International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# Synthesis of self-assembled Hollow-Sphere ZnO/rGO Nanocomposite as Anode Materials for Lithium-Ion Batteries

Shao-Chieh Weng<sup>1</sup>, Sanjaya Brahma<sup>1</sup>, Chia-Chin Chang<sup>2,\*</sup>, Jow-Lay Huang<sup>1,3,4\*</sup>

<sup>1</sup> Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan (R.O.C.)
<sup>2</sup> Department of Greenergy, National University of Tainan, Tainan 701, Taiwan (R.O.C.)
<sup>3</sup> Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 70101, Taiwan (R.O.C)
<sup>4</sup> Hierarchical Green-Energy Materials (Hi-GEM) Research Center, National Cheng Kung University, Tainan 70101, Taiwan
\*E-mail: <u>ccchang@mail.nutn.edu.tw</u>, jlh888@mail.ncku.edu.tw

Received: 22 June 2018 / Accepted: 18 August 2018 / Published: 10 March 2019

We investigate the lithium storage properties of two kinds of materials as anode for LIB: graphene oxide (GO) and self-assembled hollow-sphere zinc oxide/reduced graphene oxide (ZnO/rGO) nanocomposite. GO is obtained by Hummers method controlled by the various process parameters. The ZnO/rGO hollow sphere nanocomposite is synthesized by a low temperature (95 °C) chemical solution reaction. For ZnO/rGO composite, the capacity is increased remarkably as compared to GO sheets, and this is due to the synergistic effects of both the components in the composite. The GO acts as a conductive buffer layer that promotes the conductivity, and suppresses the volume expansion of ZnO during the charge/discharge process. ZnO/rGO hollow sphere structure nanocomposite has higher capacity 605.36 mAh g<sup>-1</sup>, which is 4.5 times higher than GO (133.82 mAh g<sup>-1</sup>), after 20 cycles. The capacity variation with the charge-discharge rate of ZnO/rGO nanocomposite showed a higher capacity (299.95 mAhg<sup>-1</sup> at 1700 mAg<sup>-1</sup>) than GO (20.09 mAhg<sup>-1</sup> at 1488 mAg<sup>-1</sup>) after 32 cycles.

Keywords: self-assemble hollow sphere structure, ZnO/rGO nanocomposite, lithium-ion batteries

# **1. INTRODUCTION**

During the last few decades, people around the world are increasingly aware of the importance of energy storage devices that can provide energy to a range of electronic devices. Ultra-high capacity slim devices are used in electric vehicles and, it is therefore essential to develop energy storage systems for future requirements.

Li-ion battery (LIB) and supercapacitor are the key energy storage devices developed for electric vehicles/ motorcycles [1]. LIBs have high energy density, long cycle life, low self-discharge, environmental friendly, no memory effect, rapid recharge, and light weight [2]. LIBs can be used to many application fields, such as portable device, home appliances, transportation, and industry. The instruments of LIB include electrodes (cathode and anode), separator and electrolyte [3, 4]. The performances of electrodes is the most important factor affecting the cycle life, stability and safety of LIBs. Graphite is widely used in commercially available LIB, in which lithium forms graphite intercalation compounds (GICs) and the highest level can be LiC<sub>6</sub>, corresponding to a theoretical capacity of 372 mAh g<sup>-1</sup>, but this type of anode does not meet the safety requirements for large size battery applications [5-13]. Graphene, consists of a single layer of sp<sup>2</sup> bonded carbon atoms arranged in honeycomb structure, with high surface area, and high electron mobility (15,000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) at room temperature. Single layer graphene has theoretical lithium storage capacity of 744 mAh g<sup>-1</sup>, if lithium is attached to both sides of the graphene sheets. The enhanced lithium storage capacity of graphene has attracted tremendous attention in replacing graphite, for use in anode active material of LIB [14-18]. Graphene derivate with different oxygen-containing groups such as graphene oxide (GO) and reduced graphene oxide (rGO) can serve as electrode materials with higher capacity. Graphene-based materials can be used as 2D buffer layer for the anisotropic growth of various metal (M)/metal oxides (MOs) nanoparticles (NPs) and effectively suppressed the aggregation of these NPs [19].

