

Effect of Acetylene Black Content in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Xerogel Solid-State Anode Materials on Half-Cell Li-ion Batteries Performance

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Abstract. The effect of Acetylene Black (AB) additive contents in lithium titanate/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode on Li-ion Batteries performance is studied in this work. The LTO active material for Li-ion batteries anode was successfully synthesized using sol-gel method to form TiO_2 xerogel continued by mixing process with LiOH in ball-mill and then sintered to obtain spinel LTO. The LTO powder is characterized by X-Ray Diffraction (XRD), scanning electron microscopy-Energy Dispersive Spectroscopy (SEM-EDS), and Brunauer–Emmett–Teller (BET). The spinel LTO and TiO_2 rutile were detected by XRD diffractogram. The LTO powder is in the form of agglomerates structure. This powder then was mixed with PVDF binder (10%wt) and AB additives with various amount from 10%wt (LTO2 Ac-1), 12%wt (LTO2 Ac-2), and 15%wt (LTO2 Ac-3) of total weight solid content to form electrode sheet. Half-cell coin battery was made with lithium metal foil as a counter electrode. Cyclic voltammetry (CV), Electrochemical-impedance spectroscopy (EIS), and charge discharge (CD) test used to examine the battery performance. The highest resistance value is obtained in LTO2 Ac-3 sample with 15%wt of AB. It might be caused by the formation of side reaction product on electrode surface at initial cycle due to high reactivity of LTO2 Ac-3 electrode. The highest initial capacity at CV test and CD test was obtained in LTO2 Ac-1 (10%wt AB) sample, due to the best proportion of active material content in the compound. While, in the charge-discharge test at high current rate, the best sample rate-capability performance belongs to LTO2 Ac-3 sample (15%wt AB), which still have 24.12 mAh/g of discharge capacity at 10 C with 71.34% capacity loss.

1. Introduction

Battery is one of the energy storage medium that have a good capacity and energy densities performance. It should have a good rechargeable performance and more safe to use as well. However, Li-ion Batteries (LiB) to be used for electric vehicle (EV) needs to have high power density as one of the basic properties [1].

On their development, graphite is selected as anode materials in LIB. However the poor cyclic life performance of the graphite, makes the LIB with graphite based anode is less durable. It can be caused



by unavoidable solid electrolyte interface (SEI) film formation on electrode surface and thickening on the graphite anode, lithium plating while charging at low temperature, and other side reaction [2].

Recently, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) based anode materials is considered to substitute the graphite based anode, due to high safety, and excellent cyclic performance, compared to graphite based anode materials [3]. LTO based anode has a zero strain properties, no SEI film formation, fast charging ability, and good thermal stability, therefore makes LTO based anode has a long cycle life, high safety, and can be implemented for EV LIB anode materials [3]. However, LTO has a low intrinsic conductivity ($10^{-9} \text{ S.cm}^{-1}$) [4]. Thus, a conductive agent additives must be added into LTO mixing slurry to improve the conductivity of anode materials. Acetylene Black (AB) is often used for conductive agent additives to improve the conductivity of electrode.

In this research, the LTO compound prepared by sol gel process to produced TiO_2 anatase and then by a solid-state process to form $\text{Li}_4\text{Ti}_5\text{O}_{12}$ mixed with AB with various contents, then it is assembled into a half cell LiB to observed the influence of Acetylene Black (AB) content to the performance of the battery cell.

2. Experimental

2.1 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder preparation and characterization

LTO powder is synthesized through a sol-gel process, calcination, ball-milling, and sintering process. Sol gel process is started by making primary solution that contain titanium tetra-n-butoxide (Kanto chemical, Co. Inc.) and ethanol (Merck) and mixed that with secondary solution that contains ethanol and distilled water. Mixing process is carried out in magnetic stirring for about 2 h until gel formed. The gel is then allowed to dry in room temperature for about 12 h to form xerogel. Calcination is carried out at 300°C for 2 h to make anatase TiO_2 . The high energy ball milling (HEBM) is used to mix anatase TiO_2 with LiOH for 1 h in an intermittent way. Sintering process is then carried out at 750°C for 3 h to form spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) that ready to be used as an active electrode material.

