

Titania and Cu-Titania Composite Layer on Graphite Substrate as Negative Electrode for Li-Ion Battery

Fitria Rahmawati, Nuryani, and Liviana Wijayanti

Abstract—This research study the application of the immobilized TiO_2 layer and Cu- TiO_2 layer on graphite substrate as a negative electrode or anode for Li-ion battery. The titania layer was produced through chemical bath deposition method, meanwhile Cu particles were deposited electrochemically. A material can be used as an electrode as it has capability to intercalates Li ions into its crystal structure. The Li intercalation into TiO_2 /Graphite and Cu- TiO_2 /Graphite were analyzed from the changes of its XRD pattern after it was used as electrode during discharging process. The XRD patterns were refined by Le Bail method in order to determine the crystal structure of the prepared materials. A specific capacity and the cycle ability measurement were carried out to study the performance of the prepared materials as negative electrode of the Li-ion battery. The specific capacity was measured during discharging process from fully charged until the cut off voltage. A 300Ω was used as a load. The result shows that the specific capacity of Li-ion battery with TiO_2 /Graphite as negative electrode is $230.87 \pm 1.70 \text{mAh.g}^{-1}$ which is higher than the specific capacity of Li-ion battery with pure graphite as negative electrode, i.e $140.75 \pm 0.46 \text{mAh.g}^{-1}$. Meanwhile deposition of Cu onto TiO_2 layer does not increase the specific capacity, and the value even lower than the battery with TiO_2 /Graphite as electrode. The cycle ability of the prepared battery is only two cycles, due to the Li ribbon which was used as cathode became fragile and easily broken.

Keywords—Cu- TiO_2 , electrode, graphite substrate, Li-ion battery, TiO_2 layer.

I. INTRODUCTION

THE Li-ion battery usage has already wide in everyday life of human kind, especially for many portable electronic devices. This battery also has the highest power density between the other secondary batteries [1]. It can produce voltage of 3.6 Volt until 4 Volt. This is higher than NiCd and NiMH batteries which are only 1.2 Volt [2]. Beside higher power density, the Li-ion battery also environmentally save due to does not contains of weight metal, such as Ni and Cd. The other advantages are it has no memory effect, therefore it can be charged anytime and the charging time is fast, which is

2-4 hours due on high charging current, i.e 0.5 – 1 Ampere, the dropping rate of battery efficiency is low, i.e 5 – 10% in a month and also could reach 3 years [3]. The commercial Li-ion battery usually use carbon crystal as anode, LiCoC_2 as cathode, a polymer as separator and an electrolyte of lithium salt solution, such as LiPF_6 , LiBF_4 or LiClO_4 in organic solven [4].

Some problems are still existed in Li-ion battery such as the electrochemical characteristic of graphite prevent Li ions migration and large particle size of graphite lead to longer path of Li ions to be freely released from graphite structure, this tend to decrease the produced energy. The electrochemical of graphite also lead the non-intercalated Li ions agglomerate on the graphite surface and lead to energy decreasing. During charging process, Li ions are deposited inside graphite structure and they will be released during discharging process. These entering and releasing of Li ions provide expansion and shrinkage of graphite crystal size in order to accomodate the ions [5]. These repetitive shrinkage and expansion tend to damage the graphite structure and reduce the battery lifetime. This Li ion battery shortcoming can be overcome through cathode and anode materials modification. The materials that are usually used in electrode modification such as Co, Mn or phosphate [5] or by deposit metal which is unreactive to Li ions, therefore the battery is more stable, has longer lifetime and higher power density.

TiO_2 is a chemically inert material, unexpensive and also chemically stable in almost all solven, except in very strong acid and fluoride contained solven [6]. TiO_2 is also existed commercially and non toxic. Due to these reasons and the nano size of its structure, TiO_2 is become a good candidate for electrode material [7]. TiO_2 has also been proven has capability to intercalate Li ions inside its lattice structure. Sun *et al.* [8] used anatase TiO_2 pillared by Al_3 as cathode and produce the specific capacity of 191.4mAh.g^{-1} .

The quality of anode material is determined by its capability to intercalate Li ions into its crystal lattice. The transition metal oxide has open crystal structure which can accomodate ions, it has an electronic structure that can serve as electron acceptor and also has suitable electronic and ionic conductivity as electrode. The transition metal oxide such as TiO_2 has all criteria, therefore it become a potential candidate for developing high energy density of battery [7].