It is known that MOs such as zinc oxide (ZnO) [20], RuO<sub>2</sub> [21], NiOx [22], SnO<sub>2</sub> [23], and MnO<sub>2</sub> [24] have gained lot of interest as electrode materials in lithium-ion batteries in the last decades not only because of their higher theoretical capacity but also they can improve the capacity of carbon-based lithium-ion batteries [25]. Zinc oxide is a wide band gap semiconductor (3.37 eV) with large exciton binding energy of 60 meV at room temperature [26], and is considered as a multifunctional material for a various applications such as light-emitting devices [27], UV Photodetectors [28], supercapacitors [29], water splitting [30], and piezoelectric nano-generator (PZG) [31] due to its excellent physical and chemical properties. ZnO, as an anode material of lithium ion batteries, has a theoretical capacity of 978 mAh g-1 [25]. However, some disadvantages of ZnO, such as the poor electronic conductivity, large volume expansion during lithium/delithium process, and fast capacity fading are major challenges for its industrial applications. Recently, various hybrid nanostructures of ZnO nanoparticle and carbon-base materials, which can improve mechanical durability of ZnO and shorten the diffusion paths for Li ion transport, have been developed and thereby improving cycling performance and facilitating fast lithium-ion diffusion [20].

Herein, we demonstrate a possible strategy to combine ZnO and reduced graphene oxide (rGO) in the form of a composite that can be used as anode materials with improved electrochemical properties for applications in LIBs.

# 2. EXPERIMENTAL

## 2.1 Synthesis of graphene oxide (GO) [32, 33]

Commonly used Hummers' method was slightly altered for the synthesis of GO (graphene oxide) by using graphite powder (ALDRICH graphite, 1-2 micron) and the complete procedure was reported

elsewhere [32,33]. 2g of the graphite powder was taken in a glass beaker followed by the addition of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and the mixture was stirred for 10 minutes [34] room temperature. Then, sodium nitrate (2g NaNO<sub>3</sub>) was added to the above mixture followed by continuous stirring for another 30 minutes in an ice bath condition. Potassium permanganate (12 g of KMnO<sub>4</sub>) was slowly added to the above mixture followed by continuous stirring for another 30 minutes. Temperature of the mixture was increased to 78 °C and maintained for 2 hours to which 80 ml of deionized water was added (stirring for 15 minutes) and the reaction is completed by mixing 200 ml of distilled water and 30% H<sub>2</sub>O<sub>2</sub> solution (10 ml) leading to yellowish colored mixture [35]. Finally, hydrogen chloride (20 ml HCl) was added to the solution mixture and stirring is continued for a while. GO was then filtered, washed repeated by alcohol/deionized water and finally dried at 45 °C overnight in a vacuum oven.

#### 2.2 Synthesis of ZnO/rGO hollow sphere nanocomposites

GO(40~50 mg) was added in to 40 ml dimethyl formamide (DMF) and ultrasonicated for 10 min [34]. Zinc acetate dihydrate [Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O] (0.92 g) was dispersed in 200 ml of DMF by magnetic stirring. Subsequently, GO solution was added into the zinc acetate solution with continuous magnetic stirring to prepare stable reaction precursor, then, the mixture is heated to 98 °C and maintained at this temperature for 5 hr. In the reaction, the color changed from dark gray to bright gray. The as obtained ZnO/rGO hollow sphere nanocomposites powder was washed repeatedly by ethanol and DI water by and finally collected by centrifugation. The final ZnO/rGO hollow sphere nanocomposites powder was obtained after drying the product at 55 °C.

## 2.3 Characterization of GO and ZnO/rGO hollow sphere nanocomposite

The crystallinity, surface morphology, the microstructure and the crystallographic phases of GO and ZnO/rGO hollow sphere nanocomposites was studied by X-ray diffraction (XRD, Model No: GADDS/D8 DISCOVER diffractometer) equipped with CuK $\alpha$  ( $\lambda = 1.54$  Å) as the X-ray radiation source, field emission scanning electron microscopy (FE-SEM, Model: AURIGA-39-50, EHT=5kV) and transmission electron microscopy (TEM, JEOL JEM-2100F CS STEM). Raman spectra were recorded on a laser micro-Raman spectrometer with an excitation of 514 nm laser light. Thermogravimetric Analysis (TGA, Perkin Elmer, Pyris 1 TGA) was carried out within 20 °C - 800 °C (heating rate 15 °C per min) in N<sub>2</sub> atmosphere.

