Effect of coating thickness of Al-doped Li$_4$Ti$_5$O$_{12}$ (LTO) on the electrochemical performance of half cell battery

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Abstract. Effect of coating thickness of Al-doped Li$_4$Ti$_5$O$_{12}$ (LTO) sheet on the electrochemical performance of battery cells is reported. A 0.025 mol Al-doped LTO powder was synthesized by solid state reaction method, for the anode sheet was made by the doctor blade method. The sheet manufacturing was carried out by varying the coating thickness from 100, 200, 300 and 400 $\mu$m to determine the effect on the electrochemical performance of the battery cell. The analysis of phase was conducted by X-ray diffraction (XRD); for electrochemical performances were conducted by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and charge discharge (CD) method. XRD analysis showed that there are two phases formed, i.e. LTO and rutile phases (TiO$_2$) of 75.6% and 24.4%, respectively. EIS results showed that the thicker the coating layer, the conductivity of the sample become slower. Furthermore, the results indicate that the sample with thickness of 100, 200 and 300$\mu$m indicated sharp redox peak, and 400 $\mu$m showed wide redox peaks. The specific capacity and specific power of the half cell battery decreases with the increasing of coating thickness. The best cell capacity is obtained by sample with 100 $\mu$m thickness with specific discharge capacity of 134.3 mAh/g.

1. Introduction
Lithium batteries were firstly proposed in 1976 [1] and have been widely adopted for commercial since the early 1990s. Lithium batteries can be divided into three different groups, i.e. lithium metal, lithium-ion and lithium-ion polymer. Lithium metal batteries are primary batteries with non-rechargeable, while lithium-ion and lithium-ion polymer batteries are the rechargeable one. The main difference between lithium-ion and lithium-ion polymer, the electrolyte of lithium-ion is based on a lithium salt in an organic solvent (such as LiPF$_6$), while lithium-ion polymer use solid composite polymer (such as oxymethylene-linked polyethylene glycol, PEMO) [2]. Lithium ion batteries are the most promising energy storage device for both portable electronic, electric vehicles and large-scale energy storage. Lithium ion battery consist of four main part, including cathode, anode, separator and electrolyte. The performance of lithium ion battery depends on the properties of those materials. Therefore, lithium ion batteries areas have spurred extensive research to make new electrode materials with high safety level and good electrochemical performance.
Li$_4$Ti$_5$O$_{12}$ (LTO), which was first proposed by J.R. Dahn et al [3], has been suggested as potential alternatives material to replace graphite as anode. LTO, one of spinel structure materials, is promising anode material for lithium ion batteries because it has many advantages compared to the conventional anode like graphite. LTO has small lithium diffusion coefficient and experience large volume variation about 9%. There is no structure change under charge-discharge condition, so it is called as “Zero strain materials”. This material has a good Li-ion intercalation/de-intercalation, good reversibility, and structural stability and does not form solid-electrolyte interphase (SEI) layer because of high potential around 1.5 V. Additionally, LTO has more lithium ion mobility than graphite, hence promising for high rate battery applications [3, 4].

Although LTO has many advantages for anode lithium ion battery, LTO shows poor electronic conductivity due to empty Ti 3d state with a band energy of about 2eV, and its electron conductivity is $10^{-13}$-$10^{-19}$ S cm$^{-1}$. However, when Li$_4$Ti$_5$O$_{12}$ (LTO-spinel) transforms into Li$_7$Ti$_5$O$_{12}$ (LTO-rock-salt) in Li-ion insertion process, its electron conductivity become $10^{-5}$-$10^{-9}$ S cm$^{-1}$. In order to improve electrochemical properties, LTO is doped by some metal ion. Doping by metal ion is the best way to increase electron conductivity. There are many choices of metal ion for doping that can be applied, such as: Mg$^{2+}$, Ni$^{3+}$, Al$^{3+}$, Cr$^{3+}$, Co$^{3+}$, Fe$^{3+}$, Mn$^{3+}$, Ga$^{3+}$, Zr$^{4+}$, Mo$^{4+}$, V$^{5+}$, Ta$^{5+}$, F$^-$ and Br$^-$ in Li, Ti or O site [5].

