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Z A I Supardi

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Electrochemical performances of lithium-ion coin cell based on Li₄Ti₅O₁₂ anode

Z A I Supardi^{1*}, Munasir¹, A I Najihah¹, S Priyono² and B Prihandoko²

¹Physics Department, Universitas Negeri Surabaya, Indonesia 60231

²Research Centre for Physics, Indonesian Institute of Science (LIPI), Serpong, Banten, Indonesia, 15314

*E-mail: zainularifin@unesa.ac.id

Abstract. Recently many portable devices need electrical energy which instant and high capacity. Lithium-ion battery is one of very popular as mobile electrical energy source for them. This experiment focused to elaborate the electrochemical performances of Lithium-Ion (LI) coin cell based on $Li_4Ti_5O_{12}$ (LTO) Anode with variation of calcination holding time (2, 4) and 6 hours) at temperature 900 $^{\circ}$ C. They are electrical conductivity, specific capacity and coefficient of ion diffusion. Sol-Gel method and doctor Blade technique were used to produce LTO anode material. Vacuum technique was used to assembly LI coin cell. Electrochemical Impedance Spectroscopy and Cyclic Voltammetry were used to measure the electrochemical performances of theses coin cells. The best result of these experiments showed that coefficient of ionic diffusion is 3.48×10^4 cm²/S, the specific capacity value is 304 mAh/g and electrical conductivity value is 6.87×10^{-3} S/cm. So, this experiment has shown strongly a prospective for application in the future to produced commercially lithium-ion coin cells

1. Introduction

Recently many devices need mobile electrical energy sources for supporting and help our life easily. Lithium-ion battery (LIB) in portable electronics and electric vehicles, there has been intense interest in developing advanced electrode materials with higher energy and power densities in recent years [1]. Many materials have been exploited as anodes based on different electrochemical mechanisms including intercalation, alloying, and conversion reactions [2-11].

The main problem is to get electrical energy sources which properties high energy density, higher output power, fast charging, support green environmental principle, small and light weight in size, and durable [12]. For this reason, LIB is the promising electrical energy sources for supporting mobile, lite and compact energy.

One of the important lite weight prototypes of LIB is coin cell. It can be assembled from LTO anode, lithium foil cathode, polypropylene separator, and PF_6 electrolyte [13]. They have many advantages to develop LI coin cell because it has good conductivity, higher energy capacity, easy and cheaper in fabrication, durable and full support to green technology.

Various popular methods are used to prepare battery anode, i.e. solid state method, hydrothermal route, solvothermal process, electrospinning deposition, microwave-hydrothermal method, and sol-gel method have been proposed by many researchers [14-18]. In this work sol-gel method, Doctor Blade and solid state reaction were used to prepare the anode material. Moreover, the electrochemical performances of LI coin cell are also carefully investigated.

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2. Experimental and Measurement

LI coin cell formation contained three stages, i.e. preparation of components, assembly process, and measurement of electrochemical performances. For detailing each stage is explained as follows.

2.1. Preparation Components LI coin cell

The main components of LI coin cell consist of anode, cathode, separator, electrolyte, and coin jacket. Anode material was prepared through three stages, i.e. formation of: (1) high purity LTO powder, (2) slurry, and (3) anode composite. LTO powder was prepared from Sigma Aldrich product lithium acetate (CH₃COOLi) 99.95%, tetra butyl titanate (Ti(OC₄H₉)₄) 97%, hydrochloric acid (HCl) 37% and ethanol (C₂H₅OH) from Merck product as solvent using sol-gel method with the special heat treatment [19]. The LTO powder were calcinated with variation of holding time 2 (LT192), 4 (LT194) and 6 hours (LT196).

Slurry was prepared from LTO powder, polyvinylidene difluoride (PVDF) and Super P (Carbon) with percentage ratio 80:10:10. They were dissolved and Stirred (250 rpm and 75°C) in N,N-Dimethylacetamide (N,N-DMAC). The slurry was superimposed to copper foil using doctor blade equipment with tape casting method. Then it was dried and cut which diameter 16 mm using special heat treatment [19]. Standard Lithium foil was used as cathode material (diameter 16 mm) and polypropylene as separator material with diameter size in 19 mm. Further, commercial electrolyte PF_{6} -EC:DEC was completed as LI coin cell components.

