Lithium Ion Battery Cell Fabrication With $Li_4Ti_5O_{12}$ /C Anode And $LiMn_2O_4$/C Cathode Synthezed By Solid State Reaction Method

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Abstract. Lithium ion batteries using Lithium Titanate Oxide anodes ($Li_4Ti_5O_{12}$ / LTO) and Lithium Manganese Oxide cathodes ($LiMn_2O_4$ / LMO) have been successfully manufactured. The active components, LTO and LMO, were synthesized utilizing the solid state reaction technique at an 850°C sintering temperature and 4 hours holding duration in a free air atmosphere. The active components are crushed and sieved through 400 mesh after sintering. The active material, which contains 5% super-P carbon, is subsequently pyrolyzed in a tube furnace at 600°C for 2 hours while nitrogen gas flows. Following the carbon plating process, the material is formed into cathode-anode sheets and assembled into a cylindrical battery cell in the glove box. The results of characterized the sample findings the potential difference ranges for Cyclic Voltammetry (CV) are (0.8-2.7 and 3 - 4.6 V), Charge Discharge (CD) with a range of potential difference (0.9 - 2.4 V), respectively, and the speeds ranges are 0.1C and 0.05 mA (0.1 C), 3.3V-4.6V.

Keywords: $Li_4Ti_5O_{12}$, $LiMn_2O_4$, Charge Discharge (CD), Cyclic Voltammetry (CV), Solid State Reaction Method.

1 Introduction

Nowadays, LIB (Lithium Ion Battery) has been widely applied in mobile phones, notebook computers and other portable electronic devices. because this type of battery has many advantages including light weight, high energy density, high operating voltage, environmental friendliness, and long cycle life. However, for a long time, the safety of LIB (Lithium ion battery) has been one of the main issues related to its application. Graphite is the main source of anode material for commercialized LIB (Lithium ion battery). In the charging and discharging process, lithium dendrites are gradually formed on the graphite surface because Li^+ enters and does not enter it [1]. However, graphite has a safety problem when used, namely graphite will experience the formation

S. Hadi et al. (eds.), *Proceedings of the 5th International Conference on Applied Sciences, Mathematics, and Informatics (ICASMI 2024)*, Advances in Physics Research 13,
https://doi.org/10.2991/978-94-6463-730-4_4

of lithium dendrites which will cause an explosion or fire. So for other alternatives, other materials are given to replace graphite as the anode, namely $Li_4 Ti_5 O_{12}$ [2].

Lithium Titanate ($Li_4Ti_5 O_{12}$/LTO) has several advantages, namely LTO has a higher working voltage of 1.55 V vs Li / Li^+, far above the voltage for the formation of the interfacial solid electrolyte layer (SEI) and the growth of Lithium dendrites (at a voltage of ~ 0.8 V), thus ensuring battery safety when used. LTO is included in in safe, cheap, and thermally stable materials. For other advantages, LTO is known as a *"zero strain" material* [2]. In addition, $Li_4Ti_5O_{12}$ is a promising material to replace graphite as an anode material for Lithium Ion Batteries [3]. However, LTO also has disadvantages including low electron conductivity in the range of 10^{-13} Scm^{-1} and low diffusion coefficient in the range of 10^{-8} $cm^2 S^{-1}$. This weakness causes high polarization when used at high current densities, therefore it is necessary to overcome these shortcomings [4].

LiMn2O4 (LMO) is materials used as cathodes in solid lithium batteries, Lithium manganese oxide as the most favorite cathode material used because it is cheap, environmentally friendly and easy to synthesize. The advantages of Lithium manganese oxide have a host in three dimensions, so that the direction of the crystals that intersect between grains does not affect much [5], has high chemical stability properties, has profile characteristics with very good voltage, relatively cheap and safe [6]. However, lithium manganese oxide has disadvantages where it has a low level of capability, this is due to the low electronic conductivity of manganese oxide, and low coulomb efficiency.

Both LTO and LMO have the disadvantage of low electronic and ionic conductivity. This problem can be overcome by applying a carbon layer on the surface of LTO and LMO. Carbon on the surface of the active material can act as an electron path to the current electrons. In addition, carbon has electrical and ionic conductivity, so carbon layers have been widely used to improve interphase chemical bonds [7] Carbon coating is used to increase electronic conductivity. Therefore, in this study, LTO and LMO materials that function to serve carbon will be fabricated using the solid-state reaction method.

