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Variation of Carbon Coating on $Li_2Na_2Ti_6O_{14}$ as Anode Material of Lithium Battery

B Prihandoko[1], S Priyono[1], A Subhan[1] and A Mulya[2]

[1]Research Center for Physics, Indonesian Institute of Sciences, Tangerang Selatan Indonesia
[2]University of North Sumatera, Medan Indonesia

Email: bamb012@lipi.go.id

Abstract. $Li_2Na_2Ti_6O_{14}$ was developed from $Li_5Ti_4O_{12}$ as a good active material for anode of the lithium battery. $Li_2Na_2Ti_6O_{14}$ was prepared by a preliminary formation of $Li_2Na_2Ti_6O_{14}$ through solid state reaction with calcination temperature at 700 ^oC, and sintering temperature at 800 ^oC for 8 hours. By analysis of XRD patterns, $Li_2Na_2Ti_6O_{14}$ shows spinel structure which similar as $Li_5Ti_4O_{12}$. Carbon coating on $Li_2Na_2Ti_6O_{14}$ was done by using pyrolysis method at a temperature of 700 ^oC for 2 hours. The process of carbon coating was done under variation of comparison between $Li_2Na_2Ti_6O_{14}$ and tapioca powder as a carbon source, i.e. 8:1, 10:1 and 12:1. The working voltage of $Li_2Na_2Ti_6O_{14}$/C product was 1,2 volt. The other analysis were conductivity, cyclic voltammeter, and charge – discharge.

1. Introduction

Lithium ion batteries have been widely applied as power sources for electronic devices such as cameras, mobile phones, computers and other related equipment. The Recent development of lithium ion batteries as electric sources for electric and hybrid electric vehicles (EVs and HEVs) also widely investigated[1]. In fact, high power and high energy density of lithium ion batteries is the major key to application in EVs and HEVs [2]. A search of new electrode materials exhibiting high charge/discharge current rates are urgently required. The spinel lithium titanate ($Li_4Ti_5O_{12}$) has been demonstrated as a potential candidate for the anode electrode material in high power Li-ion batteries as well as hybrid supercapacitors because it has some unique characteristics as compared with carbon-based anode materials [3].

Spinel $Li_4Ti_5O_{12}$ is a promising anode material for high safety due to the absence of solid electrolyte interphase (SEI) film [4, 5,6]. Furthermore, its discharge platform at about 1.55 V, which is higher than the reduction potential of most organic electrolytes, can restrain the origination of SEI film and avoid the formation of metallic lithium dendrite [7]. However, bare $Li_4Ti_5O_{12}$ suffering from low electronic conductivity (10^{-13} S cm^{-1}) shows poor lithium storage properties at high rates, which have a huge negative effect on its commercial applications [8,9].

In this problem, the most improvements have been focused on improving the electronic conductivity and electrochemical properties of $Li_4Ti_5O_{12}$ by developing nanostructures of material, by using different doping of element and coating techniques [10, 11]. $Li_4Ti_5O_{12}$ was successfully doped with Na. This doping changed to new anode active material of $Li_2Na_2Ti_6O_{12}$ and made the lower working potential of 1.3 V. $Li_2Na_2Ti_6O_{12}$ has been regarded as a novel promising anode material to replace $Li_4Ti_5O_{12}$ in recent years [7]. Unfortunately, it also suffers from low electronic conductivity which hinders its further research. In this work, the problem will be an improvement with a carbon coating. The coating technique was used for increasing of electronic conductivity. Under carbon coating, that carbon can give an effect on the electrochemical characterization of $Li_2Na_2Ti_6O_{14}$. Carbon coating with local cassava powder as carbon sources was done as well.

2. Experimental Method

Preparation of $Li_2Na_2Ti_6O_{12}$ has been carried out with the technical grade raw materials of TiO_2 (Japan), Na_2CO_3 (Merck), and $LiOH.H_2O$ (Germany) using powder metallurgy method. After the stoichiometric weighing and mixing, the mixture was calcined at 700^0C for 1 hour. After milling, calcined powder material was sintered at 800 ^{o}C for 8 hours. Carbon coating on $Li_2Na_2Ti_6O_{14}$ was done with pyrolysis method at a temperature of 700 ^{o}C for 2 hours [12]. The process of carbon coating was done under variation of comparison between $Li_2Na_2Ti_6O_{14}$ and tapioca powder as a carbon source, i.e. 8:1, 10:1 and 12:1. The crystal structure of $Li_2Na_2Ti_6O_{14}$/C powders was observed by using X-Ray. For the electrochemical test, the working electrode was prepared by dispersing a mixture of as-prepared active material, carbon black, and polyvinyl difluoride binder with a weight ratio of 8.5:0.5:1 in DMAC solvent to form a homogeneous slurry and then passing the slurry on copper foil to form a thin film. This film was dried at 80 ^{o}C. In the coin-type half cells, metallic lithium foils were used as the counter and reference electrodes; the electrolyte was 1 mol L_1 solution of $LiPF_6$. The method of EIS (Electrochemical Impedance Spectroscopy) from HIOKI equipment was used primarily to test the conductivity of the material. Cyclic Voltammeter of sample was done by using WBCS3000 automatic battery cycler.