In this research, Al$^{3+}$ ion will be used as dopant to substitute a small portion of Ti$^{4+}$ in LTO. There are so many research about Al$^{3+}$ doped on LTO. Research done by Huang et.al [6] showed that Al$^{3+}$ ion increased reversible capacity and cycle stability when charging and discharging. Lin, et al.[8] synthesized Al doped on LTO by using sol-gel process. The result showed that there is significantly increasing on discharge capacity and rate capability. Based on previous report, 0.025 mol Al doped LTO is the best result by showing cycling stability and lower polarization [7, 8]. In order to make battery cell, making electrode sheet is most important to be consider. Electrode sheet must have precise composition, good adhesive power, and high conductivity. The electrode sheet is made by mixed active materials with binder (i.e. PVDF), conductive carbon, and organic solvent (i.e. DMAC). There are some parameters that have to be considered in preparing electrode sheet, such as: material composition, mixing time, temperature process, mixing speed, viscosity, thickness, coating speed, drying temperature, and drying time.

Coating thickness will effect on cell performance, because it related with the length of electron path from electrode/electrolyte interface into current collector [9]. If the coating is thicker, electron path will become longer so that the efficiency of the battery cell decreases as the electron flow will be
resisted in the active material. Additionally, the increased of thickness coating can also cause internal resistance increase and lead to self-discharge. The illustration of electron path from interface to the collector is shown in figure 1.

The power and energy density of the battery depend on coating thickness of the layer of active material on the current collector. Thicker coating of the electrode material layer provides higher energy because of the amount of the active ingredient which is great, but it also increases the length of ion diffusion in the material resulting in lower specific power. Instead, a thin layer electrode provides a short diffusion path so that a higher power density. But much less active material and consequently the specific energy decrease. In addition, optimization of the thickness of coating can minimize costs production [10, 11]. In this report, the effect of coating thickness on the electrochemical performance specifically on specific power and specific energy will be reported.

2. Experiment

Al doped LTO was synthesized by a solid-state reaction method. The 0.025 mol Al$_2$O$_3$ was used as Al ion to replace Ti ion in LTO. Stoichiometric LiOH.H$_2$O, TiO$_2$ and Al$_2$O$_3$ with technical grade used as raw materials. The raw materials were mixed and followed by screening #200. Finally, the product were sintered at 850°C for 4 h with heating rate of 10°C/min in air atmosphere to obtain active material of Al doped LTO. The crystal structure and phase of active material was identified and confirmed by X-ray diffraction (XRD) using Cu-Kα radiation.

The electrochemical properties of samples were measured using CR2032 coin cells. Active materials (Al doped LTO, 85 wt.%), poly-vinylidene fluoride (PVDF, 10 wt.%) and acetylene black (5 wt.%) were mixed in DMAC solvent until become slurry. The slurry was coated on Cu foil by varying thickness coating i.e., 100, 200, 300 and 400 µm become electrode sheets and the samples were called as G1, G2, G3 and G4, respectively. The cells were assembled using electrode sheets as working electrode, lithium metal as the counter electrode, and Celgard film as the separator. The electrolyte was LiPF$_6$ dissolved in organic solvent, i.e., ethylene carbonate (EC) and diethyl carbonate (DEC). The cells were assembled in a glove box filled with high purity argon gas and tested by LCR HIOKI to measure Electrochemical Impedance Spectroscopy (EIS). While, cyclic voltammograms (CV) and charge-discharge (CD) were recorded using WBCS battery tester. Cyclic voltammetry was carried out using scan rate of 0.16 mV/s from 0.7 – 2.8 V. Charge-discharge was measured at 0.1 C rate from 0.5 – 2.6 V to obtain capacity, specific capacity, and specific power.

3. Result and discussion

Figure 2 displayed the XRD patterns of the obtained Al doped LTO powder. There are two phases identified, i.e., LTO (75.6%) and rutile TiO$_2$ (24.4%) which denoted by filled diamond and circle shapes, respectively. The co-exist of two phases can be explained due to high heating rate when sintering process carried out; and in this work, there is no initial calcination process. The calcination process is usually needed to remove volatile from raw material while slow heat rate will make perfect reaction. However, from the XRD result, the percentage of LTO phase seems enough to be used as anode material. The Al doped LTO powder showed high crystallinity as host of lithium ion, this benefit for charge-discharge of materials. The XRD peaks can be adjusted to pristine LTO spectra from the ICDD card No 00-049-020, at three main peaks at two theta of 18°, 43° and 36°.
Figure 2. XRD of Al doped LTO.

Figure 3. EIS spectra of Al doped LTO with thickness variation of electrode sheet.

