

Electrochemical performance of natural graphite coated by amorphous carbon using two step synthesis processes at various temperatures for anode material in Li-ion battery

F Rohman¹, S M Nikmah² and J Triwibowo¹

¹Research Center for Physics – LIPI, Kawasan Puspiptek Gd. 441 – 442 Setu
Tangerang Selatan, Banten 15314, Indonesia

²Department of Physics, Faculty of Science and Technology – UIN Maulana Malik
Ibrahim, Jalan Gajayana 1 Malang Jawa Timur, Indonesia

E-mail: fadlirohman@gmail.com

Abstract. Electrochemical performance of natural graphite as anode material in the Li-ion battery has been modified by coating this particle with amorphous carbon through two step synthesis process. Citric acid as the amorphous carbon source was mixed with natural graphite (NG) in the ethanol solvent at 80 °C using magnetic stirrer. In the first step, the mixture of NG and CA were dried at 350 °C for 5 hours under argon atmosphere to evaporate the solvent. This dried mixture was then sintered at different temperature i.e. 500 °C (labeled CNG500), 600 °C (CNG600) and 700 °C (CNG700) under argon atmosphere to form amorphous carbon layer on the surface of NG. The crystal structure and morphology of the particles were characterized by using XRD, SEM and TEM. Electrochemical performance and charge-discharge of amorphous carbon-coated graphite has been evaluated by cyclic voltammetry and WBCS 3000, respectively. Cyclic voltammogram showed the working potential and redox reaction peak of the sample. Charge-discharge data was obtained to determine the specific capacity of the sample at 0.1C.

1. Introduction

Li-ion battery has been used as energy storage for several applications such as mobile phone, notebook computer, gadget, cameras [1] and also for electric vehicles and hybrid electric vehicles [2] due to its high performance i.e. the energy density, safety, rate capability, low cost, sustainability [2], and cycle life [3]. Graphite was the promising and standard active material for anode in Li-ion battery over last two decades due to its excellent performance such as low operating potential, structural stability, moderate cost, and good life cycle [4].

The rate performance on the anode material of Li-ion battery depends on stability of the surface electrolyte interface (SEI) layer formed during charge-discharge cycle. One of the roles of SEI on graphite anodes is to ensure effective passivation of the active anode material against mechanical exfoliation and to impact kinetic stability against electrochemical reactions of the electrolyte in further charge-discharge cycles [5]. Surface modification on the graphite based anode materials have been reported by many researcher. This modification can achieve the high rate performance of the Li-ion battery. The surface chemistry on the interface of electrode-electrolyte has been controlled by modifying the graphite with introducing ion-functional groups, metal oxide, and carbon composite



[4].

Surface modification through by coating graphite with amorphous carbon was also reported by many researchers for enhancing the battery performance. Coal tar pitch (called CTP) was a kind of carbon source of coating layer on the graphite that enhance the rate performance of the battery [4]. CTP derived amorphous carbon coating could effectively decrease charge transfer resistance on the graphite electrode-electrolyte interface.

The characteristic of the coating material using amorphous carbon for the graphite anode in Li-ion battery should have several properties i.e.: isotropic properties, high carbonization yield, and uniform coating electrode. In this study, all the samples are prepared by a citric acid as a carbon source assisted using sol gel method dissolved in the ethanol. The temperature of heat treatment is varied and its effect on the electrochemical performance of the graphite is studied.

2. Experimental methods

2.1. Material preparations and characterizations

A natural graphite (uncoated), labelled UNG, was selected for raw material to evaluate surface modification as anode material for Li-ion batteries. Citric acid as a carbon layer source was dissolved in the ethanol solvent then mixed and stirred with UNG. Further, the samples were dried over night at 80°C in the oven. In the first step, these samples were heat treated at 350°C for four hours for evaporation process. In the second step, the samples were sintered at various temperature i.e. 500°C (CNG500), 600°C (CNG600), and 700°C (CNG700).

The crystal structure of the products was characterized by powder X-ray diffraction (XRD) (Rigaku, Japan) using Cu α radiation $\lambda = 1.541862 \text{ \AA}$ at 40 kV (30 mA) with continuous theta-2-theta in a range 20°-90°. The surface morphology of the products was observed using a scanning electron microscopy (SEM) (SU3500, Hitachi, Japan) operated at 20 kV accelerating voltages with different magnification. Transmission electron microscope (TEM) (Tecnai, FEI, the Netherlands) images and selected area electron diffraction (SAED) were performed at 200kV accelerating voltage to evaluate the coating product on the surface of the graphite.