The *solid state* method has several advantages such as a simple, inexpensive synthesis path, and ease of commercial application. Based on several studies, this study will conduct fabrication of Li4Ti5O12 / C and LiMn2O4 / C battery cells synthesized by the solid state reaction method.

2 Research Methods

2.1 Tools and materials

The materials used in this study include LiOH.H2O (technical, Germany), TiO2 (technical, Germany), *PVDF* (technical, Yin Li Gelon China), *Acetylene Black* (technical, MTI-China), NN *Dimetyl Acethamide* pro analis (sigma Aldric), *Carbon Super-P*, *Lithium Ferro Phosphate* (LFP), electrolyte fluid, *positive aluminum terminal*, *negative nickel terminal*, *casing*. While the tools used in this study include electric scales, *mixer*

machines, *glove boxes*, *press machines*. Material characterization is carried out by testing WBCS3000S (Wonatech, Korea) for *cyclic voltammetry* and *charge discharge tests*.

2.2 Experimental Procedure

Synthesis of LTO and LMO. The synthesis of $Li_4Ti_5O_{12}$ was carried out using the *solid state reaction method* with raw materials $LiOH.H_2O$ and TiO_2. Each material was weighed based on the following stoichiometric equation calculation:

$$4LiOH.H_2O + 5T_iO_2 \rightarrow Li_4Ti_5O_{12} + 6H_2O \quad (1)$$

The raw materials were mixed homogeneously and milled for 4 hours with a planetary ball mill (PBM) at a speed of 20 *rpm*. The milling results were then sintered at a temperature of 850 ° C for 4 hours in a free air atmosphere. The $Li_4Ti_5O_{12\ powder}$ from the sintering was ground and sieved with a 400 mesh sieve. For the carbon coating process, 5 wt.% Super-P Carbon was mixed with L TO powder and then ground until black. Then the mixture was pyrolyzed at a temperature of 600 ° C for 2 hours under conditions of nitrogen gas (N_2).

The synthesis of $LiMn_2O_4$ was carried out by using raw materials $LiOH.H_2O$ and MnO_2 through the *solid state reaction* method, with stoichiometric calculations:

$$4LiOH.H_2O + 8MnO_2 \rightarrow 4LiMn_2O_4 + 6H_2O + O_2 \quad (2)$$

The materials were mixed and homogenized using a mortar then milled for 4 hours. The mixture was then sintered at a temperature of 800˚C for 4 hours. Carbon Super-P as much as 5% was mixed with $LiMn_2O_4$ powder then ground until black. Then the material is sintered at a temperature of 600 ° C for 2 hours under conditions of nitrogen gas (N_2).

Anode and Cathode Sheet Manufacturing. Li4Ti5O12 |C anode sheets and LiMn2O4 |C cathodes was carried out using the *doctor blade method.* The active material powder (LTO anode and LMO cathode) was mixed with additives , namely PVDF and AB with a composition of 85:10:5 into the *N,N-DMAC solution* until *a slurry was obtained* . The coating process on Cu and Al foils, each anode and cathode, with a thickness of 100 μm, a length of 80 cm and a width of 10 cm. Then dry in an oven at a temperature of 80 o C for 60 minutes and LTO anode sheets and LMO cathodes were formed.

Assembling Process. the experiment using this assembling process.

Battery Performance Test. *Coin cell* battery cells were subjected to *Cyclic Voltammetry* with a voltage of 0.8-2.5 V and a *scan rate* of 100 mV/s and *charge-discharge* with a voltage of 1-3.5 V. CD testing was only carried out at a speed of 0.1 C.

3 Results and Discussion

3.1 *Cyclic Voltammetry* (CV) testing on LTO and LTO/C

Cyclic Voltammetry (*CV)* test was carried out in half-cell conditions use a *coin cell* as a sample . In this test, LTO which acts as an anode is paired with lithium metal which acts as a cathode because its voltage is lower than LTO. The *CV test result data* obtained as a curve that illustrates the relationship between voltage (V) as *input* with current (I) as *output* at a scan rate variation *of* 100 μV/s and has a potential range of 0.8 V-2.5 V. CV LTO and LTOC test result curves can be seen in Figure 1.