## 2.4 Electrochemical analysis [24, 35]

Electrochemical measurements were carried out by using CR2032 type coin cells at room temperature. The working electrode was prepared by mixing the active material (80 wt. %), the conductive additive (10 wt.% of Super P), lithium hydroxide (5 wt. %) and the binder (5 wt.% of polyacrylic acid) [36-38]. The PAA based binders were lithiated by titration using aqueous LiOH (Li-PAA) and controlled by adjusting the pH value of the solution [36]. The four components were mixed

with a suitable amount of deionized water to produce a slurry. This was then uniformly loaded on a copper foil with a doctor blade as a current collector. The sample was cut into circular electrodes and dried for 30 min at 70 °C in an electric oven. The cells were assembled in an Ar-filled glove box with lithium foil as the counter electrode, and a solution of 1.0 M LiPF<sub>6</sub> dissolved in 1:1 (v/v) EC/ DEC as the electrolyte. Galvanostatic Li<sup>+</sup> charge/discharge analysis was carried out using a Wonatech WBCS3000 automatic battery cycler. All electrochemical measurements were conducted in the potential range from 0.002 V to 3 V (vs Li<sup>+</sup>/Li).

## **3. RESULTS AND DISCUSSION**

Figure 1 shows the XRD spectra of GO and ZnO/rGO composite. The XRD pattern of GO exhibits a broad and weak diffraction peak centered at  $2\theta = 10.13^{\circ}$ , which correspond to the interlayer spacing of 0.8623 nm. The dramatic increase in interlayer spacing of GO is ascribed to the embedding of oxygen-containing functional groups during the oxidation process. The standard diffraction pattern of ZnO (JCPDS, card NO.: 36-1451) is provided for comparison with the as-prepared ZnO/rGO nanocomposite. The major diffraction angles at  $2\theta = 31.77^{\circ}$ ,  $34.42^{\circ}$ ,  $36.25^{\circ}$ ,  $47.54^{\circ}$ ,  $56.60^{\circ}$ ,  $62.86^{\circ}$ ,  $66.38^{\circ}$ ,  $67.96^{\circ}$ ,  $69.10^{\circ}$ ,  $72.56^{\circ}$ , and  $76.95^{\circ}$ , can be assigned to the (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) crystal phases, respectively. All the diffraction peaks of as-prepared ZnO/rGO nanocomposite agree well with the hexagonal wurtzite structure (P63mc, a = 3.2495 Å, c = 5.2069 Å, JCPDS, card NO.: 36-1451) of ZnO.



**Figure 1.** XRD patterns of (a) graphene oxide, (b) ZnO PDF #36 - 1451 and (c) self-assembled hollow-sphere ZnO/rGO nanocomposite..

FESEM images reveals the surface morphologies of GO, ZnO nanoparticles and ZnO/rGO hollow sphere nanocomposite which are presented in Figure 2. The surface of GO is randomly folded

and have wrinkled structure (Fig. 2a) due to the presence of oxygen-containing functional groups on GO nanosheets. From Figure 2b, it shows that the typical diameter of ZnO nanoparticle is  $80 \pm 20$  nm. ZnO nanoparticles uniformly disperse on the substrate without aggregation. When zinc ion react with GO and forming ZnO/rGO nanocomposite, the morphology would be hollow sphere structure self-assembly (Fig. 2c), which consists of many nano-size ZnO nanoparticles (diameter:  $60 \pm 10$  nm).



Figure 2. FESEM images of as-prepared (a) graphene oxide, (b) ZnO nanoparticles and (c) self-assembled hollow-sphere ZnO/rGO nanocomposite.





**Figure 3.** Bright field TEM images of (a) graphene oxide, (d) ZnO nanoparticles and (g) ZnO/rGO nanocomposite. HRTEM images of (b) graphene oxide, (e) ZnO nanoparticles and (h) ZnO/rGO nanocomposite. Electron diffraction pattern of (c) graphene oxide, (f) ZnO nanoparticles and (i) ZnO/rGO nanocomposite.