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The anode material usually applied as anode is graphite, which has specific capacity of 372mAh.g^{-1} [9]. However, researchers still keep in searching other materials with higher capacity, such as nanoparticle SnO_2 and composite of SnO_2 -graphite [10], Sn nanoparticle and also composite of Sn-KS6 graphite [11]. However, Sn metal anodes provide problem on the structural instability regarding large change on volume during discharging process and this lead to cracking and fragility of electrode material [12]. It inspired Son *et al.* [9] to use FeO_4 nanoparticles as anode and it produces capacity of $485\text{-}375\text{mAh.g}^{-1}$ and the cycle ability is 30. However, the specific capacity is still below SnO_2 -carbon with 604mAh.g^{-1} and after 40 cycles, it still has 57% of initial capacity; meanwhile, pure SnO_2 produce 652mAh.g^{-1} with 40 cycles and 39.4% of capacity remaining after 40 cycles [11].

Researchers used various methods to prepare a semiconductor layer, such as electrodeposition [13], chemical vapor deposition [14], chemical bath deposition (CBD) [15], [16], and laser induced vapor deposition (LICVD) [17]. The CBD has advantages compare to other methods, those are it does not need a specific and expensive equipment, low energy intake and it allows to be applied for wide area of deposition. Therefore, this research preferred to use CBD method due to these advantages.

Meanwhile copper, Cu, is a transition metal with standard reduction potential, i.e. 0.3419V (vs. SHE standard). Therefore when $\text{Cu-TiO}_2/\text{Graphite}$ is applied as anode, Cu will be oxidized to Cu^{2+} due to the fully charged of this battery will be around 3V . Cu^{2+} ions may interact with oxygen to form cupric oxide, a metal oxide with monoclinic structure, which has tetragonal and octahedral site which can also accommodate Li ions. Therefore if this cupric oxide is formed and proven can increase the performance of $\text{TiO}_2/\text{Graphite}$ as anode, in the next Li ion-battery can be fabricated under oxygen atmosphere. Eventhough, still there is possibility that Cu^{2+} will compete the intercalation of Li ions into TiO_2 structure, and may even lower the performance of battery.

II. EXPERIMENTS

Chemicals used in this research were on pro analysis grade which are purchased from E- Merck, Indonesia. Graphite rods from ABC battery industry, Indonesia were slid into small discs with diameter of 0.8cm and 1mm of thickness. The graphite discs then were heated at 450°C for 4 hours, then were cooled at room temperature and were analytically balanced.

The precursor solution of TiO_2 is 0.1M of TiCl_4 in hydrochloride solution and added with cetyl trimethyl ammonium bromide (CTAB) at defined amount to reach 16mM of concentration in 100mL of precursor solution. The pre-heated graphite discs were dip into the precursor solution using a wire and keep in the oven at 60°C for 4 days, as it described in our previous paper [18]. After being washed with deionized water then being heated at 450°C for 4 hours, the Cu was electrodeposited from 0.2 ; 0.3 and 0.4M of CuSO_4 solution at 0.03Ampere in Electrolytic Analyzer Electrolysis

Yanaco AES-2D for 30 minutes. The $\text{Cu-TiO}_2/\text{Graphites}$ were then weighted analytically and subtracted by TiO_2/G weight in order to find the weight of deposited Cu. The Cu depositions were conducted four times for each variation. The average weight ratios of $\text{TiO}_2:\text{Cu}$ were then calculated.

The prepared materials then were analyzed by X-ray diffraction, Shimadzu 6000 with $\text{Cu K}\alpha$ λ 1.5418\AA as radiation source. The XRD patterns were compared to ICSD and JCPDS standards and refine by Le Bail Method.

The electrochemical testing were carried out to get specific capacity (mAh.g^{-1}) and the cycle ability with the set up of testing device as described in Fig. 1. The prepared materials were applied as anode, Li ribbon as cathode and the electrolyte is 1M of LiPF_6 in the mixture of ethylene carbonate and diethyl carbonate at $50:50$ of weight ratio.

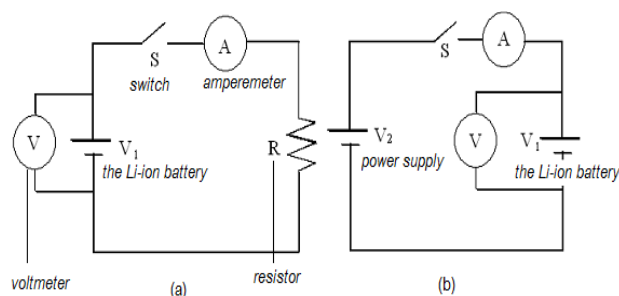


Fig. 1 Set up of electrochemical testing device of (a) discharging process and (b) charging process