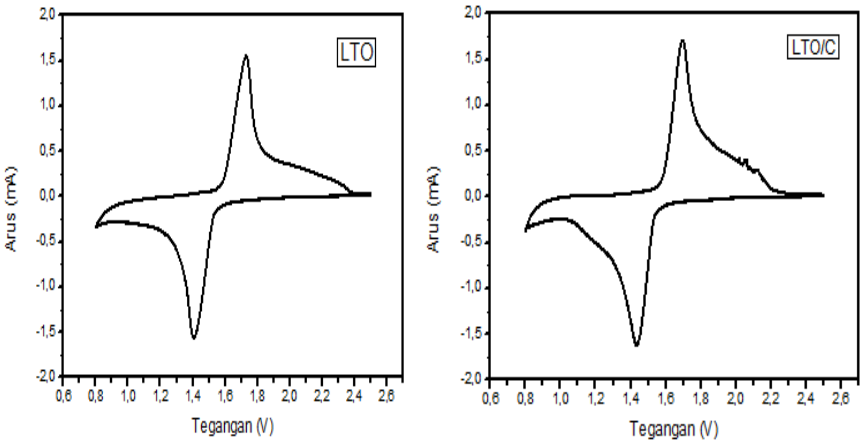

Fig. 1. *Cyclic Voltammogram* Curve LTO and LTO/C.

The anodic peak on the curve indicates the oxidation process, whereas the cathodic peak indicates the reduction process. Each peak on the curve points higher. The oxidation process occurs during *charging* , namely when lithium ions move from the cathode (Li metal) towards the cathode (LTO), while the reduction process occurs during *discharging* , namely when lithium ions move in the opposite direction, from the anode to the cathode. The process of lithium moving from the anode to the cathode or vice versa is called the intercalation and de-intercalation process of lithium ions. The presence of a pair of oxidation-reduction peaks indicates that the process is *reversible* or can be recharged. Can be seen in Figure 1 *Cyclic Voltammogram Curve* on LTO/C has a higher peak current compared to Figure 1 *Cyclic Voltammogram* Curve on LTO. This is due to the addition of carbon to LTO/C so that the current value is higher than LTO.

The addition of carbon to LTO/C also causes a phase difference, namely the LTO phase and the Anatase phase.To determine the value of the lithium diffusion coefficient, you can use the Randles – Sevcik equation:

$$DLi = \frac{Ip^2}{2.659\,x\ 10^5\,(n^{1,5})A^2\,C^2 v} \quad (3)$$

For n is the number of electrons per molecule (3), A is the surface area (2.0096 cm ^{2}) , C is the concentration of Li ions (0.00437 mol/cm ^{3}) , D is the diffusion coefficient of Li ions (cm ^{2}/S) , v is the scan rate (V/s) , Ip is the peak current (A).

Table 1. Oxidation, Reduction, and Polarization Voltages of Each Sample.

Sample	V Oxidation (V)	V Reduction (V)	Ip Oxidation mA	Ip Reduction mA	Doxidation cm2 / s	Reduction cm2 / s	V polarization (V)
LTO	1.72	1.40	1.55	1.53	1.05x10 - 10	1.04x10 - 10	1.52
LTO/C	1.70	1.42	1.67	1.60	1.13x10 - 10	1.08x10 - 10	1.53

Table 1. From Table 1 it can be seen that the L TO sample is divided into 2, in the LTO/C sample the polarization voltage greater than the LTO sample , this is due to the addition of carbon to the LTO/C sample so that the polarization voltage of LTO/C increases , if the polarization voltage is large it will cause the battery performance to be less good. This can also happen because the thicker the layer of active material, the greater the polarization voltage. The effect of increasing the amount of active material in the battery cell causes a lot of energy required for activation so that the diffusion distance of Lithium ions is longer. In Table 1, the diffusion coefficient of LTO/C is greater than that of LTO, this is influenced by the addition of carbon to the LTO/C sample so that the coefficient value increases.

