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Heating Effect on Manufacturing $Li_4Ti_5O_{12}$ Electrode Sheet with PTFE Binder on Battery Cell Performance

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Abstract. The synthesis of $Li_4Ti_5O_{12}$ (LTO) and study of the heating effect on the manufacturing process of LTO sheet on the electrochemical performance have been investigated. LTO anode material composed with $LiOH.H_2O$, TiO_2 as raw materials were synthesized by the solid-state process. All raw materials were stoichiometrically mixed and milled with a planetary ball mill for 4 h to become the precursor of LTO. The precursor was characterized by Simultaneous Thermal Analyzer (STA) to determine sintering temperature. The STA analysis revealed that the minimum temperature to sinter the precursor was 600 °C. The precursor was sintered by using high-temperature furnace at 900 °C for 2 h in air atmosphere. The final product was ground and sieved with a screen to get finer and more homogenous particles. The final product was characterized by X-ray Diffraction (XRD) to determined crystal structure and phases. LTO sheet was prepared by mixing LTO powders with PTFE and AB in ratio 85:10:5 wt% by varrying heating process with 40 °C, 50 °C and 70 °C to become slurry. The slurry was coated on Cu foil with doctor blade method and dried at 80 °C for 1 h. LTO sheet was characterized by FTIR to analyze functional groups. LTO sheet was cut into circular discs with 16 mm in diameter. LTO sheet was arranged with a separator, metallic lithium and electrolyte become coin cell in a glove box. Automatic battery cycler was used to measure electrochemical performance and specific capacity of the cell. From the XRD analysis showed that single phase of LTO phase with a cubic crystal structure is formed. FTIR testing showed that there are stretching vibrations of Ti-O and H-F from tetrahedral TiO_6 and PTFE respectively. Increasing temperature on LTO sheet manufacturing doesn't change the structure of LTO. Cyclic voltammetry analysis showed that sample with heating of 40 °C showed better redox process than others. Charge-discharge test also showed that sample with heating of 40 °C has higher specific capacity than other samples with 53 $mAh{\cdot}g^{-1}$.

Keywords. Cyclic voltammetry, Electrode Sheet, LTO, PTFE, TiO_2.

1. Introduction

Energy consumption relying on fossil fuel is predicted having a bad future impact on the economy and ecology of the world [1] because fossil fuel is not sustainable and put carbon gas pollution on air that causing global warming. One of the enormous sector emitting carbon gas pollution into the world is transportation. This problem can be solved by replacing the conventional engine with the battery as energy sources. The battery is a device to store energy for supplying electrical power [1]. Recently, lithium-ion batteries have been emerged as the most promising energy storage technology and widely used in some applications such as portable devices and electric vehicles [2]. This is due to its advantages such as high energy density, lighter weight, no memory effect, and low self-discharge rate when compared to other rechargeable batteries [3].

Battery components include anode, cathode, electrolyte, separator and currents collector. They are assembled to be coin cells for battery performance testing. Before assembling process, the anode and cathode must be made in sheets form. Forming of anode and cathode sheets needs a binder.

Nowadays, Lithium Titanium Oxide ($Li_4Ti_5O_{12}$) called LTO and used as the anode is considered to be a better choice than conventional graphite. It is caused by its zero-strain structure, small particle size, no Solid Electrolyte Interphase (SEI) formation, etc. Therefore, lithium ion battery with LTO anode shows a very long-life cycle [4].

Binder is one of the main raw materials for making anode and cathode sheets in battery [5]. A good binder has the following requirements; right material composition, good adhesion, high conductivity, proper coating thickness, and stable or not blend with other mixed materials. The conventional binder used is PVDF (Polyvinylidene fluoride). PVDF has a drawback. It can only be deluded with N N-Dimethyl-acetamide (DMAC) solvent. However, DMAC is toxic, relatively high price, and difficult to decompose.