Figure 3 shows TEM images of GO, ZnO nanoparticles, and ZnO/rGO nanocomposite. Figure 3a shows the bright field TEM image of GO sheets, which shows wrinkled layer. The HRTEM image (Fig. 3b) shows that the graphene oxide with weak crystallized structure, and it correspond to the diffraction ring of nano-beam electron diffraction pattern (NBDP) (Fig. 3c). The result of NBDP correspond to XRD diffraction peaks of GO. Figure 3d-3f show the TEM images of ZnO nanoparticles. Figure 3d shows that the diameter of ZnO nanoparticles is around  $80 \pm 20$  nm. From the HRTEM image (Fig. 3e), the d-spacing of ZnO nanoparticle is 2.882 Å, corresponding to the crystal phase (100). However, the TEM images of ZnO/rGO nanocomposite (Figure 3g-3i) show dramatically different morphology from ZnO nanoparticles. The morphology of ZnO/rGO nanocomposite is self-assembled hollow sphere structure, and the diameter of hollow sphere are composed of nanoparticles. The NBDP of ZnO/rGO hollow sphere shown in Fig. 3i confirms the crystal phase (101) of the ZnO.

The Raman spectra for GO and ZnO/rGO hollow sphere nanocomposite were also characterized as shown in Figure 4. For both the samples, distinctive G band centered at around 1578 cm<sup>-1</sup> (tangential mode) could be observed and assigned to the  $E_{2g}$  phonon of C(sp<sup>2</sup>)-C(sp<sup>2</sup>) bond stretching vibrations; and the D band at around 1341 cm<sup>-1</sup> (disorder mode), which was a breathing mode of  $\kappa$ -point phonons of A1g symmetry. The Raman intensity ratio of D to G band ( $I_D/I_G$ ) of GO (1408.06/1315.19) and ZnO/rGO (2833.47/2510.75) are 1.071 and 1.129, respectively. It is found that the latter ZnO/rGO nanocomposite has higher Raman intensity ratio (1.129) which indicates highly disordered structures with more defects, and lesser sp<sup>2</sup> domains. The peak at 2711 cm<sup>-1</sup> corresponds to the overtone of the D band [39]. The peak located at the low frequency (328.86 cm<sup>-1</sup>) is assigned to the 2 $E_2(M)$  mode of ZnO, and the peaks at 432.22 cm<sup>-1</sup> and 1122.80 cm<sup>-1</sup> corresponds to the  $E_2(high)$  vibration mode and 2(LO)mode of ZnO, respectively [40]. The G band peak position of GO is located at 1590.31 cm<sup>-1</sup>, and the G band peak position of ZnO/rGO nanocomposite shows a measurable red shift to 1587.17 cm<sup>-1</sup>, which indicates the GO reduction phenomena. Based on the above results, we can conclude that the synthesis process itself is able to reduce GO in ZnO/rGO hollow sphere nanocomposite.



Figure 4. Raman spectra of (a) graphene oxide and (b) ZnO/rGO nanocomposites.

Figure 5 shows the thermogravimetric analysis (TGA) of GO and ZnO/rGO nanocomposite from room temperature to 800 °C in N<sub>2</sub> atmosphere. The detail weight loss is shown in the inset. The mass loss from room temperature to 180 °C is due to the loss of water molecules existing both on the surface and dominating in materials. The weight loss at intermediate temperature range (280-580 °C) is attributed to the thermolysis of oxygen-containing functional groups to generate carbon monoxide (CO) or carbon dioxide (CO<sub>2</sub>) [20, 23]. From the result of TGA analysis of GO, it shows that GO was decomposed when the temperature higher than 211 °C. The remnant after 580 °C corresponds to the amount of ZnO in nanocomposite. The weight ratio of GO and ZnO is 2 to 8 approximately.



Figure 5. TGA analysis of graphene oxide (black line) and ZnO/rGO nanocomposite (red line).

The electrochemical performance of as-prepared GO and ZnO/rGO hollow sphere nanocomposite anode are evaluated in a half-cell utilizing a metallic lithium film as the counter electrode and reference electrode. The galvanostatic charge-discharge curve for GO and ZnO/rGO nanocomposite electrodes between 0.002 and 3.0 V (vs. Li/Li<sup>+</sup>) at a current rate of 0.1C is shown in Fig. 6a-b. The first charge/discharge capacities are 1204.42 mAh g<sup>-1</sup>, 311.85 mAh g<sup>-1</sup> for GO and 1264.44 mAh g<sup>-1</sup> and 694.02 mAh g<sup>-1</sup> for ZnO/rGO nanocomposite electrodes. From the cycle performance results, the irreversible capacity of GO and ZnO/rGO nanocomposite are 74.2% and 45.1%, respectively. The initial discharge capacity increased and irreversible capacity decreased due to the GO reduction, which improved the conductivity. It is observed that not only the specific capacity is enhanced but also irreversible capacity is dramatically increased.