3.2 *Cyclic Voltammetry* (CV) testing on LMO and LMO/C

Electrochemical characterization using CV *(Cyclic Voltammetry)* , using the WBCS 3000 tool. The CV *(Cyclic Voltammetry) test* aims to see the oxidation and reduction reactions formed in the sample. The data obtained is in the form of a voltammogram graph, namely the potential curve (V) against current (A). This test was carried out with a scan rate of 0.0001 V/s and had a potential range of 3 V - 4.5 V so that the obtained Graph 2 is as follows:

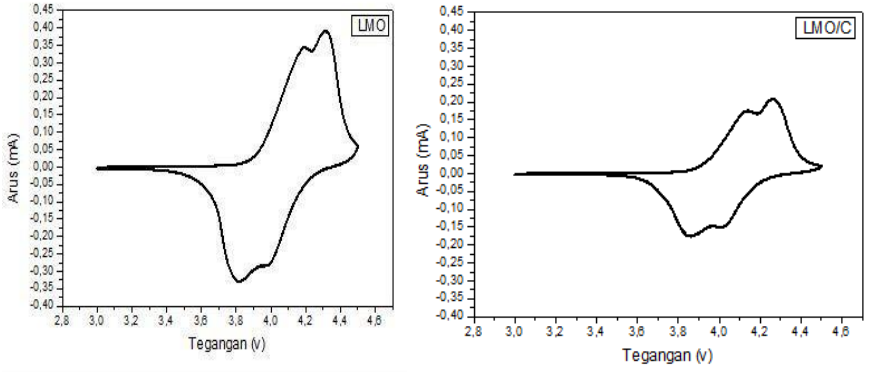

Fig. 2. Test Result Graph *Cyclic Voltammetry* Cathode of LMO and LMO/C.

Based on Figure 2 testing *Cyclic Voltammetry of LMO* and LMO/C Cathode indicates the presence of oxidation and reduction reactions. This is indicated by the emergence of a pair of oxidation and reduction peaks. The presence of a pair of oxidation-reduction peaks indicates a reversible reaction so that the sample is *rechargeable* so that it can be used to make secondary batteries. This pair of oxidation and reduction peaks occurs because manganese (Mn) has oxidation numbers of +3 and +4.

There are two oxidation peaks and two reduction peaks in every oxidation-reduction reaction. The oxidation reaction is shown in the peak that leads to above while the reduction reaction at the peak leads to below. In the picture 2 shows that each sample has excellent electrochemical performance, this is demonstrated by the formation of two oxidation peaks and two reduction peaks formed. However, the LMO/ C sample shows lower oxidation and reduction peak currents compared to the LMO sample. So that the LMO/ C sample has a fast electrochemical reaction and causes the intercalation or de-intercalation process of Lithium ions to take place at a faster rate as well. The peak on the LMO /C sample shows a sharper peak so that it has a greater capacity than the other samples. This happens because the amount of active material used is greater. From this test, it shows that the more active material used, the greater the current response. This is because there is a carbon coating on the active material of Lithium Manganese Oxide which is involved in the reduction-oxidation process.

Table 2. Peak Parameters of Cyclic *Voltammetry* Test Results on LMO and LMO/C Samples.

Sample	V_{ok1} (v)	V_{ok2} (v)	V_{re1} (v)	V_{re2} (v)	V_{po11} (v)	V_{pol2} (v)	I_{p1} (mA)	I_{p2} (mA)	P_1 (vmA)	P_2 (vmA)
LMO	4.19	4.33	3.79	3.98	0.4	0.35	0.34	0.38	1,425	1,645
LMO /C	4 ,12	4.27	3.86	3.99	0.26	0.28	0, 17	0.20	0.7004	0.854

Based on Table 2 shows that the presence of carbon coating on LMO causes polarization voltage, peak current in oxidation and reduction to decrease due to the use of large amounts of carbon. Where if the polarization voltage is large, it will cause battery performance to be less good. In addition, it can also be caused by the thicker the active material layer, the greater the polarization voltage. The effect of increasing the amount of active material in the battery cell causes a lot of energy to be needed for activation so that the diffusion distance of Lithium ions is longer. Therefore, the presence of carbon coating on the active material of LMO can increase battery conductivity so that Lithium ion batteries with LMO/C cathodes have better quality compared to LMO cathodes.

