

NATURAL POROUS Si-C COMPOSITED WITH NITROGEN-DOPED GRAPHENE AS ANODE MATERIALS IN LITHIUM-ION BATTERIES

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Abstract

Lithium-ion batteries (LIBs) have been widely used as energy storage in portable electronic devices and electric vehicles. However, graphite anode has low specific capacity and safety risks because of low operating voltage versus lithium metal which leads to battery explosion. Hence, porous silicon-carbon/ nitrogen-doped graphene (Si-C/NG) composites are good candidate anode materials for the next generation LIBs. The Si-C can be derived from bamboo leaves through a calcination process and followed by magnesiothermic reduction with the various ratio of magnesium powder. To solve the low conductivity of Si-C, nitrogen-doped graphene (NG) was added by sonication to form porous Si-C/NG composites. In this report, the NG was confirmed to have graphene structure and the nitrogen content of 8.30% by Raman and XPS techniques, respectively. The phase formation of Si-C/NG was identified by XRD along with SAED patterns, which corresponded to silicon, carbon, and silicon carbide. SEM and TEM images showed the agglomeration of porous structure Si-C which was obtained together with the wrinkled paper-like structure of NG. These composites were prepared as electrodes to study electrochemical properties including cycling stability and rate performance. Interestingly, the highest specific capacity around 500 mAhg⁻¹ at 100 mAg⁻¹ after 30 cycles was observed in the Si-C/NG-Mg0.3 electrode which was higher than commercial graphite.

Keywords: Nitrogen-doped graphene, silicon, composite, bamboo leaves, lithium-ion batteries

Introduction

Nowadays, the demand for overall energy is nonstop increasing while the supplies of fossil fuels are decreasing. These have become a great impact on finding renewable energy sources that are accessible and sustainable, for instance, solar energy, biomass

energy, wind power, and hydropower. Thus, the energy storage applications which have the rechargeable ability are necessary to store these energies (Palacín, 2009). Especially, lithium-ion batteries (LIBs) are one of the most widely used as

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energy storage because of their high energy density, long life cycling, low self-discharge rate, long shelf lifetime, no memory effect, and environmental benefits (Mauger *et al.*, 2016; Zhang *et al.*, 2018). It is well known that the most critical components in LIBs are the electrodes, which are important parts to determine the storage capacity and battery performances. Therefore, electrode materials in LIBs should have a high surface area of active site, low diffusion distance, high specific capacity, high electrical and ionic conductivity (Roy and Srivastava, 2015; Qi *et al.*, 2017). Currently, graphite has been the most common material for use as an anode material in commercial LIBs due to its stability, low cost, and high electronic conductivity (Kashhedikar and Maier, 2009). However, graphite delivers low capacity (372 mAh/g) which is not enough for the high demand of emerging applications. Moreover, the safety issue must be concerned with using graphite because of its low operating voltage which could cause the battery explosion. Hence, several researchers have attempted to look for new anode materials to replace conventional graphite anodes.

Among the potential anode materials, silicon (Si) has become the huge attention material for energy storage in the last decade because it has the highest theoretical specific capacity of 4,200 mAh g⁻¹. Also, the agricultural wastes (i.e. rice husk, corn cobs, and bamboo leaves) (Wong *et al.*, 2014; Xu *et al.*, 2016; Dutta and Nath, 2018; Zhao *et al.*, 2019) which is low-cost natural products can be easily extracted the Si element in the form of SiO₂. Thus, these can act as sustainable starting materials for Si production (Liu *et al.*, 2013). Moreover, the high operating potential of these materials (>0.5 V versus Li/Li⁺) corresponded to high safety in the use of LIBs (Yang *et al.*, 2016; Cao *et al.*, 2018). On the other hand, using Si as anode still has the major problem of high-volume expansion during cycling that could lead to the electrode cracking after using for several cycles. Then, the electrode will be lost the electrical contact and increased the internal impedance which affects the capacity fading and battery failure (Shen *et al.*, 2018). As-afore mention, Si can be stabilized by compositing with carbon matrix to achieve successful solving of the volume change problems (Zhuang *et al.*, 2017). Furthermore, the Si-C composites derived from the natural product can be modified to have a high specific surface area by introducing a porous structure which related to a more active site for Li-ion interaction. Interestingly, the porous structure of natural Si-C can improve not only shorten the transport distance for Li⁺ but also offer a large electrode-electrolyte interface in the charge transfer reaction. Therefore, porous Si-C composite will

