Effect of polymer binders on the electrochemical Performance of Al-doped lithium titanate electrode

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Abstract. The investigation of polymers as binders of Al doped Li4Ti5O12 for Li-ion battery electrode is reported. Polimer binders such as Polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA), and Polytetrafluoroethylene (PTFE) were used to make electrode sheet. Al doped Lithium Titanate (Al-doped Li4Ti5O12) were used as electrode powders. Al doped Li4Ti5O12 powders were synthesized from LiOH.H2O, TiO2 and Al2O3 via solid state reaction. X-ray diffraction (XRD) was used to analysed phase and size of particle. Electrode sheets were manufactured by used active material, binders, and acetylene black in ratio 85:10:5 wt%. Electrode sheets were cut and assembled into coin cell batteries. Coin cell samples were characterized by EIS, cyclic voltammetry and charge-discharge to get electrochemical performance. XRD result reveals that there are two phases formed from final product such as Li4Ti5O12 and rutile TiO2. EIS diagram showed that sample with PTFE binder has the best conductivity with 3.10^{-5} S/cm. While, cyclic voltammetry and charge-discharge test showed sample with PVDF binder has the best chemical performance with good redox peaks and highest specific capacity about 110 mAh/g.

1. Introduction
Lithium ion batteries are most interesting chemical power sources for electric vehicles and energy storage because they have special properties like rechargeable, high energy density, light weight, more safety, low cost and low environmental impact. Lithium-ion batteries use lithium intercalation compound as the cathode and lithium metal or graphite as the anode [1-2]. Figure 1 shows lithium ion battery that consist of anode, cathode, electrolyte and separator. When a cell battery is operating, lithium ions remove from cathode through the electrolyte and separator film and stored in the anode while at the same time electrons flow in external circuit as electricity for the load. When the cell is recharged after use, the flow of lithium ions is in the opposite direction, and they are reduced back to lithium metal or graphite to be stored in the anode [3].
The research on lithium ion battery have been focused to increase energy density, reduce weight, decrease costs, and improve recharge times. To reach all the goals, intensive research on the cathode, anode, electrolyte and separators have been done and this report we will focus on anode research. The anode is typically made from graphite, graphite had been commercial anode battery since 1990s with lithium intercalated into the graphite structure. However, graphite has some problems as anode battery if it uses in high C-rate charge/discharge. Graphite experiences volume expansion about 12% in lattice crystal, and it has very low working potential so can lead electrolyte decomposition to make solid electrolyte interface and dendrite lithium on anode surface. Conventional anode can be replaced by lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) as new anode material for lithium ion battery [1-2].

$L\text{i}_4\text{Ti}_5\text{O}_{12}$ has been an attractive candidate of anode material for lithium ion batteries because of its excellent Li-ion insertion/extraction reversibility, zero strain material under charge discharge, and higher operating voltage (1.55V vs. Li/Li+) which ensure better safety and avoiding the formation of solid electrolyte interphase and lithium dendrite [4]. However, it has weak cyclic stability because of weak Ti-O bond that restrictive for high rate application. [5] In previous and others research, Al doped on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increased conductivity and showed better cyclic stability than pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Al doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decreased polarization and can be used in high C rate while pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ only reach 0.2 C [6]. Therefore, in this report Al doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ will be used as active material.

Lithium-ion batteries are composed of several materials including metals and metal oxides, graphite and other carbonaceous materials, organic solvents, lithium salts and polymers. These latter are present in the porous separator, laying in between the electrodes (usually a polyolefin), and as binding components in the composite electrodes. Binders are counted as inactive components since they do not directly contribute to the capacity of the cells. Binders are not passive materials and have an influence on the electrochemical performance [7]. However, Binders have chemical properties such as (i) thermal stability, chemical and electrochemical stabilities, (ii) tensile strength (strong adhesion and cohesion), (iii) flexibility, and (iv) viscosity (of the slurries) [8]. The main purpose of using a binder is to form stable networks of the solid electrode components, i.e., the active materials and conducting agents (cohesion). Moreover, the binder has to ensure a close contact of the composite electrode toward the current collector (adhesion) [9]. The performance of a polymer binder in an anode is expected to depend on some parameter such as: (i) adhesion strength between the electrode and the current collector foil, (ii) the interface between the polymer and the active particles, (iii) interaction of the binder with the electrolyte, and (iv) binder mechanical properties [10].