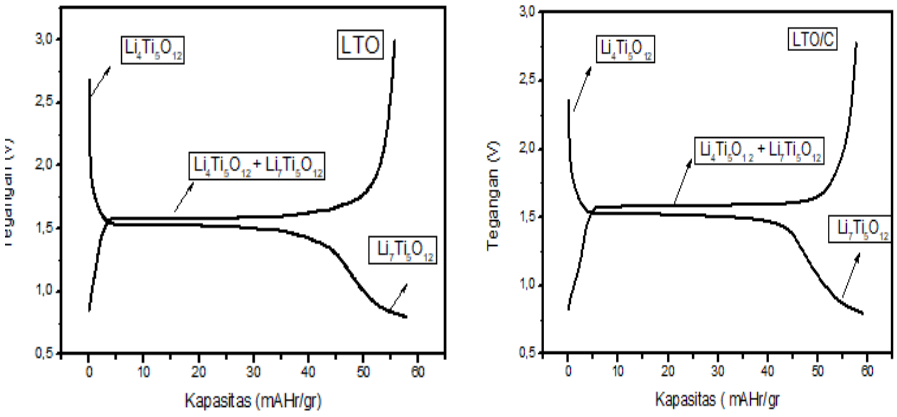

Fig. 3. Charge *Discharge* Curves a. LTO and b. LTO/C.

Figure 3 shows the results of the *charge-discharge test* of the LTO sample with a current of ±0.1 mA with a voltage of 0.8-3.0 V. Based on the graph, a *Charge graph is produced,* namely a graph that experiences an increase in voltage, and a *Discharge graph* is a graph that experiences a decrease in voltage. It can also be seen that there is a flat graph shape *on* the LTO and LTO/C voltages, there is a phase difference with the addition of 3Li and on the *charge* /discharge graph the phase is only $Li_7Ti_5O_{12}$, the difference in the flat graph *on* the LTO and LTO/C voltages is not too significant, this indicates that the addition of carbon does not cause a significant increase in working voltage with a working voltage of 1.5 V on the LTO and LTO/C samples. The *charge-discharge curve* above shows the characteristics of the use of LTO anodes in the tested *coin cells*. Figure 3 shows that the addition of carbon will increase the capacity of the LTO sample.

Table 3. Peak Parameters of *Charge -Discharge* Test Results on LTO and LTO/C Samples.

No	S ample	Capacity		Vpol (mV)	Effi-ciency Coulomb (%)
		Charge (mA H/gr)	Discharge (mA H/gr)		
1	LTO	55	60	47	109.09
2	LTO/C	57	60	52	105.26

From Table 3 It can be seen that the capacity of the LTO/C sample is 57 mAh /gr for the *charge capacity* and 60 mAh /gr for the *larger discharge* capacity . compared to LTO samples with *charge capacity* 55 mAH/gr and *disc harge* 60 mAH/gr. The LTO sample has a polarization voltage of 47 V and the LTO/C sample has a higher polarization voltage of 52 V. The smaller the polarization value, the better the battery cell performance. From the coulomb efficiency value between LTO and LTO/C, the value is not too different, the ideal coulomb efficiency value is above 100%, in the LTO and LTO/C coulomb efficiency table values have passed 100%, meaning that the sample test on the coulomb efficiency above is ideal. The Coulomb efficiency shows a balance between *charging* and *discharging* so that the battery has greater power in the CD test on LTO and LTO/C.

3.3 *Charge-Discharge* (CD) testing on LMO and LMO/C

Charge-Discharge (CD) testing is carried out to determine the ability of battery cells to store energy capacity. The energy capacity is expressed in units of mA Hr / gram or A Hr / gram. *Charge - discharge measurements* are carried out with *a current* of ± 0.06 mA with *a* potential range of 3.46 V- 4.46 V. In the charge-discharge test *, one cycle* is equal to one *charge process* or the process of a redox reaction by releasing Lithium ions and electrons to the anode, and one *discharge process* or the process of a reduction reaction by entering Lithium ions and electrons to the cathode. MnO4 has an octahedral crystal structure that shows two plateau voltages with *charge* and *discharge plateau voltages* of 4.0 V and 4.1 Volts.

The two plateaus reflect 1-phase and 2-phase reactions as in the following reaction equation:

$$LiMn2O4 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li_{1-x}Mn_2O_4 + xLi^+ + xe^- \quad (4)$$

$$Li_{1-x}Mn_2O_4 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Mn_2O_4 + (1-x)Li^+ + (1-x)e^- \quad (5)$$

