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Study of Electrochemical Performance of Amorphous Carbon-coated Graphite for Li-Ion Battery

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Abstract. Electrochemical performance of graphite coated by amorphous carbon as anode material in the Li-ion battery has been studied with citric acid (labelled CA) as a carbon source with different composition. Citric acid as the amorphous carbon source was mixed with graphite in the ethanol solvent at 80°C using magnetic stirrer with the compositions CA : graphite 2 :1, 1:1 and 1:3, respectively. The mixture of graphite and CA were dried at 350°C for 5 hours under Ar atmosphere to evaporate the solvent. This dried mixture was then sintered at 600°C under Ar atmosphere to form amorphous carbon layer on the surface of graphite. The crystal structure and morphology of the particles were characterized using XRD, SEM and TEM, respectively. Electrochemical properties of the samples have been evaluated by cyclic voltammetry and charge-discharge test using WBCS 3000. 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 – 2C.

INTRODUCTION

Li-ion battery was widely 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 cycle life [4].

The rate performance on the anode material of Li-ion battery depends on stability of the surface electrolyte interfaces (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 which to 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

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ethanol. The composition between citric acid and graphite is varied to see the effect on the electrochemical performance of the graphite in the battery.

EXPERIMENTAL METHOD

Material Preparation and Characterizations

Graphite was selected for raw material to evaluate surface modification as anode material for Li-ion batteries. Citric acid (CA) as a carbon layer source was dissolved in the ethanol solvent then mixed and stirred with uncoated graphite (labelled NG). Then the samples were dried over night at 80°C in the oven. 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 600°C for five hours with various compositions of CA : NG i.e. 2:1 (CG21), 1:1 (CG11), and 1:3 (CG13).

The crystal structure of the products were characterized by powder X-ray diffraction (XRD) (Rigaku, Japan) using Cu $\kappa\alpha$ radiation $\lambda = 1.541862$ Å at 40 kV (30 mA) with continuous theta-2-theta in a range 20°- 90°. The surface morphology of the products were 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) image and selected area electron diffraction (SAED) were performed at 200kV accelerating voltage to evaluate the coating product on the surface of the graphite.

Cell Preparation and Battery Testing

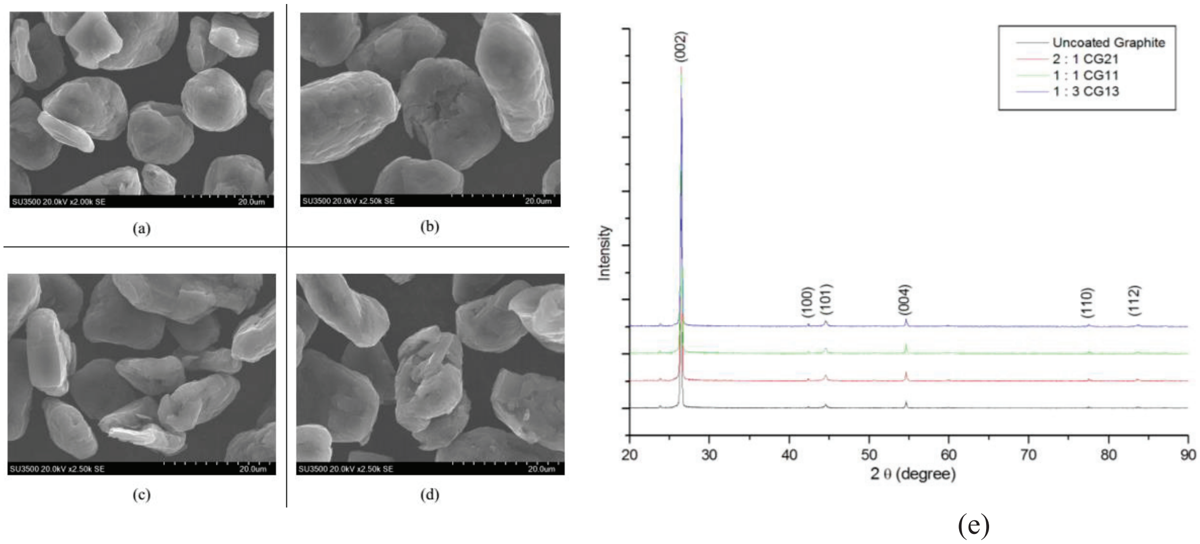
The electrochemical performance of carbon-coated graphite was investigated in the half cells CR2032-type coin cell battery. A slurry of working electrode was prepared with 85 wt% CG, 5 wt% acetylene black, and 10 wt% Polyvinylidene Fluoride (PVDF) (Sigma Aldrich) dispersed in N,N dimethyl acetamide (DMAC). The homogenous anode slurry was coated onto copper foil using doctor blade and then dried at 80°C for approximately two hours. The cell was assembled using $LiPF_6$ (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 the 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 0.1C, 0.5C, 1C and 2 C between 0 – 2.5 volt versus Li/Li^+ to determine the specific capacity at room temperature.