2.2. Assembly Process of LI coin cell

All of components above were assembled to be the coin cells in a glove box with argon environment with the structure: anode-separator-electrolyte-anode. These components were protected by metal jacket. Its complete structure as figure below.



Figure 1 Structure of one set LI coin cell [20]

2.3. Measurement of Electrochemical Performances

Electrochemical Impedance Spectroscopic (EIS) measurements were carried out with the frequency range 0.5 Hz to 20 kHz using the across voltage 0.1 volt. Cyclic Voltammetry (CV) was used to measure the redox cyclic of the process of intercalation/deintercalation of Lithium ion. Cyclic voltammogram curves were recorded from 0.0 to 3.0 V with a scan rate of 0.1 mV/s. Automatic Battery Cycler WBCS3000 Version 3.2 was used to measure Charge-Discharge (CD) with 0.1C rate.

2.3.1. Cyclic Voltammetry (CV)

CV measurement undertook by giving the voltage to the sample as input and adjusting it alternately in the 0-3 volt range with a scan rate variation of 50, 100, 150 and 200 mV/s and the amount of electric current flowing is recorded as output. Voltage and current data every second will form a graph called a

cyclic voltammogram and processed with the Automatic Battery Cycler WonAtech WBCS 3000 completed with software version 3.2. This CV data will show the reversibility of the redox process that occurs when the input voltage is applied to the coin cell and the lithium ion diffusion coefficient value can be obtained.

2.3.2 Charge-Discharge (CD)

The CD measurement analysis is performed to determine the value of the coin cell battery capacity produced. This measurement uses the same instrument as the cyclic voltammetry test, namely WonAtech WBCS 3000 and with the same treatment, which is to provide a constant current and load 0.1 C and the cut-off voltage limit is 0 - 3 volts. In this measurement, the voltage will be recorded every second. The data obtained from this measurement is also processed using the WBCS 3000 software version 3.2 by entering the value of the voltage and current multiplied by time, a voltage graph will be obtained as a function of charge-discharge capacity (mAh/g) which is also called the charge-discharge graph.

2.3.3. Electrochemical Impedance Spectroscopy (EIS)

EIS measurement is carried out by providing AC voltage as a voltage source and frequency variation to the LI coin cell anode. The results of the EIS measurement are in the form of a semicircle curve which is processed using Zview software to determine the Real (R_e) and the imaginer (R_{cl}) impedance values. EIS analysis is used to determine the interaction of electrons and Li ions that move from the cathode to the anode and vice versa. So it can be found the electrical conductivity value of the LTO anode material on the LI coin cell.

3. Results and Discussion

3.1. Results of Cyclic Voltammetry (CV)

CV measurement was carried out on samples L192, L194 and L196 in the form of half cells that had been assembled into coin cells. It was carried out to determine the electrochemical performance of the LTO anode and the Li-metal cathode. Figures 2, 3 and 4 are data curves from CV measurement in the form of curves that show the relation between voltage (V) and the scan rate variation 50, 100, 150 and 200 μ V as input voltage (V) and current (mA) as output.



Figure 2 LI coin cell L192 Sample

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Figure 4 LI coin cell L196 Sample

Figures 2, 3 and 4 show that there are two pairs of anodic and cathodic peaks that are reversible. At the anodic peak, the charging process occurs and the reaction that occurs is an oxidation reaction due to the release of Li + ions and electrons from the cathode to the anode. The cathodic peak is formed due to a reduction reaction caused by ion displacement

 Li^+ and electrons from the anode to the cathode. The anodic and cathodic peak voltages of samples L192, L194 and L196 have the same voltage range between 1.5 - 1.75 volts for each scan rate variation (50, 100, 150 and 200 mV/s). The voltage range is in accordance with the characteristic stress value of the LTO material, namely 1.5 volt [21]. The higher the scan rate will result in the curve (I vs V) of samples L 192, L 194 and L 196 also wider. It is because a lower scan rate (50 mV/s) results in slower movement of Li ions than a higher scan rate (200 mV/s). The higher scan rates also

result in higher current generated because more Li ions are transferred to the anode and cathode. Based on cyclic voltammetry data, the ion diffusion coefficient can be calculated using the Randles-Sevcik equation:

where:

n = number of electrons per molecule

A = surface area (cm²)