2.2. Cell preparation and battery testing

The electrochemical performance of CNG was evaluated in the CR2032-type coin cell battery. A slurry of working electrode was prepared with 85% CNG, 5 wt.% acetylene black, and 10% Polyvinylidene Fluoride (PVDF) (Sigma Aldrich) dispersed in N,N dimethyl acetamide (DMAC). The homogenous anode slurry was coated onto copper foil using doctor blade and then dried at 80°C for four hours. The cell was assembled using LiPF₆ (1M) in ethylene carbonate and dimethyl carbonate (EC-DMC, 1:1 v/v) as electrolyte, Celgard micro porous polyethylene (PE) film as separator, and metallic lithium as the counter electrode prepared in an argon-filled glove box.

Electrochemical characteristics were measured in the cyclic voltammetry and charge discharge test using automatic battery cycler WBCS3000. Cyclic voltammograms were performed with the scan rate 0.1 mV/s in the voltage range of 0 to 2.5 volt. The assembled coin cell batteries were also charged and discharge at 0.1 C between 0–2.5 volt versus Li/Li⁺ to determine the specific capacity at room temperature.

3. Results and discussions

3.1. Physical properties of material

The samples are heat treated at several temperatures 500, 600 and 700 °C for five hours in argon atmosphere to investigate the effect of heat treatment temperature on the electrochemical performance. Figure 1 shows the XRD patterns of graphite coated by amorphous carbon using citric acid at different temperature. According to data interpretation using Rietveld refinement method PDXL program, XRD patterns indicate that all the samples have hexagonal structures (lattice constant $a = b = 2.4607 \text{ \AA}$, $c = 6.7096 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$) with 194 : P63/mmc space group, graphite-2H phase name, and no impurity phases. This pattern also can be indexed as (002) crystal faces hexagonal (JCPDS, no. 75-1621). The results indicate graphite coated by amorphous carbon are successfully prepared. Figure 2 shows SEM images of the samples sintered at various temperatures in argon atmosphere. These images show a spherical shape and large number of micro-particles UNG and CNG with average size ranges from 2 to 20 μm . TEM images reveals the crystal area of graphite are covered by the amorphous carbon as shown in figure 3. SAED of the sample is also observed.

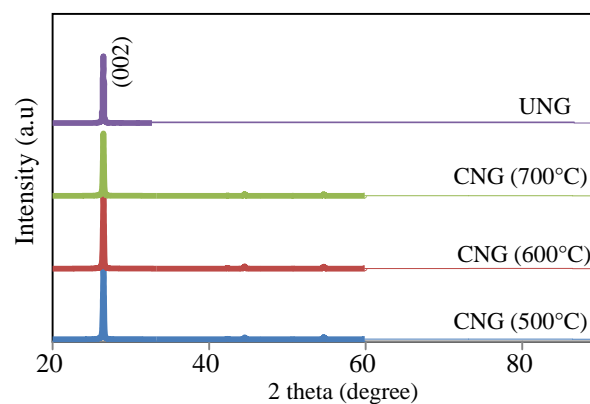


Figure 1. XRD patterns of uncoated natural graphite (UNG) and CNG for several heat-treatment temperatures.

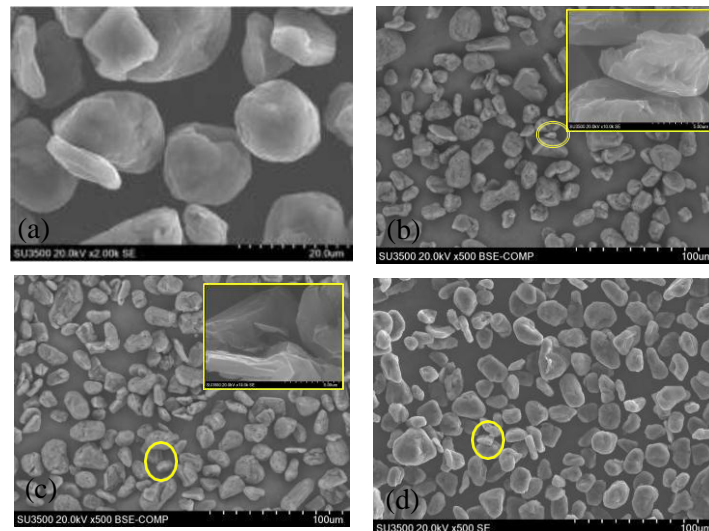


Figure 2. SEM micrographs of (a) uncoated graphite and CNG for several temperatures: (b) 500°C (CNG500), (c) 600°C (CNG600) and (d) 700°C (CNG700).