RESULTS AND DISCUSSION

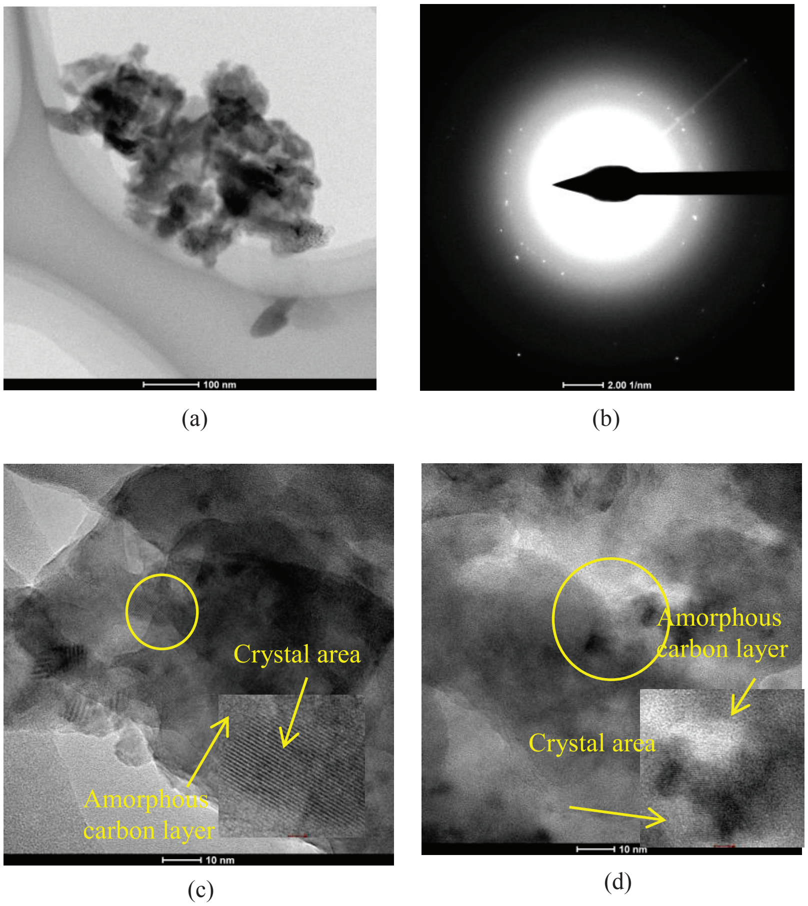
Physical Properties of Material

The samples were prepared with various compositions 2:1, 1:1, and sintered at 600°C for five hours in Ar atmosphere to investigate the effect of the compositions on the electrochemical performance in the Li-ion battery. Fig. 1 showed the XRD patterns of graphite coated by amorphous carbon using citric acid at different compositions. According to data interpretation using Rietveld refinement method PDXL program, XRD patterns indicated that all the samples have hexagonal structures (lattice constant $a = b = 2.4607$ Å, $c = 6.7096$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$) 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 indicated that the graphite coated by amorphous carbon were successfully prepared. Fig. 1 (a, b, c, and d) showed SEM images of the samples sintered at various composition in Ar atmosphere. These images showed a spherical shape and large number of micro-particles samples with average size ranges from 2 to 20 µm. TEM images revealed the crystal area of graphite were covered by the amorphous carbon as shown in Fig. 2. SAED pattern of the samples were also observed.



(a) (b) (c) (d) (e)

FIGURE 1. SEM micrographs (a) uncoated graphite, b) 2:1 (CG21), c) 1:1 (CG11) and d) 1:3 (CG13); respectively) and XRD patterns of uncoated graphite and carbon-coated graphite (CG) for several composition (e).



(a) (b) (c) (d)

FIGURE 2. TEM images of graphite coated by amorphous carbon using citric acid.

Electrochemical Properties

The cyclic voltammograms of samples were shown in Fig. 3 measured with scan rate 0.1 mV/s at range 0 – 2.5 volt. 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. Graphite has the highest specific an oxidation peak current, nevertheless CG11 has slightly higher an oxidation peak potential. It indicated that the composition has a considerable effect on the electrochemical properties of carbon coated graphite.

For further analysis, the effect of coating layer to the charge-discharge capacity of the samples was measured at 0.1C, 0.5C, 01C and 2C as shown in Fig. 4. The highest capacity of carbon coated effect which is measured by half cells is 90 mAh/g. The results showed that increasing the C-rate can decrease the capacity of the sample.

