

# 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  $\text{TiO}_2$  layer and Cu- $\text{TiO}_2$  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  $\text{TiO}_2$ /Graphite and Cu- $\text{TiO}_2$ /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  $300\Omega$  was used as a load. The result shows that the specific capacity of Li-ion battery with  $\text{TiO}_2$ /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  $\text{TiO}_2$  layer does not increase the specific capacity, and the value even lower than the battery with  $\text{TiO}_2$ /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- $\text{TiO}_2$ , electrode, graphite substrate, Li-ion battery,  $\text{TiO}_2$  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,  $\text{LiCoC}_2$  as cathode, a polymer as separator and an electrolyte of lithium salt solution, such as  $\text{LiPF}_6$ ,  $\text{LiBF}_4$  or  $\text{LiClO}_4$  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.

$\text{TiO}_2$  is a chemically inert material, unexpensive and also chemically stable in almost all solven, except in very strong acid and fluoride contained solven [6].  $\text{TiO}_2$  is also existed commercially and non toxic. Due to these reasons and the nano size of its structure,  $\text{TiO}_2$  is become a good candidate for electrode material [7].  $\text{TiO}_2$  has also been proven has capability to intercalate Li ions inside its lattice structure. Sun *et al.* [8] used anatase  $\text{TiO}_2$  pillared by  $\text{Al}_3$  as cathode and produce the specific capacity of  $191.4\text{mAh.g}^{-1}$ .

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  $\text{TiO}_2$  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  $372\text{mAh.g}^{-1}$  [9]. However, researchers still keep in searching other materials with higher capacity, such as nanoparticle  $\text{SnO}_2$  and composite of  $\text{SnO}_2$ -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  $\text{FeO}_4$  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  $\text{SnO}_2$ -carbon with  $604\text{mAh.g}^{-1}$  and after 40 cycles, it still has 57% of initial capacity; meanwhile, pure  $\text{SnO}_2$  produce  $652\text{mAh.g}^{-1}$  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.  $0.3419\text{V}$  (vs. SHE standard). Therefore when  $\text{Cu-TiO}_2/\text{Graphite}$  is applied as anode, Cu will be oxidized to  $\text{Cu}^{2+}$  due to the fully charged of this battery will be around  $3\text{V}$ .  $\text{Cu}^{2+}$  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  $\text{Cu}^{2+}$  will compete the intercalation of Li ions into  $\text{TiO}_2$  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 slided into small discs with diameter of  $0.8\text{cm}$  and  $1\text{mm}$  of thickness. The graphite discs then were heated at  $450^\circ\text{C}$  for 4 hours, then were cooled at room temperature and were analytically balanced.

The precursor solution of  $\text{TiO}_2$  is  $0.1\text{M}$  of  $\text{TiCl}_4$  in hydrochloride solution and added with cetyl trimethyl ammonium bromide (CTAB) at defined amount to reach  $16\text{mM}$  of concentration in  $100\text{mL}$  of precursor solution. The pre-heated graphite discs were dip into the precursor solution using a wire and keep in the oven at  $60^\circ\text{C}$  for 4 days, as it described in our previous paper [18]. After being washed with deionized water then being heated at  $450^\circ\text{C}$  for 4 hours, the Cu was electrodeposited from  $0.2$ ;  $0.3$  and  $0.4\text{M}$  of  $\text{CuSO}_4$  solution at  $0.03\text{ Ampere}$  in Electrolytic Analyzer Electrolysis

Yanaco AES-2D for 30 minutes. The  $\text{Cu-TiO}_2/\text{Graphites}$  were then weighted analytically and subtracted by  $\text{TiO}_2/\text{G}$  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  $\text{Cu K}\alpha$   $\lambda$   $1.5418\text{\AA}$  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 ( $\text{mAh.g}^{-1}$ ) 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  $1\text{M}$  of  $\text{LiPF}_6$  in the mixture of ethylene carbonate and diethyl carbonate at  $50:50$  of weight ratio.

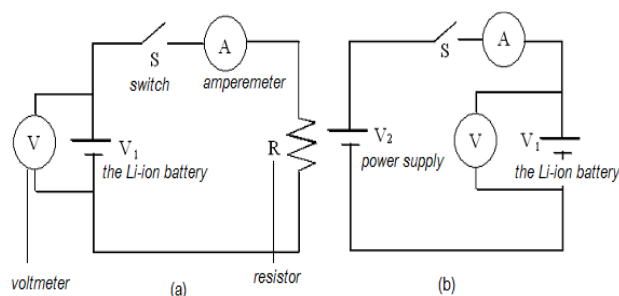


Fig. 1 Set up of electrochemical testing device of (a) discharging process and (b) charging process

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 ( $0.008\text{ h}$ ) 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 polynomial function and applying Newton-Cotes integration to solve those polynomial 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  $\text{TiO}_2$  and it is founded that the  $\text{TiO}_2$  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  $c= 2.9490\text{\AA}$ .