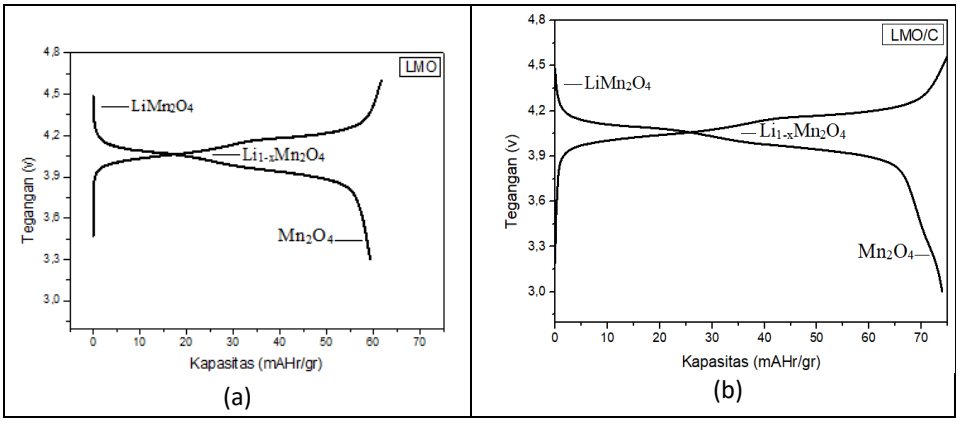

Fig. 4. Charge-Discharge graphs of samples (a) LMO and (b) LMO/ **C**.

Based on Figure 4, it can be seen that the LMO and LMO/C samples have stepped working voltages due to the formation of oxidation and reduction peak pairs in Figure 4.1. The left oxidation and reduction peak pair occurs because manganese (Mn) has an oxidation number of +4. While the right oxidation and reduction peaks occur because manganese (Mn) is +3. The LMO sample has a working voltage of 4.067 Volts. While the LMO/C sample has a working voltage of 4.058 Volts. This means that the LMO/C cathode has a smaller working voltage than the LMO cathode.

Table 4. Charge-Discharge Analysis Data on LMO and LMO/C Samples,

No	Sample	Capacity		Efficiency
		Charge (mAh)	Discharge (mAh)	Coulomb (%)
1	LMO	0, 403	0, 387	96.03
2	LMO/ C	0, 602	0.591	98.17

Based on Table 4 shows that the LMO /C sample has a larger *charge-discharge* capacity value , namely the *charge capacity* of 0.602 mAh and a *discharge capacity* of 0.591 mAh. While the LMO sample has a lower capacity value , namely a *charge* capacity of 0.403 mAh and a *discharge capacity* of 0.387 mAh. Both samples have good Coulomb efficiency values because they are close to 100%. Where the LMO/C sample has a higher Coulomb efficiency value of 96.03%. Thus, the Coulomb efficiency shows a balance between *charging* and *discharging* so that the battery has greater power. Thus, the presence of carbon coating causes its capacity to increase.

Table 5. Analysis Data on LMO and LMO/C Samples.

Sample	Mass	Thick-ness	Voltage (v)		Vpolarization
	(gr)	(mm)	Charge	Discharge	(v)
LMO	0.008	0.1	4,182	3,948	0.234
LMO/ C	0.00456	0.1	4,161	3,958	0.203

Based on Table 5 shows that the LMO sample has a greater polarization voltage, namely of 0.234 Volts. While the LMO/C sample has a lower polarization voltage of 0.203 Volts. The polarization voltage itself is the difference between the *charge voltage* and the *discharge voltage*. The smaller the polarization value, the better the battery cell performance. Thus, the presence of carbon coating on the LMO causes its polarization voltage to decrease. So that the LMO/C cathode has better battery cell performance compared to the LMO cathode.

4 Conclusion

The active materials of LTO/C and LMO/C electrodes were successfully made using the *solid state reaction method* with the percentage composition of LMO, PVDF and Super-P carbon materials, namely 85:10:5. The sheet analysis of LTO/C and LMO/C electrode sheets were successfully fabricated using the *solid state reaction method* with the percentage composition of LMO, PVDF and Super-P carbon materials of 85:10:5. The results of the CV and CD tests show that each polarization voltage decreases, namely in LTO/C by (1.52 V-1.53 V), while in LMO/C it is (0.4 V-0.26 V), (0.35 V-0.28 V) and (0.234 V-0.203 V). The addition of carbon provides good coulombic efficiency in the LTO sample of 109.09% and LTO/C 105.26%. Furthermore, the characterization of *(Cyclic Voltammetry*) CV test results show that the lithium diffusion value increases with the addition of carbon to the LTO diffusion of $1.05x10^{-10}$ - 1.0 4 $x10^{-10}$ become $1.08\ x10^{-10}$ - 1, 13 x1 0^{-10} on LTO/C.

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