**Figure 6.** Charge/discharge curve of (a) graphene oxide and (b) ZnO/rGO nanocomposite. Capacity vs. cycle number plots of (c) graphene oxide and (d) ZnO/rGO nanocomposite.

As other metal oxides and previously reported of ZnO-based materials [20, 25, 41], there is voltage plateau at 0.5 V which is mainly from the irreversible reduction of ZnO to Zn and the formation of Li-Zn alloy. The conversion reactions between ZnO and Li ions can be expressed by the following two equations:

$$\begin{array}{c} charge \\ Conversion reaction:  $ZnO + 2Li^{+} + 2e^{-} \rightleftharpoons Zn + Li_{2}O \quad (1) \\ discharge \\ charge \\ Alloying reaction:  $Zn + Li^{+} + e^{-} \rightleftharpoons LiZn \quad (2) \\ discharge \end{array}$$$$

The capacity vs. cycle number plots of GO and ZnO/rGO nanocomposite are shown in Fig. 6cd. The discharge capacities of 20<sup>th</sup> cycle are 133.82 mAh g<sup>-1</sup> for GO and 605.36 mAh g<sup>-1</sup> for ZnO/rGO nanocomposite, respectively, which prove that the positive effect of combining ZnO with GO forming ZnO/rGO nanocomposite and facilitate the performance.

It has been reported that the combination of ZnO with carbon based materials (carbon nanotubes, reduced graphene oxide, graphene) can improve the performance (cyclic stability, rate capability etc.) of lithium ion batteries. Table 1 provides a brief review of the electrochemical properties of ZnO/carbon-based material composite [20, 41-47] that shows that the combination of ZnO and GO/RGO/CNT have higher capacity and better cyclic stability than pure ZnO material.

Authors	Materials and Structure	Current density	Reversible capacity of 1 <sup>st</sup> cycle (mAh g <sup>-1</sup> )	Voltage range	Capacity retention after n cycles (cycling range)	Ref.
J. Wu et al.	ZnO/rGO composites	200 mA g <sup>-1</sup>	450 mAh g <sup>-1</sup>	0.01 to 3.0 V	360 mAh g <sup>-1</sup> (n=2- 200)	[41]
H. Li et al.	ZnO/NCNT composite	100 mA g <sup>-1</sup>	1005 mA g <sup>-1</sup>	0.005 to 3.0 V	664 mAh g <sup>-1</sup> (n=2- 100)	[20]
Y. Zou et al.	ZnO/MWCNTs nanocomposites	100 mA g <sup>-1</sup>	802 mA g <sup>-1</sup>	0.01 to 3.0 V	437 mA g <sup>-1</sup> (n=2-100)	[42]
CT. Hsieh et al.	ZnO@Graphene composites	0.1 C	606 mA g <sup>-1</sup>	0.01 to 3.0 V	475 mA g <sup>-1</sup> (n=2-50)	[43]
M. Yu et al	ZnO/graphene nanocomposite	100 mA g <sup>-1</sup>	783 mA g <sup>-1</sup>	0.01 to 2.5 V	610 mA g <sup>-1</sup> (n=2-500)	[44]
C. Kim et al.	self-assembled ZnO@GO composite	100 mA g <sup>-1</sup>	798 mA g <sup>-1</sup>	0.02 to 3.0 V	517 mA g <sup>-1</sup> (n=2-65)	[45]
F. Li et al.	ZnO nanospheres	0.5 C	657 mA g <sup>-1</sup>	0.05 to 2.5 V	381 mA g <sup>-1</sup> (n=2-30)	[46]
HJ. Yang et al.	mesoporous ZnO nanowires	0.1 C	728 mA g <sup>-1</sup>	0.01 to 2.0 V	432 mA g <sup>-1</sup> (n-2-10)	[47]
This work	Self-assembled hollow-sphere ZnO/rGO nanocomposite	85 mA g <sup>-1</sup>	694 mA g <sup>-1</sup>	0.002 to 3.0 V	605 mA g <sup>-1</sup> (n=2-20)	This work