Commercial Li-ion batteries have been using polyvinylidene-difluoride (PVDF) as binder due to excellent adhesion properties and electrochemical stability. However, this polymer used volatile and toxic solvent such as N-methyl-pyrrolidone (NMP) or N, N-Dimethylacetamide (DMAC), and also high cost. In addition, the recycling of battery component will cause firing or dissolution of PVDF (in NNH or DMAC), and it leads environmental problems. These problem can be eliminated by using water soluble binders such as polyvinyl alcohol (PVA) or polytetrafluoroethylene (PTFE). So, water-soluble binders must be used to make cheaper, safer and environmentally friendlier batteries [11].

PVA and PTFE binder containing numerous hydroxyl groups in its polymer chain makes strong hydrogen bonds with active materials and the current collector, which is favourable for decreasing volumetric change and preventing excessive electrolyte uptake [12]. In other research, PTFE used as
cathode binder mixed with active material and it could significantly enhance capacity and rechargeability [7, 13]. PTFE is used to avoid water contain in electrode sheet because it has hydrophobic properties. PVA and PTFE were commonly used for cathode material but there is no report for these binders that can be used in anode materials.

In this paper, the roles of polyvinylidene fluoride (PVDF), Polyvinyl acetate (PVA) and polytetrafluoroethylene (PTFE) as anode binders have been studied to know the effect of binders on the electrochemical performance of Al doped Li$_4$Ti$_5$O$_{12}$.

2. Eksperiment
Active materials, 0.025 Al-doped Li$_4$Ti$_5$O$_{12}$, were synthesized by solid state reaction. LiOH.H$_2$O, TiO$_2$ and Al$_2$O$_3$ were used as raw materials. All raw materials were mixed, mased and screned to get precursor of Al doped Li$_4$Ti$_5$O$_{12}$. The precursor was sintered at 870°C for 4 h with 2°C heat rate in air atmosphere. Final product was screened 200#. The synthesized materials were characterized by using x-ray dífraactometer (XRD, Rigaku) and particle size analyzer (PSA, Cilas 1190) to know the phases and particle size of the Al-doped Li$_4$Ti$_5$O$_{12}$ powder.

The electrochemical performance such as EIS, cyclic voltametry and charge discharge were measure by half cell test. The slurry was prepare by mixing active powder (Al doped Li$_4$Ti$_5$O$_{12}$) with binder (PVDF/PVA/PTFE) and conductive agent (acetylene black) at weight ratio 85:10:5. N-N dimethylacetamide (DMAC) was used as solvent for sample that used PVDF binder, while aquadest was used as solvent for samples that used PVA and PTFE binders. All materials were mixed, stirred, and heated in solvent to become slurry and then coated into Cu foil.

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 like 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. Cyclic voltammograms and charge-discharge were recorded using WBCS battery tester. Cyclic voltametry was carried out using scan rate of 0.2 mV/s from 0.5 - 2.8 V. Charge-discharge was measured at 0.1 C rate from 1.0 – 2.6 V to gain capacity, specific capacity, and specific power.

3. Result and discussion
Figure 2 shows XRD pattern of the Al doped Li$_4$Ti$_5$O$_{12}$ sample. There are two phases such as Li$_4$Ti$_5$O$_{12}$ and rutile TiO$_2$ which known by XRD analysis. Li$_4$Ti$_5$O$_{12}$ denoted by triangle sign while rutile TiO$_2$ denoted by circle sign. Based from riedveld analyse, Li$_4$Ti$_5$O$_{12}$ phase has quantity about 76 % while TiO$_2$ rutile has quantity about 24%. Both Li$_4$Ti$_5$O$_{12}$ and rutile TiO$_2$ peaks are sharp, which indicated high crystallinity of sample. The exitance of two phases could be caused by unhomogen of raw material mixer and there is no via calcination process. However, there is no XRD pattern for Al$_2$O$_3$ phase it indicated that Al atom succesfully entered into Li$_4$Ti$_5$O$_{12}$ lattice and substituted Ti atom.

![Figure 2. XRD patterns of the sample Li$_4$Ti$_5$O$_{12}$ doped by 0.025 mol Al](image)

![Figure 3. Electrochemical impedance spectra of Al doped Li$_4$Ti$_5$O$_{12}$ with various binders, PVA (Green), PVDF (Red ), and PTFE (Blue) in a frequency range of 0.1 – 20.000 Hz](image)
Electrochemical Impedance Spectroscopy was used to know the complex impedance behavior of material. Figure 3 showed EIS spectra of Li$_4$Ti$_5$O$_{12}$ with different binder. The measurement was taken by using AC current and then measure the impedance both real and imaginer. EIS spectra will show semicircle and straight line. Semicircle was correspond with electronic resistance ($R_e$) and charge transfer resistance ($R_{ct}$). The existance $R_{ct}$ was caused by electrode contact between anoda (LTO) and electrolyte. While straight line correspond with lithium diffusion that called warburg diffusion. Good sample will show small semicircle and straight line with high gradient. Some parameters values like electron resistance, charge-transfer resistance, conductivity, warburg coefficient, diffusion coeffisien can be known from EIS pattern and all parameters values are listed in Table 1. There is no significant different conductivity values for all samples, it indicate binder does not effect the conductivity. Although sample with PVDF binder gave smallest conductivity but its sample showed highest diffusion coefficient which will affect the electrochemical properties.