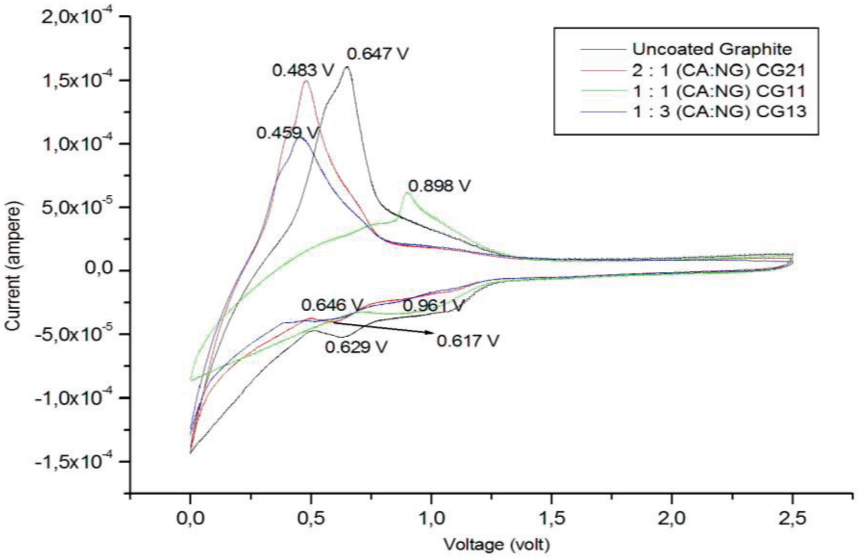


FIGURE 3. Cyclic voltammograms of uncoated graphite (NG) and amorphous carbon-coated graphite with different composition with scan rate of 0.1mV/s at the same cycle and voltage range of 0 – 2.5 volts.

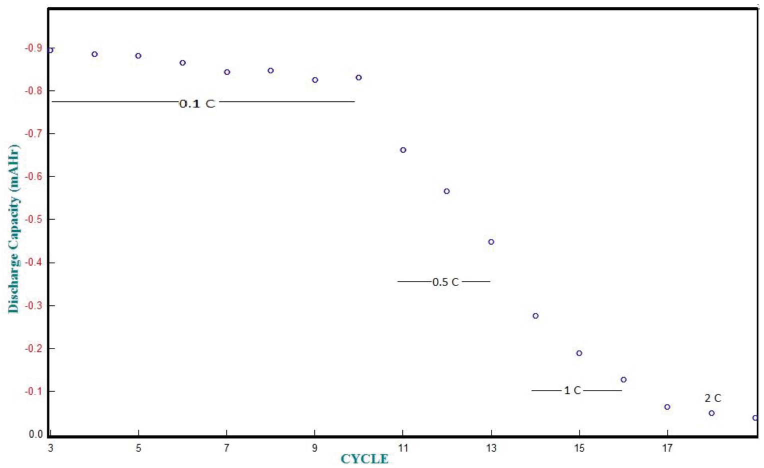


FIGURE 4. Charge discharge amorphous carbon-coated graphite with the composition of 1:3 at 0.1C, 0.5C, 1C and 2C.

CONCLUSION

Effect of the composition of citric acid / graphite to the electrochemical performance of the graphite as anode material in Li-ion battery has been studied through synthesizing the amorphous carbon layer on the surface of the graphite. Crystal structure and impurities effect of the graphite coated by amorphous carbon were investigated as revealed from XRD characterization which showed that no impurities and crystal structure change in the graphite. Amorphous carbon layer and graphite area were observed through electron microscopy analysis (SEM and TEM observation). From the CV and CD test can be concluded that amorphous carbon layer on the surface of graphite improved the electrochemical performance through redox reaction in cyclic voltammogram and charge-discharge capacity which has the specific discharge capacity of 90 mAh/g for the graphite coated by amorphous carbon.

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REFERENCES

1. Changseng Ding, Toshiyuki Nohira, Rika Hagiwara, Atsushi Fukunaga, Shoichiro Sakai, Koji Nitta, *Electrochimica Acta* **176,** 344 – 9 (2015).
2. Ruofei Wu, Guofeng Xia, Shuiyun Shen, Fengjuan Zhu, Fengjing Jiang, Junliang Zhang, *Electrochimica Acta* **153**, 334 – 42 (2015).
3. D. Miranda, C.M. Costa, S. Lanceros-Mendez, *J.Electroanal. Chem.* **739**, 97-110 (2015).
4. Yu-Jin Han, Jandee Kim, Jae-Seong Yeo, Jung Chul An, Ik-Pyo Hong, Koji Nakabayashi, Jin Miyawaki, Jin-Do Jung, Seong-Hoo Yoon, *Carbon* **94**, 432 – 8 (2015).
5. Nidia C. Gallego, Cristian I. Contescu, Harry M. Meyer III, Jane Y. Howe, Roberta A. Meisner, E. Andrew Payzant, Michael J. Lance, Sang Y. Yoon, Mathew Denlinger, David L. Wood III, *Carbon* **72**, 393 – 401 (2014).