Water is a saver and more secure that can be used in making a slurry. Nevertheless, PVDF is not able to dissolve into it. Therefore, it is needed another binder to replace PVDF, that is PTFE. PTFE (Polytetrafluoroethylene) is environmentally friendly. It uses water solvent that is not harmful to health. PTFE has excellent chemical resistance, high heat, and cold resistance, insulating, resistant to UV rays (ultraviolet), good weather resistance, low friction coefficient, anti-fracture, flexural, high resistance to fire and low water absorption.

In this research, anode powder, $Li_4Ti_5O_{12}$ (LTO), had been made with raw materials of $LiOH{\cdot}H_2O$ and TiO_2. Following that, anode powder was used to make electrode sheet. In this study is focused on using PTFE binder with varying temperature on the heating process to know the characteristic of battery performances.

2. Materials and methods

The $Li_4Ti_5O_{12}$ powder was synthesized via Solid state reaction with using raw materials such as $LiOH{\cdot}H_2O$ (technical) as Lithium (Li) source, and TiO_2 (technical) as Titanium (Ti) source. The synthesized material follows stoichiometry formula as stated in Equation 1:

$$4LiOH{\cdot}H_2O + 5TiO_2 \rightarrow Li_4Ti_5O_{12} + H_2O + O_2 \quad (1)$$

All raw materials were mixed, mashed and screened to get precursor of $Li_4Ti_5O_{12}$. The precursor was milled with Planetary Ball Milling (PBM) with speed 400 rpm for 4h. Following that, the precursor was sintered at 900 °C for 2 h with 2 °C heat rate in an air atmosphere. The final product was screened 200#. The synthesized materials were characterized by using X-ray diffractometer (XRD, Rigaku) to know the phases.

The slurry was prepared by mixing active powder ($Li_4Ti_5O_{12}$) with a binder (PTFE) and conductive agent (acetylene black) at weight ratio 85:10:5. Aquadest was used as a solvent to soluble the binders. All materials were mixed, stirred, and heated by varying temperature heating at 30 °C, 50 °C and 70 °C in a solvent to become slurry and then coated with Cu foil.

The anode sheet was cut into a circular form with a diameter of 16 mm. The circle sheet was tested by FTIR (Thermo Scientific Nicolet iS10) to study the functional group of the sheet. The testing was conducted at a range of 500 cm^{-1} to 4000 cm^{-1} wavenumbers.

Before battery performance testing, the sheets were assembled in cell coin in the glove box. Cyclic Voltammetry (CV) and Charge-Discharge (CD) testing by WBCS instrument (WBCS 3000, Automatic Battery Cycler Ver.3.2) were performed on the coin cells to observe the battery performance. In CV testing, battery voltage used was starting from 2.8 V to 0.5 V at a scan rate of 0.1 $mV\cdot s^{-1}$ in 1 cycle. Meanwhile, in CD testing, it was starting from 1.0-2.8 V with a scan rate of 0.1 C for 1 cycle.

3. Results and discussion

The XRD result displayed in Figure 1 showed that LTO crystal phase is formed without any impurities. All the peaks are high and sharp, and those indicate high crystallinity of the sample. The diffraction peaks of LTO peaks are at 2θ of 18.33°, 35.57°, 37.21°, 43.24°, 47.35°, 57.21°, 62.83°, 66.07°, 74.34°, 75.36°, and 79.34°. The crystal planes (hkl) are 111, 311, 222, 400, 331, 333, 440, 531, 533, 622, and 444. The peaks pattern is corresponding to LTO ICDD database No #00-049-0207. The crystal structure of LTO sample is cubic with a space group of Fd-3m and lattice parameter of 8.373 Å.