deliver high specific capacity and surface interaction in the electrode (Feckl *et al.*, 2012; Liang *et al.*, 2018). Nevertheless, Si-C composite still suffers from poor electrical conductivity because of Si and amorphous carbon. Due to the poor electrical conductivity, the slow lithium diffusion kinetics and low electric conductivity which occurred in Si-C affect significantly the rate capability and full capacity utilization of electrodes in LIBs (Liu *et al.*, 2020). For these reasons, the electrical conductivity of this material is one of the factors that need to be developed to obtain high specific capacity and excellent electron transportation in LIBs (Roy and Srivastava, 2015).

To gain the electronic conductivity improvement of Si-C composites, the catalytic graphitization process can transform the amorphous carbon to graphite. Thus, the conductivity will increase because electrons can delocalize on π -bonds and then lithium-ion intercalate and diffuse appropriately in the electrode structure (Wang *et al.*, 2018a; Gaikwad *et al.*, 2019). Besides these techniques, the composite with conductive materials (carbon nanotube, graphene, n-doped graphene, etc.) is a good technique to increase the conductivity of anode materials (Wang *et al.*, 2017; Xiang *et al.*, 2017; Xiong *et al.*, 2017). Especially, the nitrogen-dope graphene (NG) material, which is one of the most attractive modified graphene, not only provides excellent cycling stability but also has a higher specific capacity than bare graphene. Due to the nitrogen defect sites in graphene structure, the active sites in the anode electrode were increased corresponded to the increasing of specific capacity. Moreover, the doped nitrogen elements which are good electron-donor can generate electron delocalization in the graphene structure. For these reasons, NG, which has high conductivity, has become the popular anode material in LIBs (Li *et al.*, 2011).

Besides, the Si-C uniformly distributed and embed in the structure of graphene sheet which its flexible structure can buffer the large volume change and enhance electrical conductivity, leading to fast charge transfer (Wang *et al.*, 2015a; Huang *et al.*, 2019; Laokawee *et al.*, 2019). Therefore, these techniques will be the most attractive processes to enhance the good characteristic of anode materials.

This research focused on the synthesis and development of Si-C composite materials which can be prepared from bamboo leaves through a facile chemical treatment and calcination process followed by magnesiothermic reduction procedures. The amorphous carbon of Si-C composites was improved by catalysts graphitization and conductive composite method to produce Si-C composited with NG sheets. These composites have good characteristic for anode materials and have the

potential to be used as an alternative anode for next-generation high energy density LIBs.

Materials and Methods

Materials

The bamboo leaves which were used as a raw material in this research were collected in Thailand. Hydrochloric acid (HCl, AR grade, 37%) was provided by RCI labscan with analytical grade. Magnesium powder (Mg, reagent grade, 98%), Zinc chloride (ZnCl_2 , reagent grade, >98%) were purchased from sigma-aldrich. Deionized water was used for all the experiments.

Preparation of Si-C/NG Composites

In these synthesized strategies, the bamboo leaves were cleaned with water to remove soil and dust and then dried at 100°C for overnight. The cleaned bamboo leaves were soaked in ZnCl_2 solution which the weight ratio of 1 g ZnCl_2 per 1 g dried bamboo leaves, for 12 h and then dried at 100°C overnight. After that, the porous silica-carbon ($\text{SiO}_2\text{-C}$) was synthesized by heat treatment of the treated bamboo leaves at 500°C for 1 h and then 800°C for 3 h with a heating rate of 5°C min^{-1} under N_2 atmosphere. Next, the $\text{SiO}_2\text{-C}$ product was ground to a fine powder. To prepare the Si-C composite material, the $\text{SiO}_2\text{-C}$ powder was undergone a magnesiothermic reduction together with a catalytic graphitization. The $\text{SiO}_2\text{-C}$ powder was homogeneously mixed with magnesium powder in the mass ratio of 1:0.7, 1:0.5, and 1:0.3. After that, the mixed powder was heated in a nitrogen tube furnace using a heating rate of 5°C min^{-1} and dwelled at $1,000^\circ\text{C}$ for 3 h to reduce SiO_2 to Si. The as-prepared products were then soaked in 10% HCl solution at ambient temperature for 6 h to eliminate the metal oxide impurities. After that, all products were washed and adjusted to neutral by deionized water and then dried to obtain the Si-C composites. To prepare the Si-C/NG composites, the Si-C products, and NG sheets, which the synthesis of NG followed the previous report (Autthawong *et al.*, 2018), were sonicated for 2 h in the mass ratio of 1:1 in the ethanal solvent. Then, the suspension was collected by centrifugation. The final products were dried overnight at 60°C to obtain the Si-C/NG composites. All final products were denoted as Si-C/NG-xMg, whereas the x is the weight ratio of Mg powder.