Table 1. Physical properties and electrochemical Li cycling data of ZnO/carbon-based material

The Nyquist plots of GO and ZnO/rGO nanocomposite (Fig. 7) shows two different regions: a semicircle in the high frequency and a slope line in the low frequency, which describe various resistances obtained in the materials [23, 48, 49]. The semicircle at high frequency, which is mainly contributed from active material (GO or ZnO/rGO) and the electrolyte, of ZnO/rGO nanocomposite is smaller than the GO electrode, indicating that ZnO/rGO nanocomposite has smaller surface film resistance and charge transfer resistance. Meanwhile, the slope line can be attributed to the diffusion of lithium ion into electrode materials [48-50]. ZnO/rGO nanocomposite exhibits smaller diameter of the high-frequency semicircle as that with GO, revealing lower charge-transfer resistance, which may be attributed to the highly electric conduction performance of GO and high capacity of ZnO.



Figure 7. EIS analysis of GO (square-solid black line) and ZnO/rGO nanocomposite (circle-solid red line).

Figure 8 shows the capacity variation with charge-discharge rate of GO and ZnO/rGO nanocomposite. The capacity of GO is 136.17 mAhg<sup>-1</sup> in 74.4 mAg<sup>-1</sup> (0.1C) during first seven cycles. When the current density was 148.8 mAg<sup>-1</sup> (0.2C), 372 mAg<sup>-1</sup> (0.5C), 744 mAg<sup>-1</sup> (1C), and 1488 mAg<sup>-1</sup> (2C), the GO electrode showed reversible capacities of 98.22 mAhg<sup>-1</sup>, 55.81 mAhg<sup>-1</sup>, 33.48 mAhg<sup>-1</sup>, and 20.09 mAhg<sup>-1</sup>, respectively. The capacity of ZnO/rGO nanocomposite is 650.87 mAhg<sup>-1</sup> in 85 mAg<sup>-1</sup> (0.1C) during first seven cycles. When the current density was 170 mAg<sup>-1</sup> (0.2C), 425 mAg<sup>-1</sup> (0.5C), 850 mAg<sup>-1</sup> (1C), and 1700 mAg<sup>-1</sup> (2C), the ZnO/rGO nanocomposite electrode showed reversible capacities of 635.19 mAhg<sup>-1</sup>, 595.98 mAhg<sup>-1</sup>, 511.68 mAhg<sup>-1</sup>, and 299.95 mAhg<sup>-1</sup>, respectively [51]. This further implies that the ZnO/rGO nanocomposite structure is highly stable at high charge-discharge rate leading to relatively high capacity (299.95 mAhg<sup>-1</sup>) which is 15 times higher than GO (20.09 mAhg<sup>-1</sup>). When the charge-discharge rate is reversed to 0.1 C (74.4 mAg<sup>-1</sup> and 85 mAg<sup>-1</sup> for GO and ZnO/rGO nanocomposite reaches to113.85 mAhg<sup>-1</sup> and 558.73 mAhg<sup>-1</sup> for GO and ZnO/rGO nanocomposite at 32<sup>nd</sup> cycle. The capacity retention for both GO (ZnO/rGO) nanocomposite is as high as 83.6 % (85.8 %) which indicates that the ZnO/rGO nanocomposite has high structural stability leading to better capacity after 32 cycles.



**Figure 8.** Capacity versus cycle number of GO (square-solid black line) and ZnO/rGO nanocomposite (circle-solid red line); the cell was first cycled at 0.1C for 7 cycles with the voltage ranging between 0.002 and 3.0 V, after which the rate was increased in stages to 0.2C for 5 cycles, 0.5C for 5 cycles, 1C for 5cycles, 2C and 0.1C for final 5 cycles.