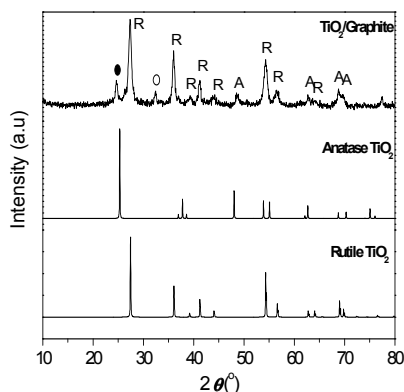


Fig. 2 XRD pattern of  $\text{TiO}_2/\text{G}$  in comparison with standard rutile and anatase  $\text{TiO}_2$ . R : rutile, A : anatase, ○ : Titanium oxide (TiO) and ● : CTAB

There are two peaks at  $2\theta$   $24.4312^\circ$  and  $2\theta$   $32.2161^\circ$  which are not  $\text{TiO}_2$  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  $\text{TiO}_2$  layer, although it has been heated at  $450^\circ\text{C}$ .

The diffraction pattern of  $\text{Cu-TiO}_2/\text{Graphite}$ , as it is described in Fig. 3 shows new peaks at  $2\theta$   $43.379^\circ$ ,  $50.375^\circ$  and  $74.152^\circ$  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.

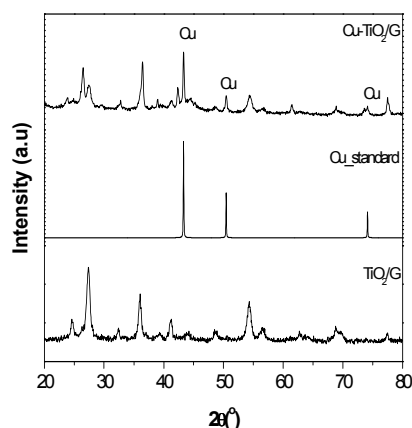


Fig. 3 XRD pattern of  $\text{Cu-TiO}_2/\text{G}$  in comparison with Cu and  $\text{TiO}_2/\text{G}$

TABLE I  
WEIGHT RATIO OF  $\text{TiO}_2:\text{Cu}$  AT DIFFERENT  $\text{CuSO}_4$  CONCENTRATION

$\text{CuSO}_4$ concentration (M)	Average of $\text{TiO}_2$ weight (mg)	Average of deposited Cu weight (mg)	Weight ratio of $\text{TiO}_2:\text{Cu}$ (mg/mg)
0.2	$3.250 \pm 0.208$	$1.725 \pm 0.171$	1.9
0.3	$3.175 \pm 0.096$	$3.175 \pm 0.096$	1.0
0.4	$3.225 \pm 0.150$	$4.125 \pm 0.096$	0.8

XRD analysis on  $\text{TiO}_2/\text{G}$  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  $\text{TiO}_2$  structure and forming 2 phases of Li-titanate, those are  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  and  $\text{Li}_4\text{TiO}_4$ . Meanwhile, Li ions were intercalated in  $\text{Cu-TiO}_2$  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  $\text{Cu}^{2+}$  during discharging process, then  $\text{Cu}^{2+}$  was dissolved into  $\text{LiPF}_6$  electrolyte. If those  $\text{Cu}^{2+}$  reacted with the dissolved oxygen in electrolyte and forming copper oxide, it apparently did not deposited on the  $\text{TiO}_2$  surface, because the diffraction pattern did not record the existence of copper oxide on the  $\text{TiO}_2$  layer, as it is described in Fig. 5.

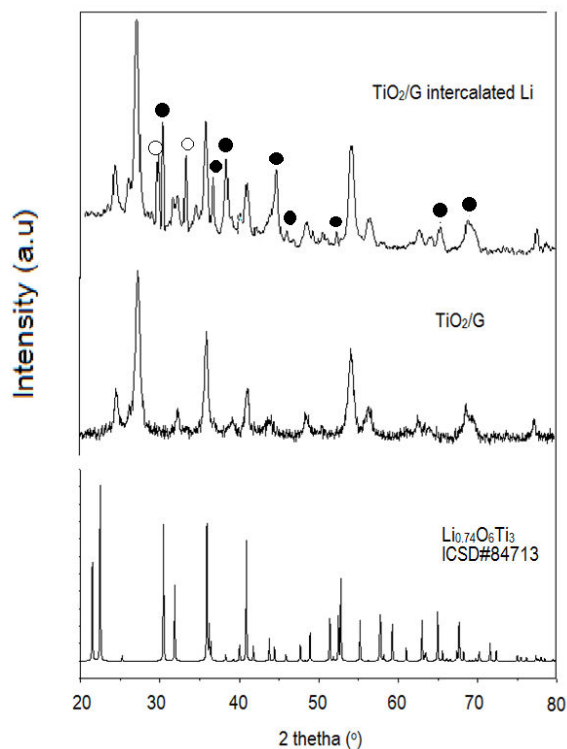


Fig. 4 XRD pattern of Li intercalated  $\text{TiO}_2/\text{G}$  in comparison to  $\text{TiO}_2/\text{G}$  and standard Li-titanate ( $\text{Li}_{0.74}\text{O}_6\text{Ti}_3$ ) ICSD#84713. ● refers to  $\text{Li}_{0.74}\text{O}_6\text{Ti}_3$  phase and ○ refers to  $\text{Li}_4\text{TiO}_4$  phase