Characterizations

X-ray diffractometer (XRD) was used to analyze the phase formation of synthesized products by Rigaku Miniflex II desktop diffractometer with

Cu $\text{K}\alpha$ radiation. Scanning electron microscope (SEM, JEOL JSM-7800F-Prime) along with transmission electron microscope (TEM, JEOL JEM-2010) were used to observe the morphology and structure of the prepared materials. To study the characteristic of graphitization, Raman spectra were collected by Raman spectrometer (Jobin Yvon Horiba, model T64000 triple monochromator). X-ray photoelectron spectroscopy (XPS) which is operated by AXIS ultra DLD spectrometer was used to analyze the energy loss of carbon and nitrogen element in the synthesized materials.

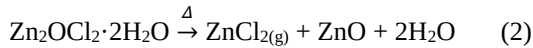
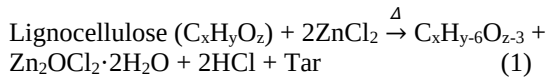
Electrochemical Measurements

To study the electrochemical performances, the Si-C/NG anode materials were fabricated as 2032-type coin cells. The working electrodes were prepared by mixing 70wt% synthesized sample, 15wt% conductive Super-P (NCM HERSBIT Chemical Co. Ltd.), and 15wt% sodium alginate (SA) binder (Loba Chemie, 99%) in DI water in order to form an as homogeneous slurry. Then, the mixed slurry was cast on Cu-foil in the thickness of $150\text{ }\mu\text{m}$ and then dried under vacuum oven at 100°C for overnight to remove the solvent and moist. Next, the prepared electrodes were cut into a circle in the diameter of 15 mm to be an anode electrode. The coin cell was fabricated in the argon-filled glove box to avoid moisture and oxygen. In the coin cell assembly, a lithium metal chip was used as the counter electrode. Both sides of electrodes were separated with polypropylene (PP, Celgard 2400) membrane as a separator and then soaked with the electrolyte of 1 M LiPF_6 solution in a consisting of ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 v/v) + 10% fluoroethylene carbonate (FEC). The electrochemical measurements were performed by a Land battery test system (LAND CT2001A) fixed a cut-off voltage window of 0.01-3.00 V at room temperature. The cycle stability of prepared electrodes was operated for 30 cycles at a current density of 100 mA g^{-1} . To study the rate cycle performance, the electrodes were measured at different current densities of 100 mA g^{-1} to $1,000\text{ mA g}^{-1}$.

Results and Discussion

The SEM images of the Si-C/NG-Mg0.3 product are shown in Figure 1. In the high magnification view (in a yellow square), the nanopores of Si-C were clearly observed in the Si-C/NG-Mg0.3 sample. The porous structure of Si-C derived from the bamboo leaves was fabricated via ZnCl_2 activation together with the heat treatment process as reported in the previous publications (Nieto-Delgado and Rangel-

Mendez, 2013; Ma, 2017). The glycosidic bonds in lignocellulose consisting with the functional groups of hydroxyl and carbonyl were eliminated by the ZnCl_2 which acted as a cutting catalyst and strong dehydrating agent. In this process, the dehydration reactions of glycosidic bonds were firstly provided, and then the biopolymer chains were cut to obtain the short biopolymer chains. While increasing the temperature, this process promoted the slippage of the short polymer chains and form the fluid phase. Then, ZnCl_2 reacted with H_2O generated from the dehydration reactions to form the zinc oxide chloride hydrate ($\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$). At the high temperature, $\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$ was decomposed to form ZnCl_2 gas. This gas was then diffused through the fluid phase to create the nanopore structure in the final Si-C product. Finally, the remaining ZnCl_2 was removed by acid treatment. All reaction mechanisms which were discussed in Yuhui Ma's work (Ma, 2017) are also illustrated in Equations 1 and 2.