The morphology of sample was observed by scanning electron microscope (SEM). The particle size of sample was measured with Image J software. Phase identification was examined by X-ray diffraction analysis (XRD) using Cu $K\alpha$ radiation in an angular range 2θ from 10° to 100° .

2.2 Cell assembly and testing

The half-cell coins battery were assembled and tested to observe the electrochemical properties and performance of LTO compound, in which LTO was prepared as cathode active material, lithium foil as an anode, and LiPF_6 1M as an electrolyte. While, DMAC, Acetylene Black (AB) and PVDF were used as solvent, conductive additive and binder, respectively. The compositions were prepared with fixed binder content of 10%wt, while the LTO and AB contents were 10%wt for LTO2 Ac-1, 12%wt for LTO2 Ac-2, and 15%wt for LTO2 Ac-3. All of these material then mixed by magnetic stirrer at 300 rpm at 70°C for 2 h to obtain slurry.

The slurry was coated at copper foil current collector by electrode coater (doctor blade) with $200 \mu\text{m}$ of wet thickness to form $100 \mu\text{m}$ of dry thickness. Coated Cu foil was then dried at doctor blade at 80°C and cut to form coin shape. The assembly process was carried out in a glove box filled with high purity argon gas.

Cyclic voltammetry (CV), Electro-impedance spectroscopy (EIS), and Charge-discharge test were performed to evaluate the cell electrochemical performance.

3. Results and Discussions

3.1 Phase analysis of the LTO

X-ray Diffraction analysis was performed to analyze phases in LTO powder after sintering process. An expected phase in XRD pattern was spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, with smoothing by X-pert High Score Plus

software corresponds to JCPDS no 26-1198 as shown in Figure 1. From the result, a spinel LTO phase was successfully identified in six angle positions of 2θ .

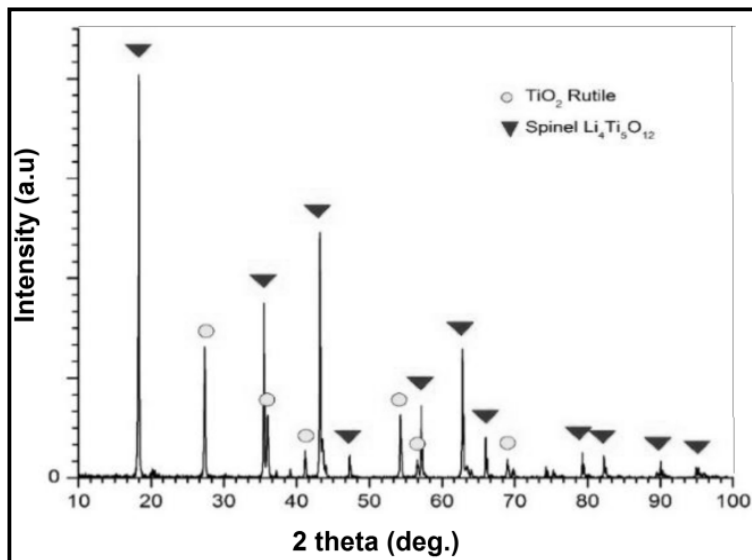


Figure 1. The XRD result pattern of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder by solid state synthesis.

The XRD result was not only identified a LTO pattern, but also TiO_2 rutile was presence in LTO powder. TiO_2 rutile identified with JCPDS no 01-076-0318. The presence of TiO_2 rutile in XRD pattern was caused by the unreacted TiO_2 anatase due to the loss of the Li^+ ion source during sintering process, and transform to TiO_2 rutile in high temperature of sintering process [5].