The battery capacity (Ampere hours, Ah) is the quantity of electrical current involved in electrochemical reaction. It was measured through current measurement (A) during discharging process. The calculation is based on (1):

$$Q = \int I dt \quad (1)$$

Q is capacity (Ah), I is current (A) and t is time (hours). In this research, the currents were recorded in every 28.8 second (0.008 h) automatically by connecting the electrochemical testing device to a computer with a prepared program. Then the data were analyzed based on (1) by constructing a polinomial function and applying Newton-Cotes integration to solve those polinomial function and to calculate the capacity value. Meanwhile, the specific capacity is the capacity of energy released in a unit of mass, w (g) of the active electrode in a battery cell [19] as it described in (2):

$$Q_{\text{specific}} = \frac{Q}{w} \quad (2)$$

The cycleability was measured from the number of charge-discharged cycles until the capacity of battery drops to 20% of its initial capacity.

III. RESULT AND DISCUSSION

The diffraction pattern was compared to standard TiO_2 and it is founded that the TiO_2 layer on graphite substrate contains of anatase and rutile phases. The comparison of diffraction pattern is described in Fig. 2. Structural refinement by Le Bail method shows that anatase is crystallized in tetragonal structure with space group of $I 41/amd$ with cell parameter $a=b= 3.71570\text{\AA}$ and $c = 9.41490\text{\AA}$. Meanwhile rutile is crystallized in tetragonal structure with space group of $P 42/mnm$ and cell parameter $a=b= 4.57080\text{\AA}$ and $c= 2.9490\text{\AA}$.

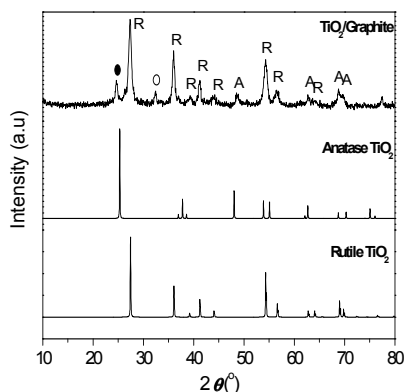


Fig. 2 XRD pattern of TiO_2/G in comparison with standard rutile and anatase TiO_2 . R : rutile, A : anatase, O : Titanium oxide (TiO) and ● : CTAB

There are two peaks at 2θ 24.4312° and 2θ 32.2161° which are not TiO_2 and are identified as cetyl trimethyl ammonium bromide (CTAB) based on JCPDS # 48-2454 and titanium (II) oxide (TiO) based on JCPDS # 23-1078, respectively. Apparently, CTAB is still remaining in TiO_2 layer, although it has been heated at 450°C .

The diffraction pattern of $\text{Cu-TiO}_2/\text{Graphite}$, as it is described in Fig. 3 shows new peaks at 2θ 43.379° , 50.375° and 74.152° which are identified as Cu, based on ICSD #43493. Meanwhile, ratio of $\text{TiO}_2:\text{Cu}$ was measured gravimetrically and listed in Table I.

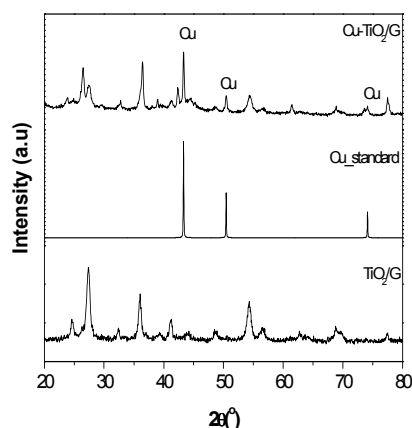


Fig. 3 XRD pattern of $\text{Cu-TiO}_2/\text{G}$ in comparison with Cu and TiO_2/G

TABLE I
WEIGHT RATIO OF $\text{TiO}_2:\text{Cu}$ AT DIFFERENT CuSO_4 CONCENTRATION

CuSO_4 concentration (M)	Average of TiO_2 weight (mg)	Average of deposited Cu weight (mg)	Weight ratio of $\text{TiO}_2:\text{Cu}$ (mg/mg)
0.2	3.250 ± 0.208	1.725 ± 0.171	1.9
0.3	3.175 ± 0.096	3.175 ± 0.096	1.0
0.4	3.225 ± 0.150	4.125 ± 0.096	0.8