The physical and chemical properties of the prepared NG material were analyzed by XRD, Raman spectroscopy, and XPS techniques as the results shown in Figure 2. The XRD pattern of NG in Figure 2(a) presents the major diffraction peaks at 26.2° and 44.3° which can be matched very well with the (002) and (101) planes of carbon (JCPDS no. 75-1621). Figure 2(b) shows the Raman spectra of NG. The NG sample was located at the Raman shift of $1,360 \text{ cm}^{-1}$ and $1,580 \text{ cm}^{-1}$ corresponds to D and G bands which are the characteristic peaks of carbon. The G band is related to in-plane, out-of-phase vibrations of sp^2 C-C bond while the D band is associated with the disorder of graphite structure. The intensity ratio of D and G peak (I_D/I_G) is 1.25. The I_D/I_G over than 1.00 indicated that the NG had higher structural defects in graphitized carbon and nitrogen atoms were doped in the graphene structure. In the case of 2D intensity at about $2,600 \text{ cm}^{-1}$, there was a small 2D band that indicated the few subsistence of multilayer structure in the NG sample (Beams *et al.*, 2015). To study the binding energy of nitrogen element in the NG sample, the XPS spectrum of N 1s is shown in Figure 2(c). In the survey element spectra, the nitrogen element was observed with a weight percentage of 8.30. In the high magnified curve fitting of N 1s, this spectrum indicated the existence of nitrogen bonding in the NG sample, consisting of pyridinic-

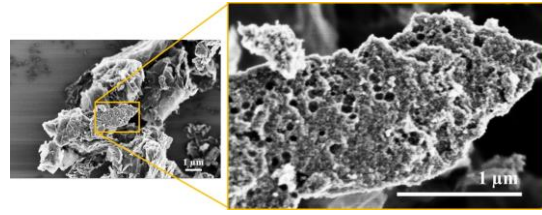


Figure 1. SEM images of the porous product of Si-C in Si-C/NG-Mg0.3 composite after activation by ZnCl_2 and heat treatment process

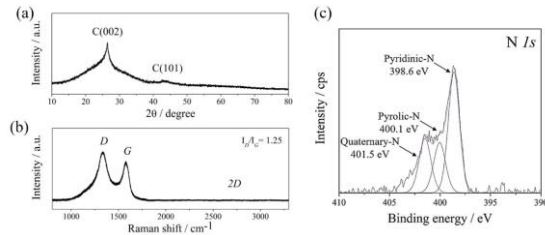


Figure 2. XRD pattern of NG (a), Raman spectrum of NG (b) and XPS N1s spectra of NG (c)

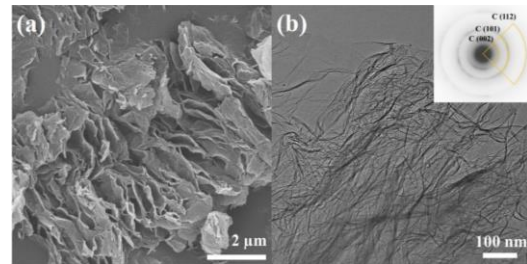


Figure 3. SEM (a) and TEM images along with SEAD pattern (b) of NG

N, pyrrolic-N, and quaternary-N which appeared at 398.6, 400.1, and 401.5 eV, respectively (Autthawong *et al.*, 2020; Jarulertwathana *et al.*, 2017).

Figure 3 represents the morphology and structure of NG which were characterized by SEM and TEM techniques. In the SEM image in Figure 3(a), the multilayered structure of NG sheets was observed as the stacked sheets. However, there was some single sheet separated from the NG stack. To study the structure of NG sheets in higher magnification, the TEM technique was used to observe which the TEM image was presented in Figure 3(b). The TEM image showed the NG as the thin wrinkled-like paper. Moreover, the SEAD pattern was taken from the NG sample. The ring pattern was successfully indexed as carbon in the plane of (002), (101), and (112) and corresponded to XRD result as discussed in the previous section.