3.2 Structure and morphology of LTO

Structure and morphology analysis of LTO powder were conducted using scanning electron microscopy. The magnifications used in this work were 5000X, 10000X and 20000X to see the particle size and the presence of agglomerates.

Morphology of this LTO powder can be seen in Figure 2, with 5000X magnification, an agglomerate structure was seen. With the increasing size and quantity of agglomerates, it could lead to decreasing in the reactivity and capacity of sample as a consequence of decreasing the sample's surface area. The presence of more agglomerates is caused by a quite high sintering temperature (750°C). Sintering process at high temperature could induce diffusion phenomenon and promote the LTO particle clustering generated agglomerates formation [6].

LTO particle size measurement was conducted on the SEM micrograph of microstructure by Image-J software. An average size of LTO agglomerates particle is $4.22\ \mu\text{m}$ as obtained from Figure 2a. While for the average of all LTO particles shown in the micrograph is $0.73\ \mu\text{m}$ as obtained from Figure 2b and Figure 2c.

The material contain in EDS test was Titanium, Chlor, Carbon, Oxygen with Titanium compared Oxygen contain 21,9% : 78,1%.

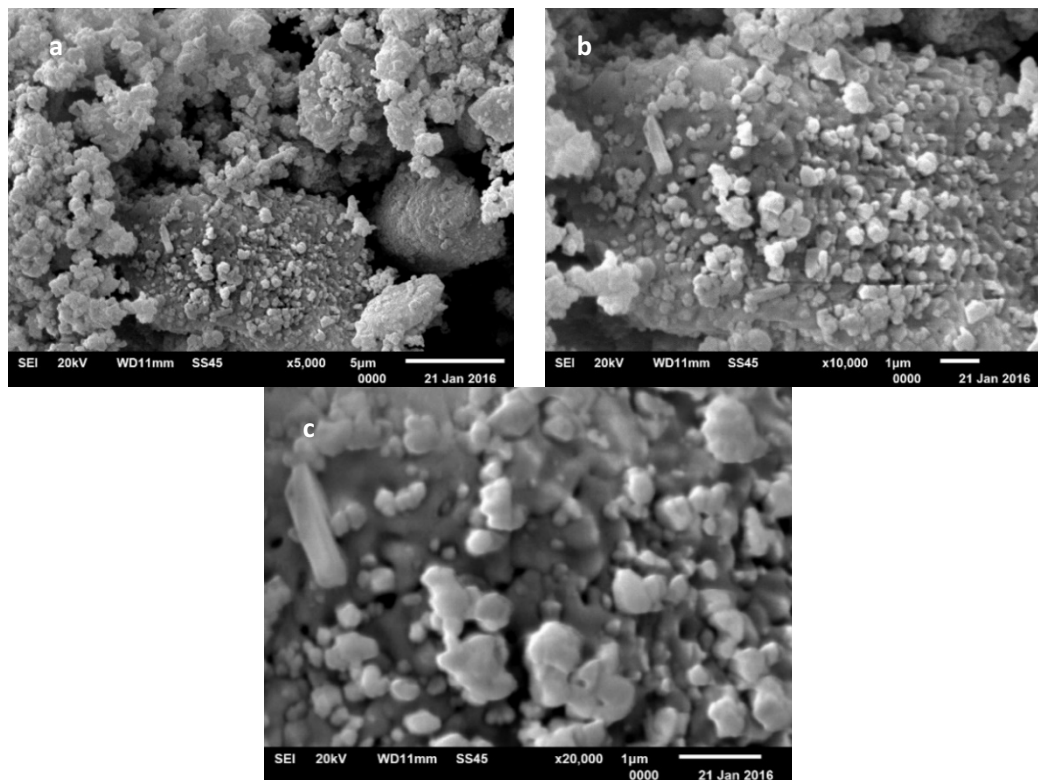


Figure 2. Microstructure of LTO by SEM test with magnification of a) 5000X, b) 10000X, and c) 20000X.