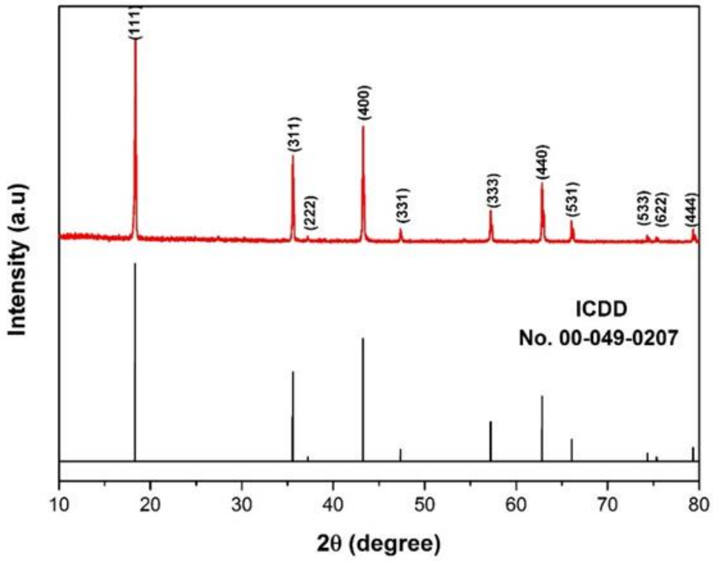


Figure 1. XRD pattern of LTO powder synthesized via solid-state reaction

Figure 2. LTO sheets with PTFE binder with the different heating process.

Figure 2 shows electrode sheets of LTO prepared by PTFE binder via doctor blade method. All samples physically show good sample, smooth, and homogenous. Samples also have well adhered and can't be brittle.

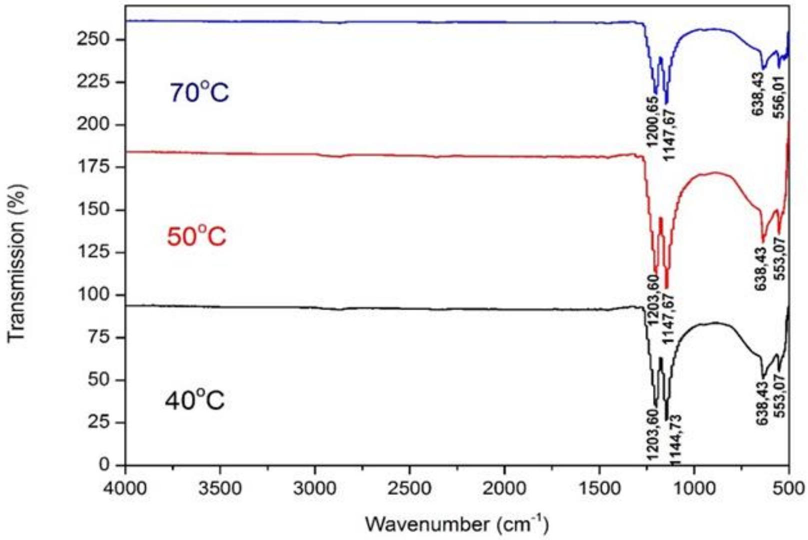
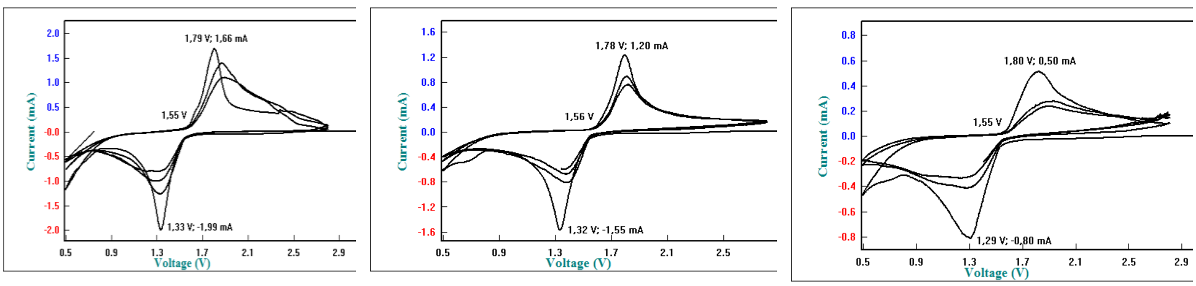


Figure 3. The infrared spectrum of the sample at a temperature of 40 °C, 50 °C and 70 °C.