Figure 4 shows the XRD patterns of Si-C/NG composite products with a different weight ratio of Mg powder. From the XRD patterns, all samples were clearly confirmed as Si (JCPDS No. 27-1402) and C (JCPDS No. 75-1621). Significantly, the broad peak around 20°-30° corresponded to the overlap peaks of amorphous carbon of Si-C composite derived from bamboo leaves and NG sheets. In addition, the sharp peaks at 28°, 47°, and 56° 2-theta corresponded to crystalline Si. In the samples of Si-C/NG-Mg0.5 and Si-C/NG-Mg0.7, the XRD patterns of silicon carbide (SiC) component (JCPDS No. 29-1129) were observed. These results suggested that the SiC content was related to increasing the weight ratio of Mg powder in the magnesiothermic reduction process. Interestingly, there was no magnesium oxide which was occurred via the reduction reaction and metal impurity from the bamboo leaves because they were completely removed after acid treatment by HCl solution. The

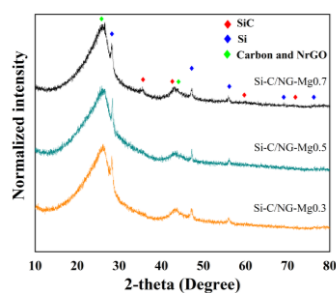


Figure 4. XRD patterns of Si-C/NG composite products with the different weight ratio of Mg powder

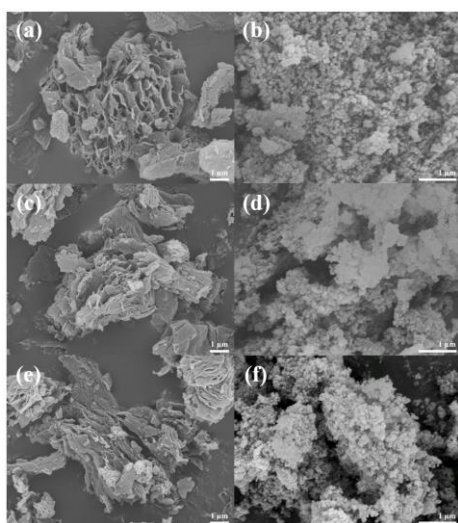
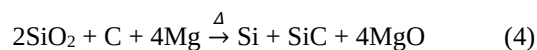


Figure 5. SEM images of Si-C/NG-Mg0.3 (a,b), Si-C/NG-Mg0.5 (c,d) and Si-C/NG-Mg0.7 (e,f) composites

overall chemical reactions of synthesized Si and SiC can be expressed as Equations 3 and 4, respectively (Niyomwas, 2011; Wong *et al.*, 2014).



To observe the morphology of prepared composite materials, the SEM images were taken from the two areas of prepared Si-C/NG composite samples as shown in Figure 5. All samples represented a similar appearance and morphology. It was clearly seen that the small particles of Si-C were agglomerated and NG was seen as the expanded layer stacking of wrinkled paper like structure. Although most of the Si-C particles were separated from the NG sheet, there were also some Si-C particles were decorated together with the expanded layered NG. The reason may come from the ultrasonic power in the composite preparation was not enough to split apart the agglomerated Si-C in order to disperse on the NG sheet.

Figure 6 shows TEM images of Si-C/NG composite with a different weight ratio of Mg powder. In the higher magnification images, the thin wrinkled-like paper of a thin layer NG sheet was observed. The NG sheets had large surface