3.3 EIS characterization of LTO electrode

Conductivity is one of the most important properties of active materials for use in the battery electrodes. Effect of AB on the conductivity is measured by EIS to obtain the impedance (resistivity) level of the electrode. The EIS results could be seen in Table 1 and Figure 3. The results show that LTO2 Ac-3 (15%wt) has the highest resistivity value, the Nyquist semicircle of LTO2 Ac-3 has the longest diameter corresponds the highest value of R_{ct} . Meanwhile, the LTO2 Ac-2 has the lowest value of R_{ct} that would result in highest level of conductivity.

Table 1. Impedance result of the samples.

Sample	$R_e(\Omega)$	$R_{ct}(\Omega)$
LTO2-Ac1	4,440	51,660
LTO2-Ac2	12	41
LTO2-Ac3	10,100	62,500

The high value level of R_{ct} in LTO2 Ac-3 sample might be caused by side reaction product formed in the early cycle of LTO2 Ac-3 sample electrode surface. The presence of side reaction product in electrode surface would block lithium ion to reach electrode surface that makes resistivity value increased.

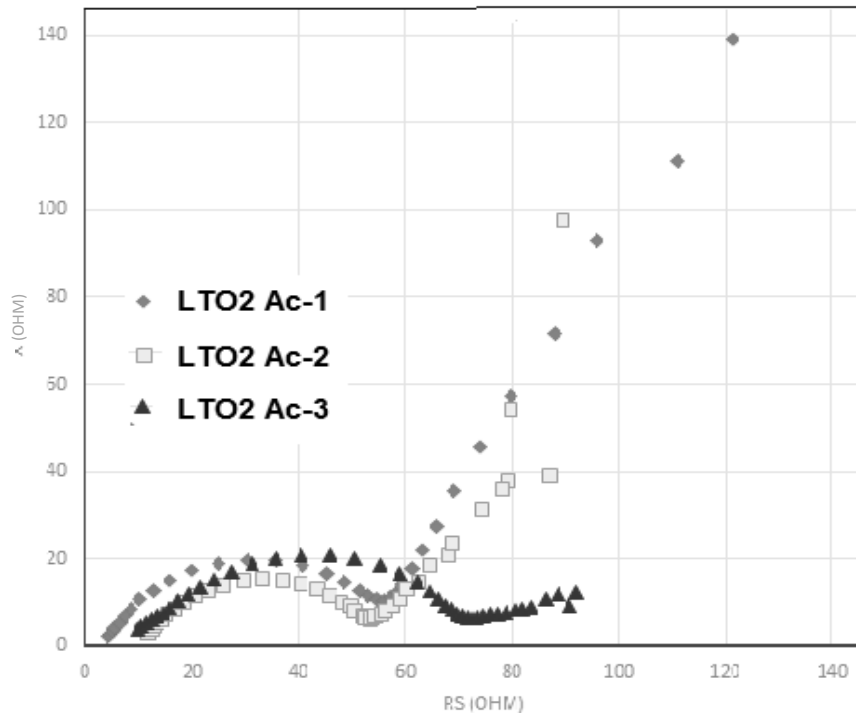


Figure 3. Nyquist semicircle-curve of the samples.

Side reaction products that formed at low cycle in LTO Ac-3 sample electrode surface might be caused by improving in electrode's reactivity due to highest content of AB. As the results, increasing reactivity would lead to a side reaction product formed even at low cycle and low rate. That phenomenon was also observed by Yan-Bing He, et al.[7]. He observed that resistivity value indicated more surface area and reactivity of electrode, the side reaction product became easier to form in early cycle and low current rate even at voltage value above 1V. This would be the reason to increased R_{ct} value at EIS test for LTO2 Ac-3 sample. This result is supported by the charge-discharge testing results.