C = Li ion concentration (mol/cm³)

D = Diffusion coefficient of Li ion

$$v = scan rate (V/s)$$

ip = peak oxidation current (A)

The results of calculating the Li ion diffusion coefficient (D) from each sample are 3.48x10⁻⁴ (L192), 3.39×10^{-5} (L194) and 2.08×10^{-5} (L196) cm²/S. These data indicate the intercalation and deintercalation processes in the LTO anode materials are slowly decreasing and running slowly correspond the duration of the holding time calcination. [22]

3.2. Charge-Discharge (CD)

CD measurements were carried out by giving a charge load of 0.1 C in the voltage range of 0 - 3 volts. Figure 5 is the result of CD measurement for each sample. Sample L192 is represented by the black line, L 194 is shown by the red line and L 196 is shown by the blue line



Figure 5. Graph of charge-discharge measurement results for Li₄Ti₅O₁₂ anode of LI coin cell with variations in the duration of calcination holding time.

In addition, the charge stored in LI coin cell is pure in the LTO anode. The formation of a plateau voltage at a voltage of ± 1.5 volt for each sample which confirms the CV results, namely the oxidation and reduction voltages located in the voltage range 1.5 - 1.75 volt. This plateau voltage value corresponds to the characteristic voltage of the LTO material, which is 1.5 volt. [23]

Based on figure 5, the L192 sample has the highest electrical capacity value, namely 304.82 mAh/g, which confirms the CV test results that the L192 sample has the highest Li ion diffusion value (3.48 x

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 10^{-4} cm²/s). The L 196 sample has the lowest electrical capacity value, namely 1.46 x 10^{-4} mAh/g, this value confirms the CV results on the L196 sample also has the lowest Li ion diffusion value (2.08×10^{-5} cm²/s). This coin cell has specific capacity performance as good as previous finding researchers [24,25]. The performance of the coin cell depend on the anode materials. As the findings of the researchers [22-25]. It had an effective charging but still had a problem in the rapid discharging process. So it would need the improvement of electrode's quality in the next research.

3.3. Electrochemical Impedance Spectroscopy (EIS)

EIS measurement is carried out to determine the conductivity value of LI coin cell with LTO anode material by varying the frequency range (0.1 - 20,000 Hz) that is inserted into coin cell. The results are in the form of a semicircle graph or nyquist plot where Z '(Z real) is the x-axis and Z "(imaginary Z) is the y-axis which can be seen in Figure 6. The black curve shows the result for sample L192, the red curve for sample L194 and the green curve for sample L196. From these three curves, it can be found that the R_e and R_{ct} values after being processed with imageJ software. Total conductivity values for each sample are 6.87×10^{-3} (L192), 3.24×10^{-2} (L194) and 3.59×10^{-2} (L196) S/cm. It is enough to meet the requirement as coin cell [9].



Figure 6 Results of EIS Measurements on LI coin cell Samples

Based on these results, sample L192 has a lower electric conductivity compared to samples L194 and L196. It corresponds to the formation of linear lines that are more upright than samples L194 and L196. While the semicircle curve in the sample L196 shows that a LI coin cell anode has the highest electric conductivity (3.59×10^{-2}) , but the ionic conductivity is low due to the downward sloping linear line on the L 196 curve. The high ionic conductivity is related to the diffusion coefficient value of Li ions in the CV, L192 has the highest diffusion coefficient value of Li ions. The linear line formed after the semicircle curve is the Warburg impedance which shows the ion transfer resistance of the LI coin cell, therefore the more perpendicular the linear line on the EIS result curve shows that the ionic conductivity of LI coin cell is also higher. The linear line on the sample curve L194 is not formed upright, it is because the frequency range is not wide enough so that the linear line is not formed.

4. Conclusion

In this paper, LI coin cell was successfully fabricated and characterized based on LTO anode material. Their best electrochemical performances: (1) coefficient of ionic diffusion was 3.48×10^{-4} cm²/S, (2) the specific capacity value is 304 mAh/g and (3) electrical conductivity value is 6.87×10^{-3} S/cm

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