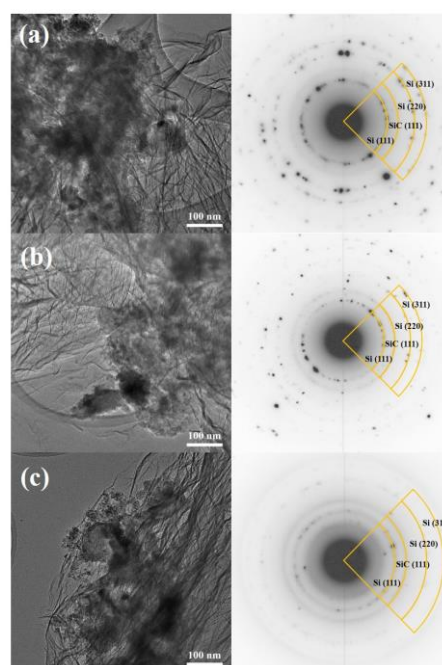


Figure 6. TEM images and the corresponding SAED patterns were taken from the composite products: Si-C/NG-Mg0.3 (a), Si-C/NG-Mg0.5 (b) and Si-C/NG-Mg0.7 (c)

corrugations indicating the disordered structures in the NG sheets. The disordered NG sheets can provide large lithium storage sites, which increased the electrochemical performance of the composites. It can be seen that the Si-C particles which were supported on the NG sheet can overcome the volume expansion-contraction of Si-C particles via charge-discharge processes. The individual Si-C in nanometer size were also agglomerated to form large clusters. In agreement with the XRD study, the inserted ring patterns revealed that the agglomerated particles were Si and SiC phases. Because of the less active materials of SiC, it was expected that the composites with high SiC content would provide lower lithium capacities, besides the composites with high Si content should have a higher specific capacity.

Figure 7 shows the charge/discharge profiles of the Si-C/NG electrodes at a current density of 100 mA g^{-1} . When considering the 1st charge/discharge capacity of all electrodes, the specific capacity rapidly dropped because of the formation of a solid-electrolyte interfacial (SEI) layer from electrolyte decomposition on the electrode surfaces. The

formation of the SEI layer was confirmed by the two plateaus at around 1.0 and 1.5 V (vs. Li/Li^+) (Yu *et al.*, 2018). In this process, the SEI layers were growing from the reaction between active lithium and electrolyte leading to the increased battery resistance (Chen *et al.*, 2010; Wang *et al.*, 2018b). Then, the two plateaus around 1.0 and 1.5 V (vs. Li/Li^+) disappeared after the subsequent cycle (2nd cycle to 25th cycle). Based on the results of charge/discharge profiles, it can be observed that the two-phase region at about 0.2 V (vs. Li/Li^+) in the discharge profile and about 0.4 V (vs. Li/Li^+) in the charge profile corresponded Li-Si alloying and Li-Si dealloying process, respectively (Ryu *et al.*, 2017). Besides, the intercalation of lithium-ion into the graphene structure was detected at a peak below 0.1 V (vs. Li/Li^+) (Jiang *et al.*, 2012).

The cycling stability operated at a current density of 100 mA g^{-1} within the voltage range of 0.01–3.00 V is shown in Figure 8(a). The initial specific capacity of Si-C/NG-Mg0.3, Si-C/NG-Mg0.5, and Si-C/NG-Mg0.7 have observed the specific capacity of 2025.8, 1862.9, and 1551.9 mAh g^{-1} , respectively, and decreased to 513.6, 482.0, and 387.7 mAh g^{-1} , respectively after 30 cycles. The dramatic reduction of capacity in the 2nd cycle was mainly due to SEI formation. It was clearly seen that all composite electrodes showed small capacity

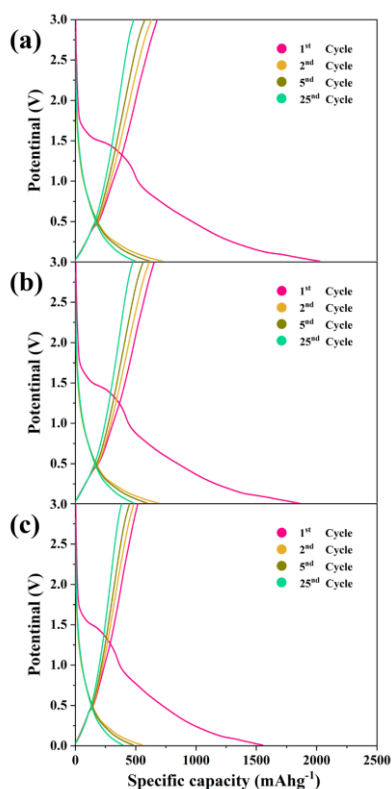


Figure 7. Charge/discharge profiles of Si-C/NG-Mg0.3 (a), Si-C/NG-Mg0.5 (b) and Si-C/NG-Mg0.7 (c) composite at a current density of 100 mA g^{-1}

