, while an *ab* value of 1.0 indicates a faradaic contribution from charge transfer with surface or subsurface atoms (pseudocapacitance effect) or a non-faradaic contribution from the electrical double layer effect. Quantitatively, the capacitive contribution can be determined by separating the *current* (*I*) at a certain *potential* (*V*) into capacitive (linear relationships with sweeps rates marked as $k1(V)V$ and diffusion control (proportional to $V^{1/2}$) marked as $k2(V)V^{1/2}$ as in the equation (1) and (2):

$$I(V) = k1(V)V + k2(V)V^{1/2} \quad (1)$$

$$I(V)/V^{1/2} = k1(V)V + k2 \quad (2)$$

Where *k1* and *k2* are constants for a certain potential (*V*) and can be calculated by plotting $I(V)/V^{1/2}$ with $V^{1/2}$ where *k1* is the slope (slope line) and *k2* is the Y-axis intersection so that we can see the area comparison diffusion and capacitive. When the sweep speed increases, the role of the capacitive contribution increases, so the addition of the amount of lanthanum affects the value of the capacitive contribution where the more the amount of lanthanum, the higher the value of the capacitive contribution.

*3.3 EIS Analysis*

Electrochemical Impedance Spectroscopy (EIS) testing was carried out to determine the value of the electrical conductivity of the electrochemical cell. The shape of the EIS curve obtained is a semicircle and a straight line. Semicircle in EIS is related to the value of electron resistance ($R_e$) and charge transfer resistance ($R_{ct}$). While the straight line indicates the presence of diffusion or the process of intercalation and deintercalation of lithium then fitting using NOVA software so that the data obtained is more specific. Where the conductivity level is inversely proportional to the resulting resistance, it can be concluded that, if the conductivity value of a material is large, the resistance value is small, and vice versa. the conductivity of each sample can b determined by equations (3), (4), and (5)

$$\sigma\ ions = \frac{t}{Rion\ x\ A}\ ; \quad (3)$$

$$\sigma_{\ materials} = \frac{t}{Rbahan\ x\ A}\ ; \quad (4)$$

$$\sigma total = -\frac{t}{Rtot\ x\ A} \quad (5)$$

where $R_{tot}$ = *Ingredients* + $R_{ion}$ , then the conductivity value of $Li_{0.2}La_{0.6}TiO_3$ is σ total = 0.76 x $10^{-5}$ S/cm.

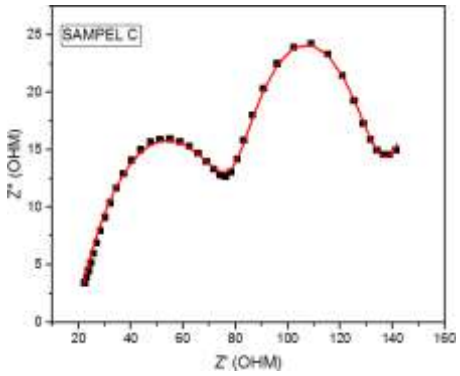



Figure 3. EIS Analysis of $Li_{0.2}La_{0.6}TiO_3$

## 4. Conclusion

In summary, XRD results state that the sample has been successfully forming the main phase of 96.4%, the results of CV show that the addition of the amount of lanthanum affects the value of the capacitive contribution where the more the amount of lanthanum, the higher the capacitive contribution the value will be by 73%, from the EIS test results show that the conductivity value of the material of 0.76 x $10^{-5}$ S/cm.

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