3.4 Chemical performance by cyclic voltammetry

The cyclic voltammetry test is conducted to examine the electrochemical performance of the sample, such as: capacity, working voltage, and other chemical performance properties of electrochemical cell. Theoretically, LTO has 1.55V of cathodic voltage peak value vs. Li with 175 mAh/g of capacity [8]. Cathodic peak relates to the intercalation process of lithium to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to form $\text{Li}_7\text{Ti}_5\text{O}_{12}$. Meanwhile, the anodic peak relates to the de-intercalation process of lithium ion from $\text{Li}_7\text{Ti}_5\text{O}_{12}$ to form $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$) [9]. The results of CV test as shown in Figure 4 were obtained with 100 $\mu\text{V/s}$ scan rate and presented in Table 2 for more detailed data.

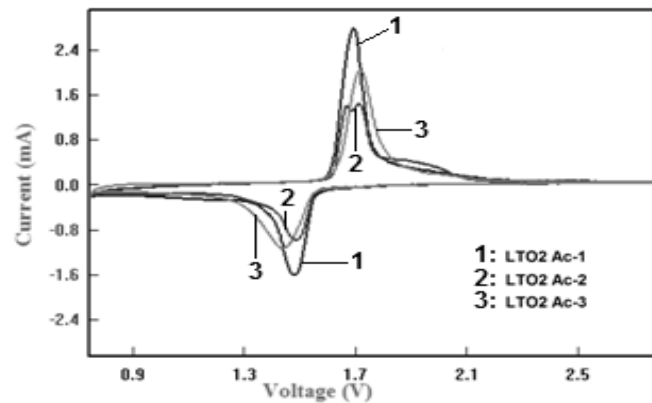


Figure 4. Cyclic voltammetry curve from sample.

Table 2. Capacity and working voltage of the samples.

	Capacity (mAh/g)	E^0 (V)
LTO2 Ac-1	129,710	1,585
LTO2 Ac-2	94,750	1,575
LTO2 Ac-3	83,350	1,573

For working potential, it was obtained by calculation using Eq.1 as follows [10]:

$$E^0 = \frac{E_{p,c} + E_{p,a}}{2} \quad (1)$$

The result in CV test shows that all of the sample has a similar working potential that similar to a LTO theoretical working potential, i.e: 1.55V for lithiation process and 1.56V for de-lithiation [11]. Thus, AB content has no effect improved the working potential of the LTO electrodes.

The graph in Figure 4 also informs a reversibility of the reactions of this LTO. The results show that all of the samples have a pair of peaks, reduction and oxidation peak of a reversible reaction[12].

Specific capacity data is also provided by CV test. As shown in Table 2, LTO2 Ac-1 sample who has smallest AB content, has the highest value in the specific capacity, i.e: 129.71 mAh/g. Besides, the LTO2 Ac-3 which contains highest AB content has the lowest value of the specific capacity, i.e: 83.35 mAh/g. The decrease of active material content (LTO) as increasing of AB content and formation of side reaction product is predicted to be the reasons of this phenomenon that consume a part of capacity in more reactive electrode [7]. This data was supported by the EIS results.

3.5 Charge-discharge test results

Charge-discharge test was performed to analyze battery performance at different given current rate. This test began from the current rate of C/3 until 10C. The results of the influence of AB content in CD test results in LTO's electrode are presented in Figure 5 and Figure 6.

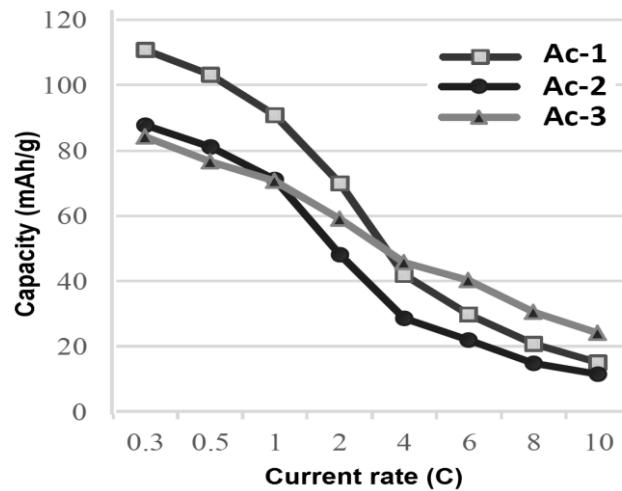


Figure 5. Discharge capacity vs. current rate.