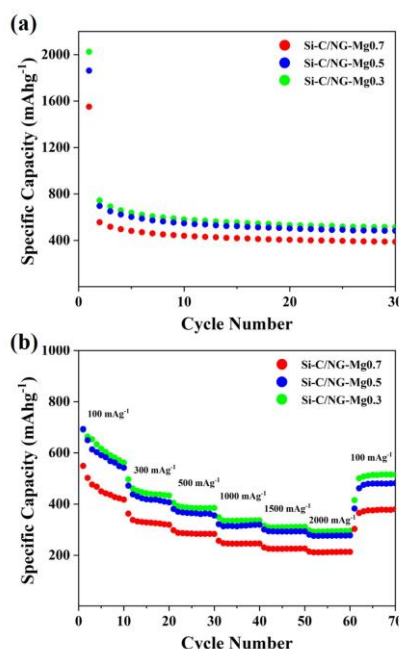


Figure 8. Electrochemical performances of prepared Si-C/NG electrodes: cycle capability (a) and rate capability at different rates increased from 100 mA g^{-1} to $2,000 \text{ mA g}^{-1}$ (b)

fading indicating the good stability of electrodes. It should also be noted that the Si-C/NG-Mg0.3 electrode exhibited the highest specific capacity compared to other electrodes because a small amount of the SiC phase was observed in Si-C/NG-Mg0.3 corresponded to XRD and TEM results. In the case of Si-C/NG-Mg0.5 and Si-C/NG-Mg0.7 electrodes, the reduction of the specific capacity was related to the increase of SiC content due to SiC not only have poor conductivity but also less active than Si. In contrast, the rigid structure of SiC is generally used as a buffer matrix of electronic materials (Wang *et al.*, 2015b). Therefore, SiC can enhance the strength of prepared composites anode in this work.

Furthermore, the rate capability was operated with the current density of 100 mA g^{-1} to $2,000 \text{ mA g}^{-1}$, as shown in Figure 8(b). The highest specific capacity was observed in the Si-C/NG-Mg0.3 electrode, which was higher than the Si-C/NG-Mg0.5 and Si-C/NG-Mg0.7 electrodes. The electrode of Si-C/NG-Mg0.3 exhibited the average specific capacity of 608.37, 442.64, 385.74, 335.32, 309.91, 293.67 mAh g^{-1} at the various current density. After applying the high current density, the current density in rate capability measurement was then reversed to conduct at the current density of 100 mA g^{-1} which recovered to a specific capacity of around 511.99 mA g^{-1} . These results indicated that the excellent reversibility and rate capability was achieved in the Si-C/NG-Mg0.3 electrode. It was obvious that the Si-C/NG-Mg0.7 electrode had the lowest capacity at every current density. After applying a high rate currently, the specific capacity of this electrode was around 375.29 mA g^{-1} at a current density of 100 mA g^{-1} . From the results of Si-C/NG-Mg0.7, it indicated that some amount of Si and C were reduced to be formed the SiC which led to a lower specific capacity. When considering the electrochemical properties of all electrodes, the Si-C/NG-Mg0.3 electrode showed obviously the best performance and had the most opportunity to be used as an anode electrode in future LIBs.

Conclusions

In this work, the prepared Si-C/NG composites were successfully synthesized where Si-C was derived from bamboo leaves. Interestingly, the porous structure was observed in the agglomerated Si-C particles which the individual particle size was obtained in the range of nanometer. From the electrochemical performances, the Si-C/NG-Mg0.3 electrode had the highest specific capacity of around 500 mA h g^{-1} after 30 cycles at a current density of 100 mA g^{-1} . Because of SiC existence in the prepared materials, the specific capacity was decreased.

In the further proposal, SiC would be against to produce in this synthesis. Therefore, this composite has the potential to be used as a promising anode material in LIBs.

Acknowledgments

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