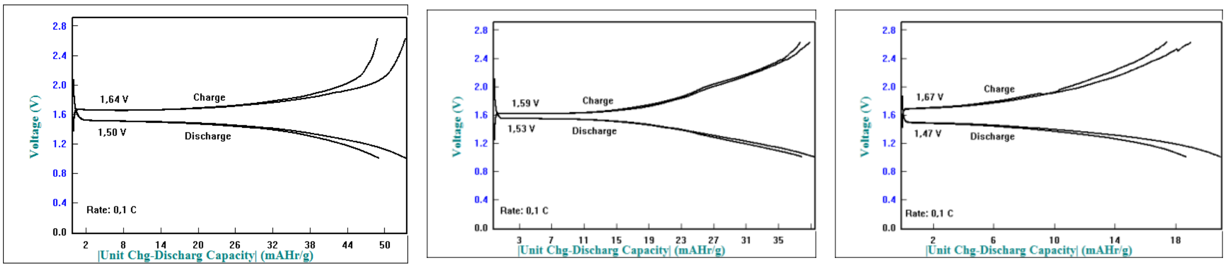
Figure 3 shows FTIR pattern of LTO sheet using PTFE as a binder with varying temperature. All samples indicate identical spectrum in fingerprint region. The peaks observed at a wave number of 553 cm^{-1} and 638 cm^{-1} denoted the symmetric stretching vibration of TiO_6 octahedral of LTO [6]. Also in the spectrum, the band at wave number 1144.73 cm^{-1} to 1200.65 cm^{-1} represent H-F bonds derived from PTFE binder [7]. Sample with heating 50 °C shows a little bit higher, wider and sharper than others in H-F bond, and it indicates that this sample has a stronger bond. There are no peaks at Hydroxyl bond (at 3000 cm^{-1} to 3500 cm^{-1}) it indicates that sample is dry enough and ready to be used as a negative electrode of the battery.



A B C

Figure 4. Cyclic voltammograms of LTO using PTFE binders with varying heating temperature (A). 30 °C, (B) 50 °C, and 70 °C

The cyclic voltammetry measurement was tested in the voltage range from 0.5 V to 2.8 V and vice versa for 3 cycles at a scan rate 0.1 $mV\cdot s^{-1}$ in order to well understand the Li^{+} intercalation/deintercalation kinetics of the electrode material. Figure 4 shows cyclic voltammograms of LTO coated onto Cu foil with PTFE binder at different heating temperature. All samples show a clear pair of redox peak observed below 2 V those indicated that samples could be rechargeable and show properties of secondary batteries. Redox peaks are associated with reduction and oxidation of Ti^{3+}/Ti^{4+} [10].



A B C

Figure 5. Galvanostatic charge and discharge curve of $Li_4Ti_5O_{12}$.

Figure 5 shows the charge-discharge curve of a cell for the first two cycles between 1.0 V and 2.8 V at a rate of 0.1 C. It can be seen from Fig 5 that the plateau is clearly in the charge-discharge curve at the potential of 1.55 V (versus Li+/Li). This behavior corresponds to the solid-state redox of Li in $LiTi_4O_{12}$ involved with Li^+ ion extraction and insertion. Sample A shows higher specific capacity than sample B and C with 54 $mAh{\cdot}g^{-1}$. Increasing in temperature slurry will decrease specific capacity and increase the polarization of samples. Higher temperature will evaporate more water content in slurry so make the bond between the active material and current collector become weak, so it will make electron difficult to across through electrode.

4. Conclusions

$Li_4Ti_5O_{12}$ powder and its electrode sheet were successfully prepared by solid-state reaction and doctor blade method respectively. The structural analysis revealed that the prepared sample was highly crystalline. Sample heated 50 °C had stronger and better bond than others, and also showed good intercalation and de-intercalation process. But sample heated 40 °C has the higher specific capacity with 55 °C, and it's greater than the previous experiment.

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