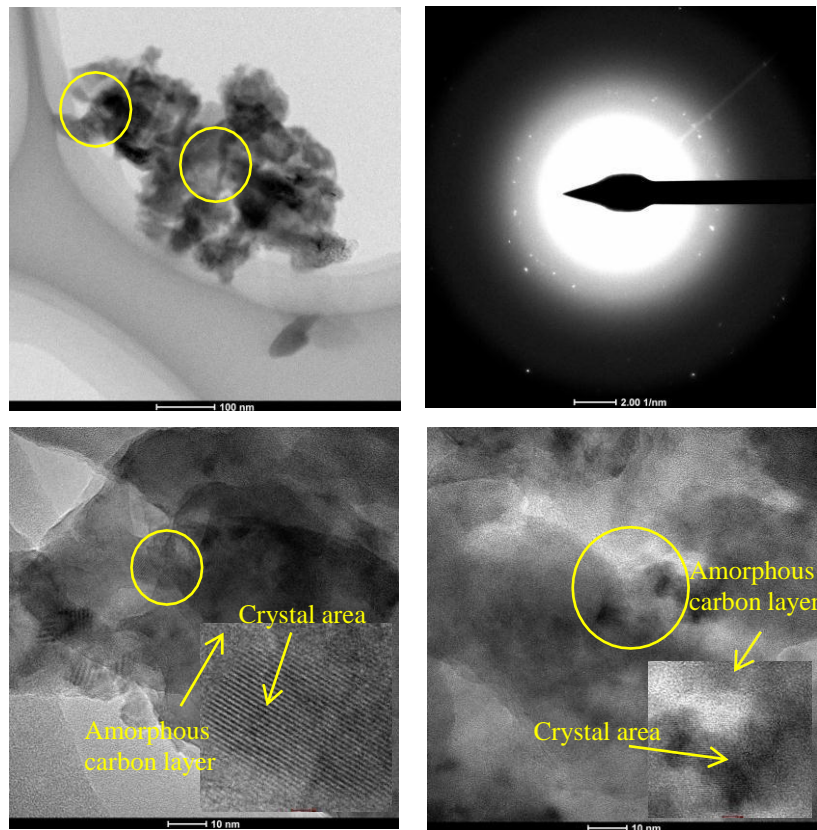


Figure 3. TEM images of graphite coated by amorphous carbon using citric acid.

3.2. Electrochemical characteristics of the sample

The cyclic voltammograms of UNG, CNG500, CNG600, and CNG700 measured with scan rate 0.1 mV/s at range 0 – 2.5 volts are shown in figure 4. In all samples, single cathodic and anodic peak is present and illustrates one electron exchange reaction through redox reaction during C_6 and LiC_6 transformation. CNG600 has the highest specific an oxidation peak current, nevertheless CNG700 has slightly higher an oxidation peak potential. It indicates that heat-treatment temperature has a considerable effect on the electrochemical properties of carbon coated graphite.

To further analyze the effect of coating on the charge-discharge capacity, UNG, CNG500, CNG600, and CNG700 are measured at 0.1 C as shown in figure 5. The highest capacity of carbon coated effect which is measured by half cells is 66 mAh/g (CNG500). The results show that coating amorphous carbon with heat treatment at 500 °C can improve the performance tested at 0.1C. The capacity of CNG600 and CNG700 almost smaller than UNG, indicating that too high heat-treatment temperature may decrease the reversible capacity of the composite coating graphite.

