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Abstract

Sodium ion battery is a promising electrical energy storage system for sustainable energy storage applications due to the abundance of sodium resources and their low cost. In this communication, the electrochemical properties of sodium ion storage in reduced graphene oxide (RGO) were studied in an electrolyte consisting of 1 M NaClO₄ in propylene carbonate (PC). The experimental results show that the RGO anode allowed significant sodium ion insertion, leading to higher capacity at high current density compared to the previously reported results for carbon materials. This is due to the fact that RGO possesses higher electrical conductivity and is a more active host, with large interlayer distances and a disordered structure, enabling it to store a higher amount of Na ions. RGO anode exhibits high capacity combined with long-term cycling stability at high current densities, leading to reversible capacity as high as 174.3 mAh g⁻¹ at 0.2 C (40 mA g⁻¹), and even 93.3 mAh g⁻¹ at 1 C (200 mA g⁻¹) after 250 cycles. Furthermore, RGO could yield a high capacity of 141 mAh g⁻¹ at 0.2 C (40 mA g⁻¹) over 1000 cycles. 2013 Elsevier Ltd. All rights reserved.

Keywords

oxide, superior, cycling, stability, rate, reduced, capability, graphene, sodium, storage

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Wang, Y., Chou, S., Liu, H. K. & Dou, S. X. (2013). Reduced graphene oxide with superior cycling stability and rate capability for sodium storage. *Carbon*, 57 (June), 202-208.

Reduced graphene oxide with superior cycling stability and rate capability for sodium storage

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Abstract

The sodium ion battery is a promising electrical energy storage system for sustainable energy storage applications due to the abundance of sodium resources and their low cost. In this paper, the electrochemical properties of sodium ion storage in reduced graphene oxide (RGO) were studied in an electrolyte consisting of 1 M NaClO₄ in propylene carbonate (PC). The experimental results show that the RGO anode allowed significant sodium ion storage, leading to higher capacity at high current density compared to the previously reported results for carbon materials. This is due to the fact that RGO possesses higher electrical conductivity and is a more active host, with large interlayer distances and a disordered structure, enabling it to store a higher amount of Na ions. RGO anode exhibits high capacity combined with long-term cycling stability at high current densities, leading to reversible capacity as high as 174.3 mAh g⁻¹ at 0.2 C (40 mA g⁻¹), and even 93.3 mAh g⁻¹ at 1 C (200 mA g⁻¹) after 250 cycles. Furthermore, RGO could yield a high capacity of 141 mAh g⁻¹ at 0.2 C (40 mA g⁻¹) over 1000 cycles.

1. Introduction

As rechargeable lithium ion battery energy storage technologies have been well developed, lithium ion batteries (LIBs) are extensively applied in various electronic devices, including electric vehicles, portable electrical devices, and smart grids. Large-scale application of LIBs, however, could face challenges related to scarcity of lithium resources and high cost. To achieve long-term energy development, rechargeable sodium ion batteries (SIBs) are gaining recognition as an intriguing candidate for such large-scale and sustainable applications. In contrast to lithium, sodium has an obvious cost advantage because of the natural abundance of Na resources, although sodium has a larger atomic mass and ionic radius than lithium. These properties mean that successful reversible intercalation hosts must possess large enough channels and interstitial sites to accept the large Na ions. Furthermore, sodium shows different thermodynamic parameters, as reflected in the higher standard reduction potential (-2.71 V vs. standard hydrogen electrode (SHE), compared to ~ 3.04 V for Li), and the gravimetric capacity is lower (1165 mAh g^{-1} compared to 3829 mAh g^{-1} for Li). Although batteries based on metallic sodium anodes would always deliver lower energy densities and exhibit lower operating voltages than those with lithium metal anodes [1], sodium ion batteries certainly are a promising option for large-scale applications in which cost rather than energy density is the overwhelming factor. Recently, great efforts have been made to find appropriate active materials for both anodes and cathodes of SIBs [2-9]. Many LIB electrode materials should theoretically show a similar electrochemistry to their counterparts in SIBs. Graphite initially drew attention because of its common use in LIBs, however, it does not allow sodium ions to intercalate to any appreciable extent and is electrochemically irreversible [10]. It is well known that the characteristics of carbon materials, including the degree of graphitization, the structural or textural disorder, and the porosity have a strong influence on the capability for and mechanisms of sodium insertion [11-13]. In recent

decades, several types of non-graphitic carbon anodes were proposed for SIBs that possess large interlayer distances and disordered structure favorable to Na-ion insertion-extraction, delivering a low reversible capacity between 100 and 300 mAh g⁻¹ [14-16]. Although those researches prove the feasibility of non-graphitic carbon materials, all of them showed rather poor cycling stability even with low charge-discharge rates at room temperature. Dramatic progresses have been made by Maier's and Liu's groups [17,18], whose results show the critical function of microstructure in the carbon materials, in forms such as hollow nanospheres and nanowires. Maier's results showed the hollow carbon nanospheres was tested at 50 mA g⁻¹ for first ten cycles and then 100 mA g⁻¹ for 100 cycles, a reversible capacity of ~160 mAh g⁻¹ could be obtained over 100 cycles. Liu's group showed a high reversible capacity of 206.3 mAh g⁻¹ after 400 cycles at 0.2 C (50 mA g⁻¹).