Increased current rate would decrease the instant capacity of the battery. As shown in Figure 5, there is a relation between AB content to rate-capability in battery. The increased of AB content would increase the rate capability of battery sample. LTO2 Ac-3 sample, with highest AB content, has the best rate-capability. Although the sample has worst initial capacity, at 4C current rate, it will surpass all of capacity of other sample and less steep slope curve than the other samples. In 10C, LTO2 Ac-3 sample reaches 24 mAh/g, while, LTO2 Ac-1 and LTO2 Ac-2 only have the capacity of 15.14 mAh/g and 11.57 mAh/g, respectively. It shown that the optimum AB content is depend at the current rate that is applied to the electrodes. When 0.3C until 4C current rate applied in the electrodes, the optimum composition was LTO2 Ac-1. After 4C until 10C, the optimum composition was LTO2 Ac-3 who highest percentage value of AB. This could indicate that AB acts to increase stability, conductivity, and also electrode's reactivity so that sample has better rate-capability or high power density. It is also confirmed that LTO2 Ac-1 sample with smallest AB content has a steepest slope in discharge capacity vs. current rate curve indicating that this sample has the lowest rate-capability. Thus, LTO2 Ac-1 composition is for highest energy density. More detailed data was provided in Figure 6, Figure 7, Figure 8 and Table 3.

Table 3. Capacity percentage at actual discharge rate.

Current Rate	LTO2 Ac-1	LTO2 Ac-2	LTO2 Ac-3
4C	37.76%	32.47%	54.22%
10C	13.65%	13.17%	28.66%

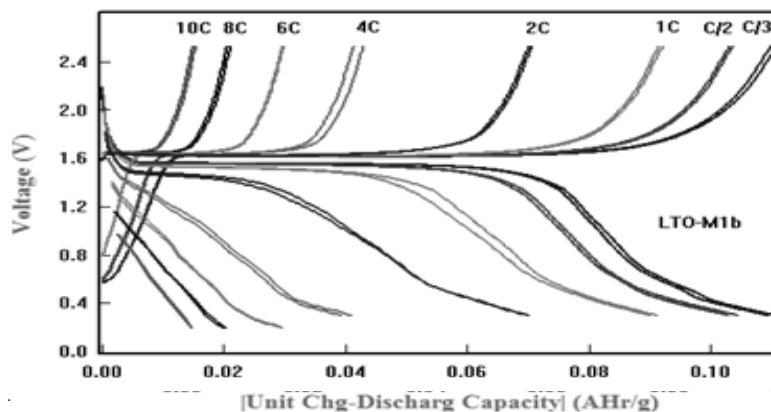


Figure 6. Charge-discharge curve of sample LTO2 Ac-1 (10wt% AB).

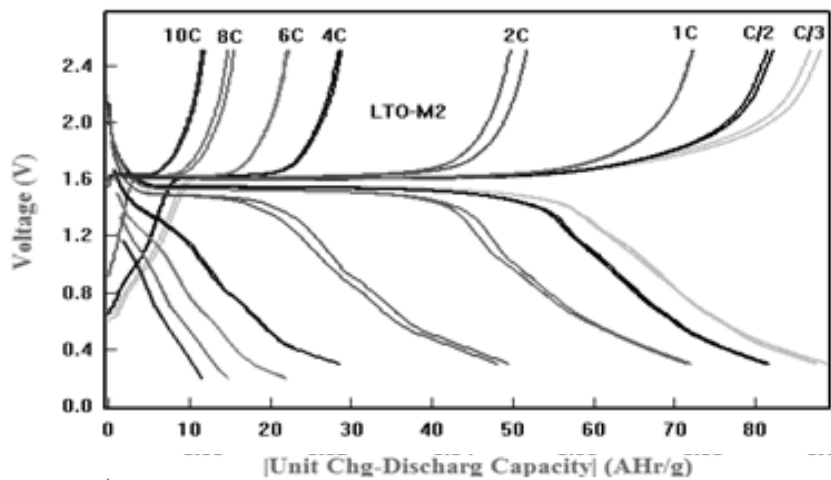


Figure 7. Charge-discharge curve of sample LTO2 Ac-2 (12wt% AB).

