Variation of Carbon Coating on Li$_2$Na$_2$Ti$_6$O$_{14}$ as Anode Material of Lithium Battery

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Abstract. Li$_2$Na$_2$Ti$_6$O$_{14}$ was developed from Li$_5$Ti$_4$O$_{12}$ as a good active material for anode of the lithium battery. Li$_2$Na$_2$Ti$_6$O$_{14}$ was prepared by a preliminary formation of Li$_2$Na$_2$Ti$_6$O$_{14}$ through solid state reaction with calcination temperature at 700 $^\circ$C, and sintering temperature at 800 $^\circ$C for 8 hours. By analysis of XRD patterns, Li$_2$Na$_2$Ti$_6$O$_{14}$ shows spinel structure which similar as Li$_5$Ti$_4$O$_{12}$. Carbon coating on Li$_2$Na$_2$Ti$_6$O$_{14}$ was done by using pyrolysis method at a temperature of 700 $^\circ$C for 2 hours. The process of carbon coating was done under variation of comparison between Li$_2$Na$_2$Ti$_6$O$_{14}$ and tapioca powder as a carbon source, i.e. 8:1, 10:1 and 12:1. The working voltage of Li$_2$Na$_2$Ti$_6$O$_{14}$/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$_4$Ti$_5$O$_{12}$) 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$_4$Ti$_5$O$_{12}$ 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$_4$Ti$_5$O$_{12}$ 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$_4$Ti$_5$O$_{12}$ by developing nanostructures of material, by using different doping of element and coating techniques [10, 11]. Li$_4$Ti$_5$O$_{12}$ was successfully doped with Na. This doping changed to new anode active material of Li$_2$Na$_2$Ti$_6$O$_{14}$ and made the lower working potential of 1.3 V. Li$_2$Na$_2$Ti$_6$O$_{14}$ has been regarded as a novel promising anode material to replace Li$_4$Ti$_5$O$_{12}$ 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$_2$Na$_2$Ti$_6$O$_{14}$. Carbon coating with local cassava powder as carbon sources was done as well.

### 2. Experimental Method

Preparation of Li$_2$Na$_2$Ti$_6$O$_{14}$ has been carried out with the technical grade raw materials of TiO$_2$ (Japan), Na$_2$CO$_3$ (Merck), and LiOH.H$_2$O (Germany) using powder metallurgy method. After the stoichiometric weighing and mixing, the mixture was calcined at 700°C for 1 hour. After milling, calcined powder material was sintered at 800 °C for 8 hours. Carbon coating on Li$_2$Na$_2$Ti$_6$O$_{14}$ was done with pyrolysis method at a temperature of 700°C for 2 hours [12]. The process of carbon coating was done under variation of comparison between Li$_2$Na$_2$Ti$_6$O$_{14}$ and tapioca powder as a carbon source, i.e. 8:1, 10:1 and 12:1. The crystal structure of Li$_2$Na$_2$Ti$_6$O$_{14}$/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 °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 Voltameter 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$_3$O$_7$/C or Li$_2$Na$_2$Ti$_6$O$_{14}$/C that was orthorhombic (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 $\alpha = \beta = \gamma = 90^\circ$. The phase of TiO$_2$ was seen in the results of XRD pattern. TiO$_2$ was tetragonal (space group = 136: P4$_{2}$/mm) with a lattice parameter of $a = 4.590$ Å, $b = 4.590$ Å, $c = 2.962$ Å, with the same angle of $\alpha = \beta = \gamma = 90^\circ$. Li$_2$Na$_2$Ti$_6$O$_{14}$ 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$_2$Na$_2$Ti$_6$O$_{14}$.](image-url)
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$_2$Li$_2$Ti$_6$O$_{14}$ phase is 96%, while the remaining phase (4%) is rutile, syn TiO$_2$.

**Table 1.** The crystal structure (lattice parameter) of NaLiTi$_3$O$_7$ 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$_3$O$_7$ | 16.485  | 5.7382  | 11.221  | 90$^\circ$                 | 3.577              |
| Rutile, syn TiO$_2$ | TiO$_2$              | 4.590   | 4.590   | 2.962   | 90$^\circ$                 | 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.

![Cyclic voltammograms](image)

**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$_2$Li$_2$Ti$_6$O$_{14}$ 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).

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 detailed numerical analysis result is 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 sample A1. The smallest coated carbon of sample A1 got the highest conductivity.

![Figure 4. Cole-cole plot of the samples](image_url)

4. Conclusion
The fabrication of Na$_2$Li$_2$Ti$_6$O$_{14}$/C composite was successfully done with 96% purity obtained from crystal structure analysis. The working voltage of Na$_2$Li$_2$Ti$_6$O$_{14}$/C was around 1.29 V. The coated carbon on anode material of Na$_2$Li$_2$Ti$_6$O$_{14}$ 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$_2$Li$_2$Ti$_6$O$_{14}$/C was achieved by the smallest amount of coated carbon with a ratio of 12:1.

5. References
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