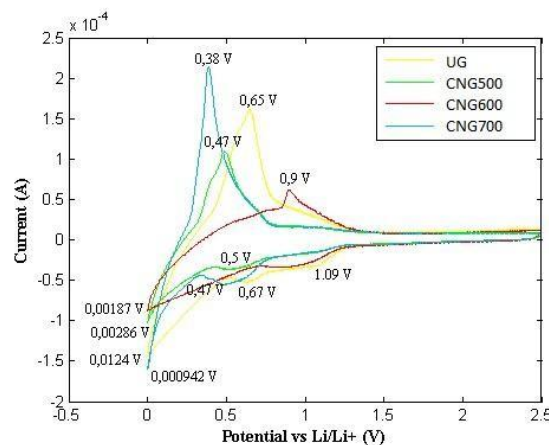


Figure 4. Cyclic voltammograms of uncoated graphite (UG) and CNG for several temperatures of 500°C (CNG500), 600°C (CNG600) and 700°C (CNG700) recorded with scan rate 0.1mV/s at range 0 – 2.5 volts.

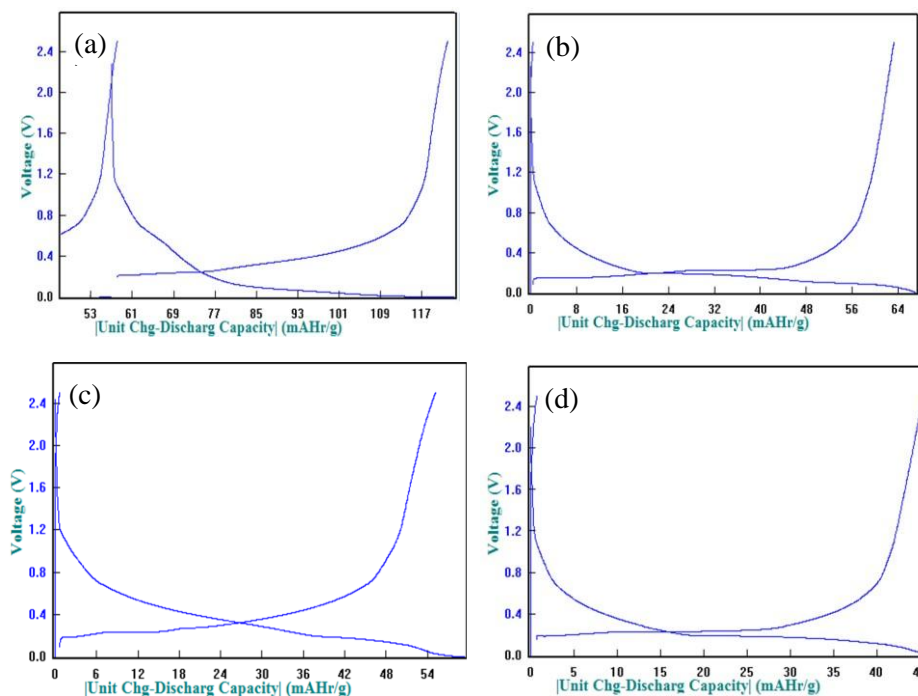


Figure 5. Charge discharge curves of (a) uncoated graphite and CNG for several temperatures: (b) 500°C (CNG500), (c) 600°C (CNG600) and (d) 700°C (CNG700) recorded for the current at 0.1C.

4. Conclusion

Effect of carbon coating layer on the surface of graphite were studied. Crystal structure and impurities effect were investigated as revealed from XRD characterization. Amorphous carbon and graphite area were observed through electron microscopy analysis. From the results can be concluded that amorphous carbon layer on the surface of graphite improved the electrochemical performance through charge-discharge capacity test which have the specific discharge capacity of 66 mAh/g.

Acknowledgements

The authors would like to acknowledge the Research Center for Physics – LIPI and Ministry of Research, Technology and Higher Education – Republic of Indonesia for financial support in this research under SINAS Research Fund Program year 2015.

References

- [1] Ding C, Nohira T, Hagiwara R, Fukunaga A, Sakai S and Nitta K 2015 *Electrochim. Acta.* **176** 344
- [2] Wu R, Xia G, Shen S, Zhu F, Jiang F and Zhang J 2015 *Electrochim. Acta.* **153** 334
- [3] Miranda D, Costa C M and Lanceros-Mendez S 2015 *J. of Electroanal. Chem.* **739** 97
- [4] Han Y-J, Kim J, Yeo J-S, An J C, Hong I-P, Nakabayashi K, Miyawaki J, Jung J-D and Yoon S-H 2015 *Carbon* **94** 432
- [5] Gallego N C, Contescu C I, Meyer III H M, Howe J Y, Meisner R A, Payzant E A, Lance M J, Yoon S Y, Denlinger M and Wood III D L 2014 *Carbon* **72** 393