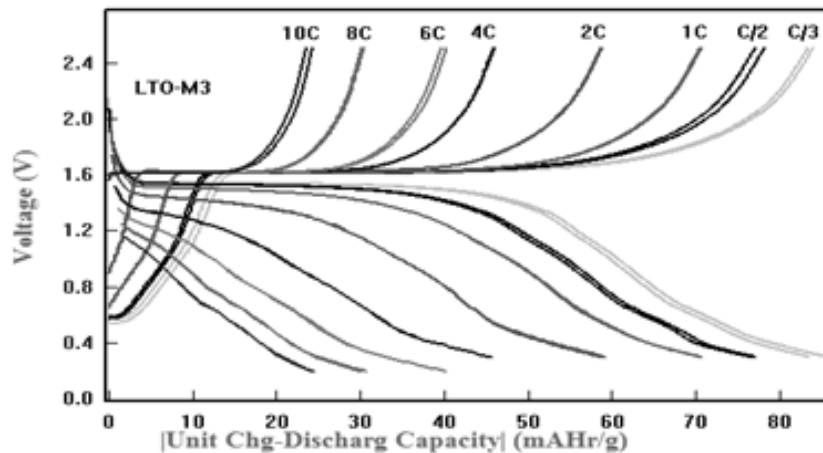


Figure 8. Charge-discharge curve of sample LTO2 Ac-3 (15wt% AB).

Low initial capacity in LTO2 Ac-3 sample might be caused by side reaction product at electrode's surface present at low cycle and low rate that consumes the initial capacity of the LTO2 Ac-3 sample. This phenomenon occurred because of AB content increased, which would increase the reactivity of the electrodes. With high reactivity, side reaction product would form easier at low rate and low cycle condition. Because of side reaction product formation has been ended at low cycle and low rate. They will not form at further rate and cycle anymore, and hinder the rate capability of the sample. Meanwhile, the less reactive electrode's is stable at initial rate and cycle, but less stable at further rate and cycle because of the formation of side reaction product at further cycle and rate that would decrease the capacity of samples in CD test [7].

4. Conclusion

Active material in the form of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structures was successfully processed by sol-gel continued with solid-state methods, and possessed agglomerates micro structure. The phase obtained has spinel LTO pattern and with little amount of TiO_2 rutile analysed by XRD. Electrochemical performance obtained from EIS test show that LTO2 Ac-3 has the highest R_{ct} value, it is predicted that the side reaction product was formed at electrode's surface. In the CV test, it is found that LTO2 Ac-1 sample has the highest specific capacity value. Charge-Discharge test, show that LTO2 Ac-3 sample has the best rate-capability and supported by CV and EIS test result. Therefore, it concluded that the effect

of acetylene black content on LiB battery's electrode composition is not significantly improved the conductivity of anode materials as the reactivity of the electrode is proportional to content of AB, and with the proper AB amount, it will obtained the best performance of LiB electrode composition. In this research, it is concluded that the optimum percentage of AB was depends on by current applied to the electrodes. For application at higher current rate (4C and above) or high power density, LTO Ac-3 has best performance. But for high density application in lower current rate (below 4C), LTO Ac-1 has best performance. Overall, considering the high initial specific capacity, LTO2 Ac-1 composition would be regarded as the optimum composition in this research. Finally, the power density or high-rate capability of this LTO compound is considered as well above the anode requirement of Li-ion batteries for electric vehicle.

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