3. Results and Discussion

The XRD results crystal structure in Figure 1 formed a phase of $NaLiTi_3O_7$/C or $Li_2Na_2Ti_6O_{14}$/C that was orthorombic (space group = 69: Fmmm) with lattice parameters of a = 16.485 Å, b = 5.7382 Å, c = 11.221 Å, with the same angle of $\alpha = \beta = \gamma = 90°$. The phase of TiO_2 was seen in the results of XRD pattern. TiO_2 was tetragonal (space group = 136: $P4_2$/mnm) with a lattice parameter of a = 4.590 Å, b = 4.590 Å, c = 2.962 Å, with the same angle of $\alpha = \beta = \gamma = 90°$. $Li_2Na_2Ti_6O_{14}$ phase is shown according to standard ICDD (International Center for Diffraction Data) with the number of 00-052-0690 and TiO2 phase is shown according to standard ICDD (International Center for Diffraction Data) with the number of 04-004-4337.

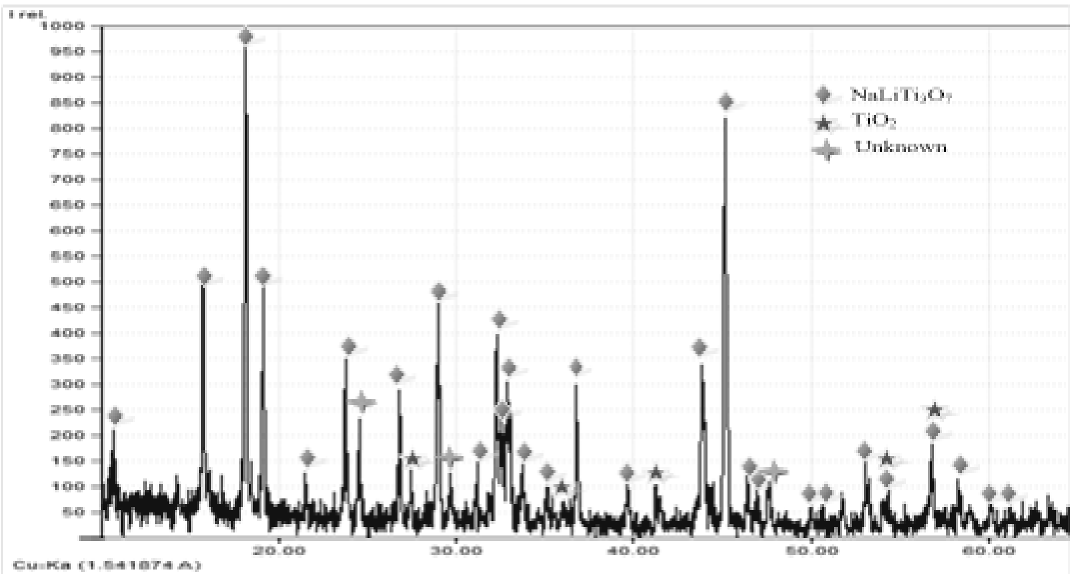

Figure 1. The X-ray pattern of carbon coated $Li_2Na_2Ti_6O_{14}$.

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Detail data of crystal structure analysis can be seen in Table 1. In generated data by quantitative analysis, the purity of sodium lithium titanium oxide $Na_2Li_2Ti_6O_{14}$ phase is 96%, while the remaining phase (4%) is rutile, syn TiO_2.

Table 1. The crystal structure (lattice parameter) of $NaLiTi_3O_7$ and TiO_2

Phase name	Chemical composition	*a* (Å)	*b* (Å)	*c* (Å)	$\alpha = \beta = \gamma$	Density (g/cm^3)
Lithium Sodium Titanium Oxide	$NaLiTi_3O_7$	16.485	5.7382	11.221	90^o	3.577
Rutile,syn	TiO_2	4.590	4.590	2.962	90^o	4.28

The test results for the four samples of CV can be seen from the graph of cyclic voltammograms in Figure 2. The working electrode of samples was prepared by dispersing a mixture of as-prepared active material, carbon black and polyvinyl difluoride as a binder. In the coin-type half cells, the samples were tested with a scan rate of 160 mV/s.