XRD analysis on TiO_2/G and $\text{Cu-TiO}_2/\text{G}$ after being used as negative electrode were also conducted in order to study the Li intercalation. The XRD patterns are depicted in Figs. 4 and 5. In comparison to standard Li-titanate, it is founded that Li ions were intercalated in TiO_2 structure and forming 2 phases of Li-titanate, those are $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$ and Li_4TiO_4 . Meanwhile, Li ions were intercalated in Cu-TiO_2 composite and forming $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$ of Li-titanate phase. It also found that the Cu peaks were disappeared after $\text{Cu-TiO}_2/\text{G}$ was used as negative electrode. This is possibly due to oxidation of Cu into Cu^{2+} during discharging process, then Cu^{2+} was dissolved into LiPF_6 electrolyte. If those Cu^{2+} reacted with the dissolved oxygen in electrolyte and forming copper oxide, it apparently did not deposited on the TiO_2 surface, because the diffraction pattern did not record the existence of copper oxide on the TiO_2 layer, as it is described in Fig. 5.

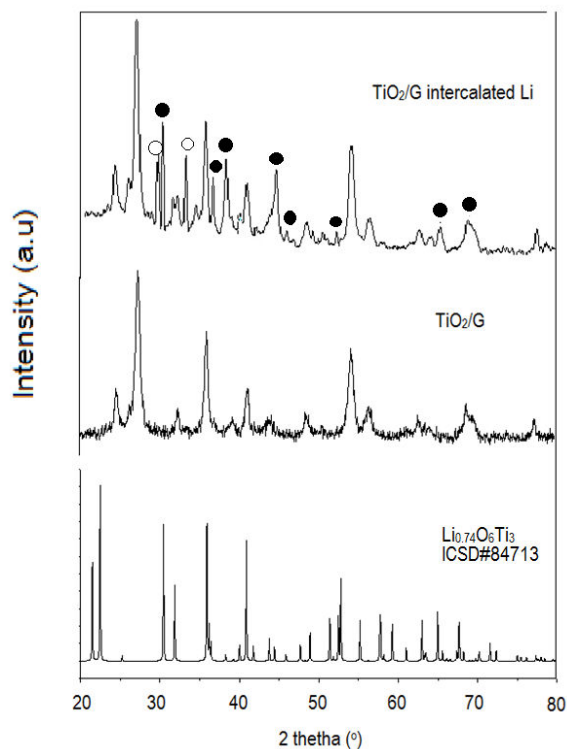


Fig. 4 XRD pattern of Li intercalated TiO_2/G in comparison to TiO_2/G and standard Li-titanate ($\text{Li}_{0.74}\text{O}_6\text{Ti}_3$) ICSD#84713. ● refers to $\text{Li}_{0.74}\text{O}_6\text{Ti}_3$ phase and ○ refers to Li_4TiO_4 phase

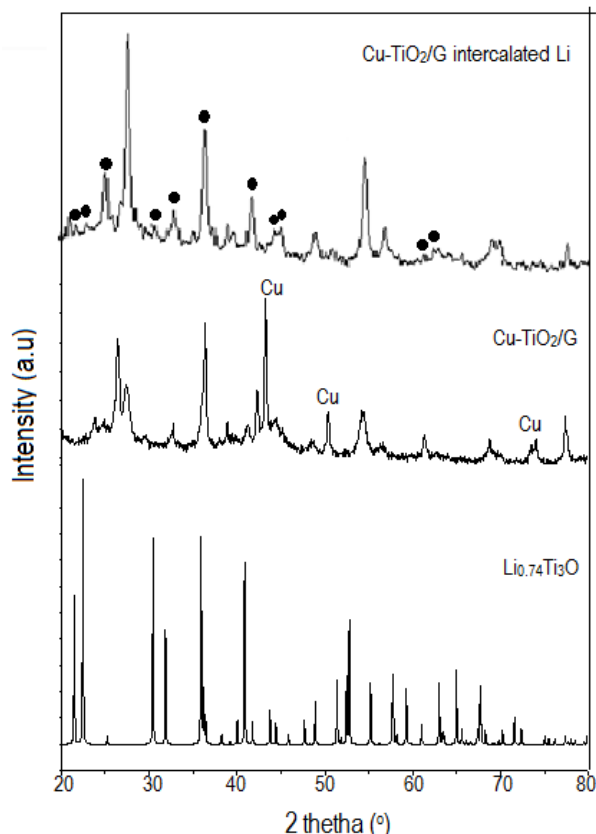


Fig. 5 XRD pattern of Cu-TiO₂/G intercalated Li and its comparison to Cu-TiO₂/G and standard Li_{0.74}Ti₃O ICSD # 84713. ● refers to Li_{0.74}Ti₃O phase and Cu refers to deposited copper

The specific capacitance was measured through discharging the fabricated battery from fully charged until cut off voltage. A 300 Ω of resistor with power of 10 watt was used as load. The current changes (Ampere) were noted during discharging time (second) automatically. The discharging time of battery that used the prepared materials are listed in Table II.