## 4. CONSLUSIONS

In summary, in this work GO and ZnO/rGO hollow sphere nanocomposite are successfully fabricated via a facile route. During the process of synthesis of ZnO/rGO nanocomposite, the formation of ZnO and reduction of GO proceed simultaneously. The electrochemical property of ZnO/rGO hollow sphere nanocomposite showed better Li storage performance and stable reversible capacity of 605.36 mAh g<sup>-1</sup>, which is 4.5 times higher than the reversible capacity of GO (133. 82 mAh g<sup>-1</sup>). GO has wide interlayer space that serves as appealing 2D substrates for the anisotropic growth of ZnO nanoparticles, and self-assembled ZnO/rGO hollow sphere nanocomposite with improved capacity and conductivity. The capacity variation with the charge-discharge rate of ZnO/rGO nanocomposite reveal relativley high capacity (299.95 mAhg<sup>-1</sup> at 1700 mAg<sup>-1</sup>) than GO (20.09 mAhg<sup>-1</sup> at 1488 mAg<sup>-1</sup>). The enhancement in the electrochemical properties of ZnO/rGO nanocomposite can be attributed to the synergistic effects of combining ZnO with rGO.

#### ACKNOWLEDGEMENT

This work was financially supported by the Hierarchical Green-Energy Materials (Hi-GEM) Research Center, from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan.

#### References

- 1. H. Kim, D.-H. Seo, S.-W. Kim, J. Kim, K. Kang, Carbon, 49 (2011) 326.
- 2. J.-M. Tarascon, M. Armand, NATURE, 414 (2001) 359.
- 3. B. Scrosati, *Electrochimica Acta*, 45 (2000) 2461.
- 4. R. Marom, S.F. Amalraj, N. Leifer, D. Jacob, D. Aurbach, *Journal of Materials Chemistry*, 21 (2011) 9938.
- 5. I. Lahiri, W. Choi, Critical Reviews in Solid State and Materials Sciences, 38 (2013) 128.
- 6. D. Bar-Tow, E. Peled, L. Burstein, Journal of The Electrochemical Society, 146 (1999) 824.
- 7. M. inter, P. Novák, A. Monnier, J. Electrochem. Soc., 145 (1998) 428.
- 8. X.-M. Liu, Z.d. Huang, S.w. Oh, B. Zhang, P.-C. Ma, M.M.F. Yuen, J.-K. Kim, *Composites Science and Technology*, 72 (2012) 12.
- 9. C. de las Casas, W. Li, Journal of Power Sources, 208 (2012) 74.
- 10. C. Zhong, J.-Z. Wang, D. Wexler, H.-K. Liu, Carbon, 66 (2014) 637.
- D.-W. Jung, S.-W. Han, J.-H. Jeong, E.-S. Oh, *Journal of Electroanalytical Chemistry*, 695 (2013) 30.
- 12. S.H. Ng, J. Wang, Z.P. Guo, J. Chen, G.X. Wang, H.K. Liu, Electrochimica Acta, 51 (2005) 23.
- 13. W. Xing, P. Bai, Z.F. Li, R.J. Yu, Z.F. Yan, G.Q. Lu, L.M. Lu, *Electrochimica Acta*, 51 (2006) 4626.
- 14. A.K. Geim, K.S. Novoselov, nature materials, 6 (2007) 183.
- 15. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science*, 306 (2004) 666.
- V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, S. Seal, *Progress in Materials Science*, 56 (2011) 1178.
- 17. G. Wang, X. Shen, J. Yao, J. Park, Carbon, 47 (2009) 2049.
- 18. E. Yoo, J. Kim, E. Hosono, H.-s. Zhou, T. Kudo, I. Honma, Nano Lett., 8 (2008) 2277.
- 19. S. Han, D. Wu, S. Li, F. Zhang, X. Feng, Small, 9 (2013) 1173.
- H. Li, Z. Liu, S. Yang, Y. Zhao, Y. Feng, Z. Bakenov, C. Zhang, F. Yin, *Materials* (Basel), 10 (2017).
- 21. P. Balaya, H. Li, L. Kienle, J. Maier, Advanced Functional Materials, 13 (2003) 621.
- 22. B. Varghese, M.V. Reddy, h. Yanwu, C.S. Lit, T.C. Hoong, G.V.S. Rao, B.V.R. Chowdari, A.T.S. Wee, C.T. Lim, C.-H. Sow, *Chem. Mater.*, 20 (2008) 3360.
- C.-C. Hou, S. Brahma, S.-C. Weng, C.-C. Chang, J.-L. Huang, *Applied Surface Science*, 413 (2017) 160.
- 24. S.-C. Weng, S. Brahma, C.-C. Chang, J.-L. Huang, Ceramics International, 43 (2017) 4873.
- 25. W. Zhang, L. Du, Z. Chen, J. Hong, L. Yue, Journal of Nanomaterials, 2016 (2016) 1.
- 26. Z.L. Wang, Journal of Physics: Condensed Matter, 16 (2004) R829.
- 27. B.P. Zhang, N.T. Binh, K. Wakatsuki, C.Y. Liu, Y. Segawa, N. Usami, *Applied Physics Letters*, 86 (2005) 032105.
- 28. T. Zhai, X. Fang, M. Liao, X. Xu, H. Zeng, B. Yoshio, D. Golberg, Sensors (Basel), 9 (2009) 6504.
- 29. Y. Zhang, H. Li, L. Pan, T. Lu, Z. Sun, Journal of Electroanalytical Chemistry, 634 (2009) 68.
- M. Liu, C.-Y. Nam, C.T. Black, J. Kamcev, L. Zhang, *The Journal of Physical Chemistry* C, 117 (2013) 13396.
- 31. M.S. Al-Ruqeishi, T. Mohiuddin, B. Al-Habsi, F. Al-Ruqeishi, A. Al-Fahdi, A. Al-Khusaibi, *Arabian Journal of Chemistry*, (2016).
- 32. P. Kumar, M.F. Wani, Jurnal Tribologi, 13 (2017) 36.
- N.I. Zaaba, K.L. Foo, U. Hashim, S.J. Tan, W.-W. Liu, C.H. Voon, *Procedia Engineering*, 184 (2017) 469.
- 34. D.I. Son, B.W. Kwon, D.H. Park, W.S. Seo, Y. Yi, B. Angadi, C.L. Lee, W.K. Choi, *Nat Nanotechnol*, 7 (2012) 465.
- 35. I. Nam, N.D. Kim, G.-P. Kim, J. Park, J. Yi, Journal of Power Sources, 244 (2013) 56.