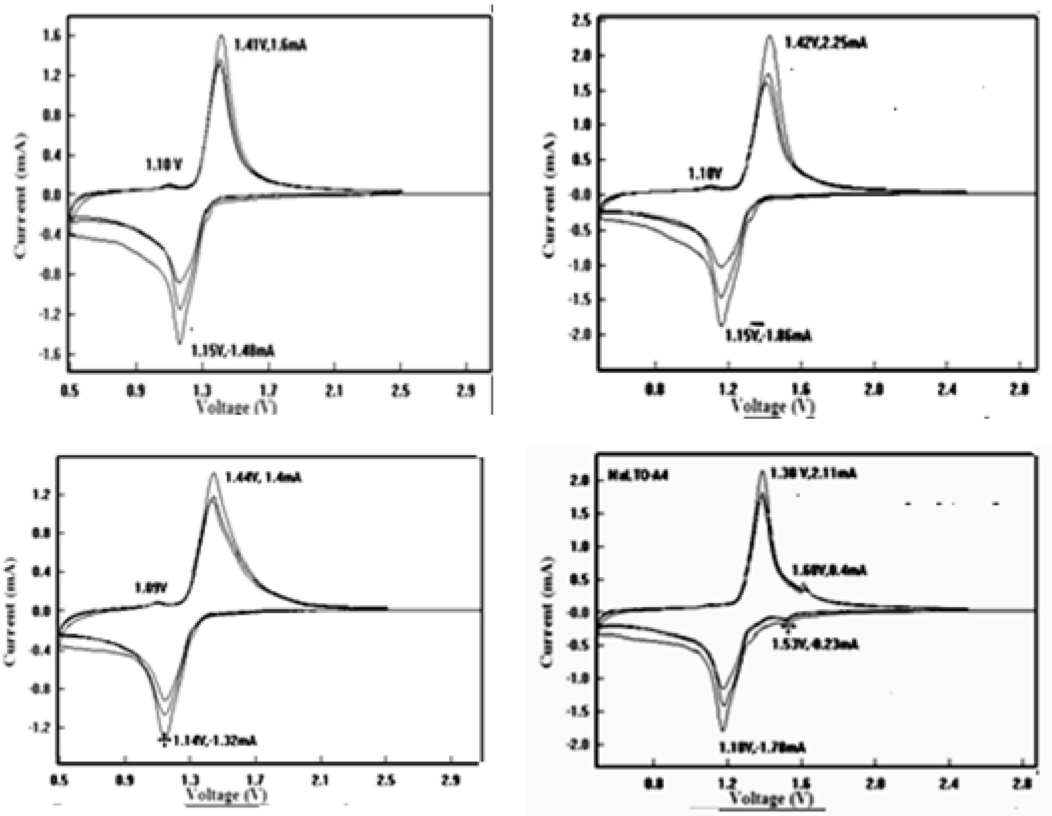

Figure 2. Results of cyclic voltammograms

From Figure 3 we can see the working voltages. Table 2 gives the detail data for working voltage of samples. From Table 2, it is obtained that each sample with a different ratio of carbon coating produced a relatively similar working voltage between 1.28 volt and 1.29 volt. The electrochemical reaction occurs nearly equally in the three samples, but uncoated samples A4 showed other signal. The working voltage of lithium titanate appeared in sample A4. In the tree samples, a coated carbon could erase an influence of the other small phase.

Table 2. The results of working voltage analysis by using cyclic voltammogram

Sample Code	Carbon coating composition	Working voltage [V]
A1	12:1	1.28
A2	10:1	1.285
A3	8:1	1.29
A4	uncoated	1.28 and 1.56

Figure 3 shows the charge-discharge results of the tests used to determine the capacity of the material $Na_2Li_2Ti_6O_{14}$ in the same coin-type half cells. The rate of 0.1 C was used in this experiment. One cycle is equal to one charge process (the oxidation reaction occurs) and one discharge (reduction reaction occurs).