Table II shows that TiO₂ layer on graphite substrate increases the discharging time of battery from 3.10 hours to 5.54 hours. This is a significant increasing. However, Cu deposition on TiO₂ layer even decrease the discharging time to 3.58 hours and higher contain of Cu actually lead to lowering the specific capacity. It seems that after self oxidation of Cu during discharging process, producing Cu²⁺, the Cu²⁺ ions prevent Li ions intercalation and possibly competes the intercalation process and they did not react with oxygen in the electrolyte to form cupric oxide, as it is not existed in the diffraction pattern. Furthermore, Luo [20] stated that in the presence of O₂ and H₂O, the intercalated Li may react with O₂ forming Li⁺ and hydroxide ions, as it described in (3).

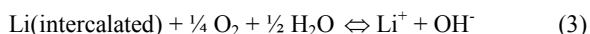


TABLE II
THE DISCHARGING TIME AND SPECIFIC CAPACITY OF BATTERY FABRICATED WITH THE PREPARED MATERIALS AS NEGATIVE ELECTRODE

The negative electrode	Average of discharging time (hours)	The specific capacity (mAh.g ⁻¹)
Graphite	3.10 ± 0.06	140.57 ± 0.46
TiO ₂ /Graphite	5.54 ± 0.07	230.87 ± 1.70
Cu-TiO ₂ /Graphite (TiO ₂ : Cu = 1.9)	3.58 ± 0.06	144.22 ± 0.55
Cu-TiO ₂ /Graphite (TiO ₂ : Cu = 1.0)	0.94 ± 0.03	57.85 ± 1.48
Cu-TiO ₂ /Graphite (TiO ₂ : Cu = 0.8)	0.40 ± 0.03	39.24 ± 1.10

The discharging time is proporsional to the specific capacity of battery. Table II shows that battery with TiO₂/G as negative electrode has higher specific capacity, i.e 230.87 ± 1.70 mAh.g⁻¹. This is higher than the battery prepared with anatase TiO₂ pillared with Al₁₃[8] i.e 191.4 Ah.g⁻¹. However, it is still far below the specific capacity of battery with SnO₂-carbon, pure SnO₂ and nano SnS₂ as anode, i.e 604mAh.g⁻¹, 652mAh.g⁻¹, and 620mAh.g⁻¹, respectively [11].

Due to the possibility of Cu self oxidation and the possibility of side reaction of intercalated Li with O₂ as it explains in (3), therefore the cycle ability of the prepared battery in this research only shows 2 cycles, it is described in Fig. 6. Moreover, the self oxidation of Li ribbon during charging process lead to damage the Li ribbon. In charging process, Li ribbon served as anode, an anodic region where the oxidation reaction occurred. By the existence of dissolved oxygen in the electrolyte, it may promotes the oxidation of Li producing Li⁺ ions that can react to oxygen to produce lithium oxide. Therefore, the Li ribbon became fragile and easily broken.

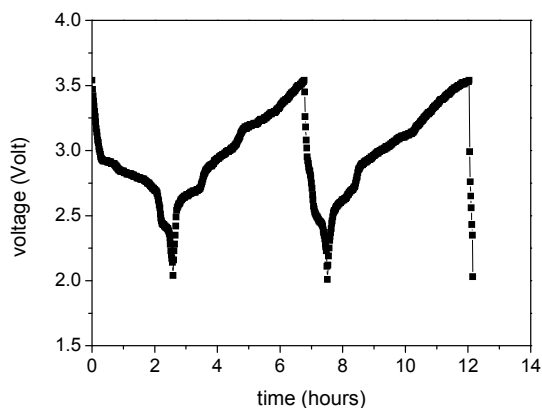


Fig. 6 The cycleability of Li ion battery with TiO₂/G as negative electrode

IV. CONCLUSION

TiO₂ layer which was deposited on graphite substrat by chemical bath deposition can be used as negative electrode or anode of Li ion-battery. This TiO₂ layer enhances the performance of graphite as negative electrode, proven by the increasing of the specific capacity (mAh.g⁻¹) and discharging time (hours) of the prepared battery. However, the deposition

of Cu actually decrease the performance of TiO_2/G as negative electrode due to self oxidation of Cu, evidenced by the loss of Cu peaks in the diffraction pattern of this material after being used as negative electrode.

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