Figure 3 showed EIS of all samples. The spectra showed semicircle at high to middle frequency and a sloping line at low frequency. The intersection of the slope line with real axis refers to a bulk resistance ($R_b$), which reflects the electronic and ionic resistance of two electrodes and electrolyte/separator. The semicircle corresponds to the charge transfer resistance ($R_{ct}$) and its related double-layer capacitance ($C_{dl}$). The sloping line at low frequency represents the Warburg impedance, which is associated with lithium-ion diffusion into the LTO particles [12]. Table 1 showed resistance and conductivity for all samples that were extracted from EIS spectra. The different in electronic resistance for all samples are quite small and it can be considered similar. But, the different of ionic conductivity of all samples are quite big. This can be explained due to the increasing in layer active material thickness causing the semicircle plot become smaller; so that the resistance become small and the conductivity become high. The results also showed that the ionic conductivity is more dominant than electronic conductivity. Increasing in conductivity can be attributed from Al doped in LTO. The thicker Al doped LTO will make more contains Al, so increasing the final conductivity. But there is no significantly different in conductivity values because it has similar power value.

Table 1. Conductivity measurement from EIS spectra of Al doped LTO with thickness variation.

| Samples | Real Thickness ($\mu$m) | $R_e$ (Ω) | $R_{ct}$ (Ω) | $\sigma$ (S/cm) |
|---------|------------------------|-----------|--------------|-----------------|
| G-1     | 80                     | 9.84      | 226          | 3.185 $\times 10^5$ |
| G-2     | 120                    | 4.86      | 259          | 4.324 $\times 10^5$ |
| G-3     | 170                    | 5.91      | 124          | 11.938 $\times 10^5$ |
| G-4     | 280                    | 6.71      | 94.8         | 23.950 $\times 10^5$ |

Cyclic voltammetry test was carried out until 3 cycles by scan rate of 160 $\mu$V/s and range potential from 0.7 V to 2.8 V. Figure 4 showed the cyclic voltamogram of Al doped LTO with varying thickness of samples. All samples showed pair oxidation/reduction peaks with working voltage at around 1.5 V. The three first samples (G1, G2, and G3) showed some sharp and narrow oxidation/reduction peaks and this indicates rapid intercalation and deintercalation process. While, G4 showing wide oxidation/reduction peak indicates slow intercalation and deintercalation process. Increasing in coating thickness showed increasing in oxidation/reduction current because more active material involved in electrochemical process.
Figure 4. Cyclic Voltamogram of Al doped LTO with varying thickness (G1) 100 um (G2) 200 um (G3) 300 um and (G4) 400 um.

Figure 5. Charge-discharge curves of Al doped LTO with varying thickness (G1) 100 µm (G2) 200 µm (G3) 300 µm and (G4) 400 µm.

Table 2. Specific capacity and capacity of samples.

| Sample | Specific Capacity (mAh/g) | Coloumbic Efficiency (%) | Capacity (mAh) | Power density (W/g) |
|--------|---------------------------|--------------------------|----------------|---------------------|
|        | Charge                    | Discharge                | Charge         | Discharge           |
| G-1    | 137.08                    | 134.30                   | 0.3692         | 0.3617              | 1.28               |
| G-2    | 103.64                    | 103.39                   | 0.6903         | 0.6886              | 1.11               |
| G-3    | 93.65                     | 93.07                    | 0.8891         | 0.8836              | 0.80               |
| G-4    | 94.73                     | 96.09                    | 2.0257         | 2.0548              | 0.36               |

Figure 5 showed charge-discharge test for all sample with rate 0.1C and it formed plateau potential at around 1.55 V. From the curves can be extracted specific capacity, coloumbic efficiency and capacity as shown in table 2. It explained that increasing thickness coating will decrease specific capacity because of Al contain and long ionic diffusion. Al contain in LTO will theoretically decrease
specific capacity. From the results, all samples have excellent coloumbic efficiency above 98%. While, increasing thickness coating will increase capacity because of more active material involved in electrochemical process. Increasing thickness coating also causin the difference between charge and discharge voltage become bigger. This indicates increasing in polarization. More active material will increase activation energy in initial electrochemical process, so the polarization increases.

Power density calculated by multiplied the current density with working voltage. Power density is significantly affected by coating thickness of active material. Table 2 showed that increasing in coating thickness decrease power density, this due to the diffusion path of lithium become longer.

4. Conclusion
Al doped LTO (Al=0.025) was synthesized by simple solid-state method in an air atmosphere. XRD result shows LTO and TiO\textsubscript{2} rutile formed. The co-exist of these phases are caused by high rate temperature when sintering process carried out. Al contained in LTO not increase electronic and ionic conductivity significantly. The sample having thickness under 300 μm showed good and rapid intercalation and deintercalation process. They consistof sharp oxidation/reduction peak and lower polarization than other thickness. Increasing in coating thickness will increase capacity but decrease specific capacity and specific power. The best electrochemical performance was showed by G-1 with specific capacity about 137.08 mAh/g, 98% coloumbic efficiency and highest specific power.

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