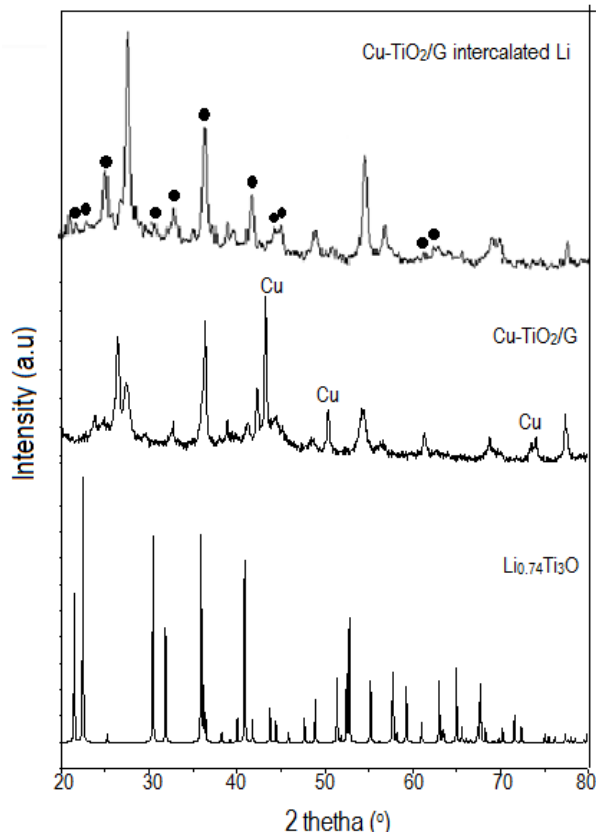


Fig. 5 XRD pattern of Cu-TiO<sub>2</sub>/G intercalated Li and its comparison to Cu-TiO<sub>2</sub>/G and standard Li<sub>0.74</sub>Ti<sub>3</sub>O ICSD # 84713. ● refers to Li<sub>0.74</sub>Ti<sub>3</sub>O phase and Cu refers to deposited copper

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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 Cu<sup>2+</sup>, the Cu<sup>2+</sup> 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 O<sub>2</sub> and H<sub>2</sub>O, the intercalated Li may react with O<sub>2</sub> forming Li<sup>+</sup> and hydroxide ions, as it described in (3).

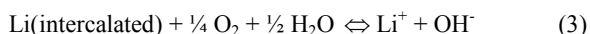


TABLE II  
THE DISCHARGING TIME AND SPECIFIC CAPACITY OF BATTERY FABRICATED WITH THE PREPARED MATERIALS AS NEGATIVE ELECTRODE

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

The discharging time is proportional to the specific capacity of battery. Table II shows that battery with TiO<sub>2</sub>/G as negative electrode has higher specific capacity, i.e 230.87 ± 1.70 mAh.g<sup>-1</sup>. This is higher than the battery prepared with anatase TiO<sub>2</sub> pillared with Al<sub>13</sub>[8] i.e 191.4 Ah.g<sup>-1</sup>. However, it is still far below the specific capacity of battery with SnO<sub>2</sub>-carbon, pure SnO<sub>2</sub> and nano SnS<sub>2</sub> as anode, i.e 604mAh.g<sup>-1</sup>, 652mAh.g<sup>-1</sup>, and 620mAh.g<sup>-1</sup>, respectively [11].

Due to the possibility of Cu self oxidation and the possibility of side reaction of intercalated Li with O<sub>2</sub> 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<sup>-</sup> ions that can react to oxygen to produce lithium oxide. Therefore, the Li ribbon became fragile and easily broken.

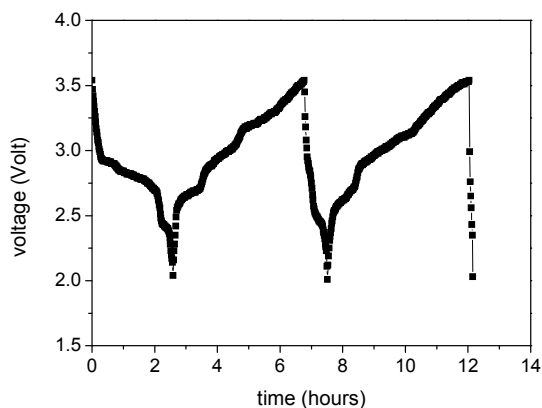


Fig. 6 The cycleability of Li ion battery with TiO<sub>2</sub>/G as negative electrode

#### IV. CONCLUSION

TiO<sub>2</sub> layer which was deposited on graphite substrat by chemical bath deposition can be used as negative electrode or anode of Li ion-battery. This TiO<sub>2</sub> layer enhances the performance of graphite as negative electrode, proven by the increasing of the specific capacity (mAh.g<sup>-1</sup>) and discharging time (hours) of the prepared battery. However, the deposition

of Cu actually decrease the performance of TiO<sub>2</sub>/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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