Table 1. Electrochemical parameters calculated from EIS patterns

| Sample | $R_{ct}$ (Ω) | $R_e$ (Ω) | $\sigma_w(\Omega cm^2 s^{-1})$ | $\sigma(Scm^{-1})$ | $i^0(Acm^{-2})$ | $D(cm^2 s^{-1})$ |
|--------|--------------|-----------|-------------------------------|--------------------|-----------------|------------------|
| PVA    | 500          | 31.2129   | 3020.9                        | 2.45248x10$^{-5}$  | 1.71248x10$^{-5}$ | 1.92542x10$^{-18}$ |
| PVDF   | 1050         | 18.0195   | 584.84                        | 9.48329x10$^{-6}$  | 8.1548x10$^{-6}$  | 5.48706x10$^{-17}$ |
| PTFE   | 400          | 11.6966   | 1023.2                        | 3.37968x10$^{-5}$  | 2.1406x10$^{-5}$  | 2.03985x10$^{-17}$ |

Table 1 showed that all samples have small conductivity, however the different for all sample is not significant. Conductivity value doesn’t effect other electrochemical properties like redox process, charge-discharge and cycling.

The cyclic voltammetry measurement was done in the voltage range from 0.5 to 2.8 V and vice versa at a scan rate of 0.2 mV/s until 3 cycles to study the Li ion intercalation/de-intercalation kinetics of electrode material. Figure 2 showed cyclic voltamogram of the samples. All samples showed three pairs good reduction/oxidation peaks and indicated reversibility process. However, samples with PVDF binder showed the best cyclic voltamogram with high and sharp oxidation/reduction peaks and indicated very fast electrochemistry process and very low polarization. Samples with PVA and PTFE binder showed wide oxidation/reduction peaks and it indicated lower intercalation/de-intercalation process Li ion from and into Al doped Li$_4$Ti$_5$O$_{12}$ lattice. The CV diagram Sample.

Figure 4. Cyclic voltamograms of Al doped Li$_4$Ti$_5$O$_{12}$ with different binder (a) PVA (b) PVDF and (c) PTFE

Fig 5 shows the first two charging-discharging profiles of Al doped Li$_4$Ti$_5$O$_{12}$ with different binder PVA, PVDF, and PTFE. The cells was charged to 2.6 V and discharged to 0 V vs Li/Li$^+$ with constant current. The charge-discharge plateau was observed at approximately 1.55 V vs Li/Li$^+$ which corespond to redox coupling of Ti$^{4+}$/Ti$^{3+}$ during insertion and extraction lithium ion. From Fig 5, it is apparent that samples with PVA and PVDF exhibited a higher charge-discharge capacity (110 mAh/g) compared to sample with PTFE binder (36 mAh/g). It caused that electrode sheet with PTFE binder
is not good, unhomogen coating and very easy loose from Cu foil as seen in figure 6 c. Although sample with PVA and PVDF binder has same capacity but sample with PVDF has lower polarization indicated from there is no difference between charge-discharge plateau as shown in figure 5. It indicated that sample with PVDF probably could be charged-discharged with higher rate.

![Figure 5. Charge/discharge characteristic of the Al doped Li$_4$Ti$_5$O$_{12}$ with different binder (a) PVA (b) PVDF (c) PTFE](image)

![Figure 6. Electrode sheet of the Al doped Li$_4$Ti$_5$O$_{12}$ with different binder (a) PVA (b) PVDF and (c) PTFE](image)

### 4. Conclusion

In this paper, spinel Al doped Li$_4$Ti$_5$O$_{12}$ materials were prepared by solid state reaction. XRD results revealed that there are two phases formed as final product. Based from riedveld analyse, Li$_4$Ti$_5$O$_{12}$ phase has quantity about 76 % while TiO$_2$ rutile has quantity about 24%. Both phases have high crystallinity with high and sharp peaks. From EIS measurement, sample with PTFE binder show highest conductivity but sample with PVDF binder show highest lithium ion diffusion. From CV diagram, sample with PVDF binder has very well oxidation/reduction peaks, it associated with very fast lithium ion diffusion. While from CD diagram, samples with PVA and PTFE binders have specific capacity about 60 mAh/g but sample with PVA has bigger polarization voltage which restrict using in high charge-discharge rate.
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