- 36. S. Chibowski, M. paszkiewicz, J. Patkowski, Physicochem. Probl. Miner. Process., 48 (2012) 317.
- J.P. Cheng, R. Ma, M. Li, J.S. Wu, F. Liu, X.B. Zhang, *Chemical Engineering Journal*, 210 (2012) 80.
- 38. A. Solís-Gómez, M.G. Neira-Velázquez, J. Morales, M.A. Sánchez-Castillo, E. Pérez, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 451 (2014) 66.
- 39. Q.-P. Luo, X.-Y. Yu, B.-X. Lei, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, *The Journal of Physical Chemistry* C, 116 (2012) 8111.
- 40. Z. Zhan, L. Zheng, Y. Pan, G. Sun, L. Li, J. Mater. Chem., 22 (2012) 2589.
- 41. J. Wu, C. Chen, Y. Hao, C. Wang, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 468 (2015) 17.
- 42. Y. Zou, Z. Qi, W. Jiang, J. Duan, Z. Ma, Materials Letters, 199 (2017) 57.
- 43. C.-T. Hsieh, C.-Y. Lin, Y.-F. Chen, J.-S. Lin, Electrochimica Acta, 111 (2013) 359.
- 44. M. Yu, D. Shao, F. Lu, X. Sun, H. Sun, T. Hu, G. Wang, S. Sawyer, H. Qiu, J. Lian, *Electrochemistry Communications*, 34 (2013) 312.
- 45. C. Kim, J.W. Kim, H. Kim, D.H. Kim, C. Choi, Y.S. Jung, J. Park, *Chemistry of Materials*, 28 (2016) 8498.
- 46. F. Li, L. Yang, G. Xu, H. Xiaoqiang, X. Yang, X. Wei, Z. Ren, G. Shen, G. Han, *Journal of Alloys* and Compounds, 577 (2013) 663.
- 47. H.-J. Yang, S.-C. Lim, S.-Y. He, H.-Y. Tuan, RSC Advances, 5 (2015) 33392.
- 48. N.-J. Song, International Journal of Electrochemical Science, 13 (2018) 452.
- 49. M.-J. Xiao, International Journal of Electrochemical Science, 13 (2018) 762.
- 50. Z. Yan, Q. Hu, G. Yan, H. Li, K. Shih, Z. Yang, X. Li, Z. Wang, J. Wang, *Chemical Engineering Journal*, 321 (2017) 495.
- 51. H. Wan, International Journal of Electrochemical Science, 13 (2018) 4115.

© 2019 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).