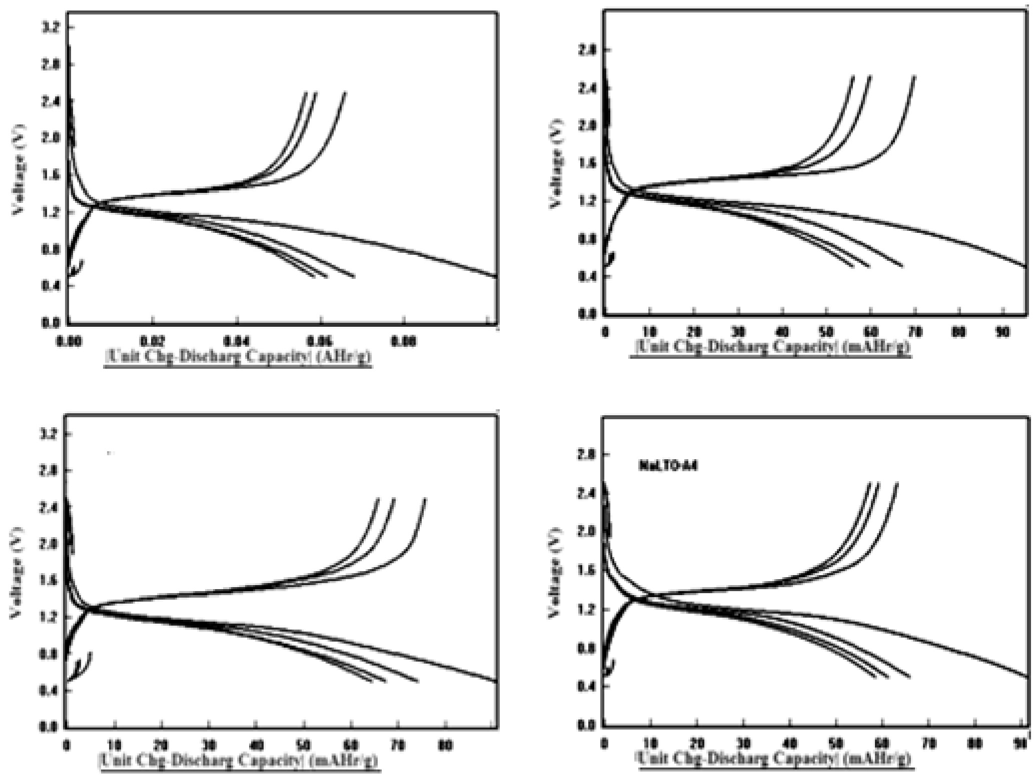

Figure 3. Results of charge–discharge test

Figure 3 shows the analysis of charge-discharge retention capacity gives a performance information to determine the materials that well interact in this process.

Table 3. The results of the analysis of charge-discharge retention capacity

Sample	Active mass [mg]	$-C_i$ [mAh/g]	$-C_f$ [mAh/g]	$-C_i$ / $-C_f$ [%]
A1	10	101.7	60.9	61.193
A2	12	94.0	59.1	55.554
A3	9.6	90.2	67.1	60.,52
A4	12	90.0	60.7	50.,63

A detail numerical analysis results are displayed in Table 3. The sample A1 showed the biggest value of charge-discharge retention capacity while sample A4 showed the lowest one. Sample with the smallest coated carbon had the best process of charge–discharge. The uncoated carbon sample was the lowest capacity.

Electrochemical Impedance Spectroscopy (EIS) was being done to identify conductivity of the samples. In Figure 4, we can see the results showing single semicircle phase. The results of wide semicircle was shown by sample A4, while smaller semicircle was demonstrated by the sampleA1. The smallest coated carbon of sample A1 got the highest conductivity.

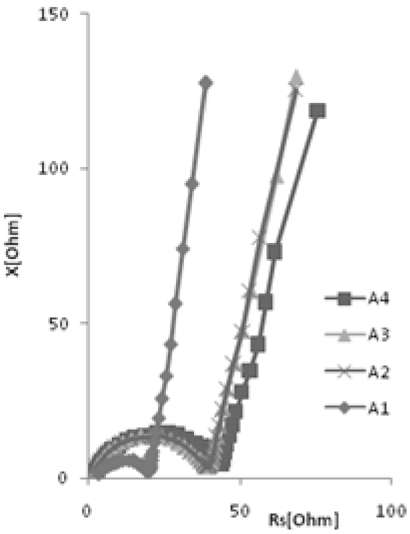

Figure 4. Cole-cole plot of the samples

4. Conclusion

The fabrication of $Na_2Li_2Ti_6O_{14}$/C composite was successfully done with 96% purity obtained from crystal structure analysis. The working voltage of $Na_2Li_2Ti_6O_{14}$/C was around 1.29 V. The coated carbon on anode material of $Na_2Li_2Ti_6O_{14}$ gave a positive effect on the electrochemical properties. We also obtained that the sample with the smallest ratio exhibited the best performance in charge-discharge process. The conductivity of $Na_2Li_2Ti_6O_{14}$/C was achieved by the smallest amount of coated carbon with a ratio of 12:1.

5. References

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