In this paper, we prepared reduced graphene oxide (RGO) in large amounts by the simple modified Hummer's method [19], which can meet the demand for large-scale applications. We used the obtained RGO as the anode in SIBs for the first time. The results show the RGO anode could deliver high capacity of 141 mAh g⁻¹ at 0.2 C (40 mA g⁻¹) with long cycling life over 1000 cycles. Outstanding rate capability also can be obtained, showing a reversible capacity of 95.6 mAh g⁻¹ at a very high current rate of 5 C (1000 mA g⁻¹).

2. Experimental

2.1 Preparation of RGO

Graphite oxide was prepared from natural graphite by the modified Hummers' method [19]. Graphite powder (2 g) was added into 46 ml concentrated H₂SO₄ then 1 g NaNO₃ was added into the above mixture under stirring and cooling in an ice bath condition for 15 min, followed by slowly adding 6 g KMnO₄. Then the mixture was continuously stirred overnight at room temperature, followed by adding 92 ml deionized water, 280 ml warm deionized water and 10 mL 30 wt.% H₂O₂ in sequence. The obtained graphite oxide was then washed

with 1:10 (v:v) HCl solution once and deionized water three times. The graphite oxide was collected by dried in a vacuum oven at 45 °C overnight. Reduced graphene oxide (RGO) was fabricated from the obtained graphite oxide through heat-treatment at 450 °C for 5 h, then 750 °C for 5 h in H₂/Ar mixed atmosphere, followed by ultrasonic treatment for 1 h to further exfoliate the graphene nanosheets.

2.2 Physical characterization

The morphology of the samples was investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA). The pass energy was 60 eV for the survey spectra and 20 eV for specific elements. Atomic force microscope (AFM) images were collected by Kelvin probe force microscopy (Asylum Research MFP-3D). The microstructure was characterized by powder X-ray diffraction (XRD; GBC MMA diffractometer) with Cu K α radiation at a scan rate of 2° min⁻¹. Raman spectra were collected with a Jobin Yvon HR800 Raman spectrometer with a 10 mW helium/neon laser at 632.8 nm excitation. X-ray photoelectron spectroscopy (XPS) was carried out on a VG Scientific ESCALAB 2201XL instrument using Al K α X-ray radiation and fixed analyzer transmission mode.

2.3 Electrochemical measurements

The electrochemical measurements were conducted by first assembling coin-type half cells in an argon-filled glove box. The slurry was prepared by fully mixing 80 wt % RGO, 10 wt % carbon black, and 10 wt % polyvinylidene difluoride (PVdF) by planetary mixer (KK-250S), then pasted on a copper film by a doctor blade with the thickness of 100 μ m followed by dried in a vacuum oven overnight at 80 °C. The working electrode was prepared by punching the electrode film into discs of 0.97 cm diameter. The sodium foil was cut by the doctor blade technique from the sodium bulk stored in mineral oil. The sodium foil was employed as both reference and counter electrode. The electrodes were separated by a glass fiber separator. The

electrolyte was 1.0 M NaClO₄ in propylene carbonate (PC). The electrochemical performance was tested by a Land Battery Test System with a cut-off voltage range from 0.01 V to 2.0 V (vs. Na/Na⁺). Cyclic voltammetry was performed using a Biologic VMP-3 electrochemical workstation between 0.01-2.0 V at a sweep rate of 0.1 mV s⁻¹.

3. Results and discussion

3.1 Characterizations of morphology and structure

The morphology and microstructure of the prepared material was characterized by field emission scanning electron microscopy (FESEM). Low magnification SEM images (Fig. 1(a)) show that the particle size of the RGO material is around 10 μm. High magnification images (Fig. 1(b)) show that the RGO possesses a layered structure. It is obvious that the RGO nanosheets overlap each other and show a thin, wrinkled structure, resulting in a large amount of free space between the graphene layers and the appearance of nanocavities and/or holes and/or defects, which is favorable to the Na ion insertion. Atomic force microscope (AFM) images (Fig. 1(c)) of RGO were used to further confirm the thickness of the RGO layers. The sample was deposited onto a mica flake from an aqueous dispersion of 0.1 mg mL⁻¹ of RGO. The results show that the thickness of the large RGO sheet in the image is ~2.0 nm (from point H to point K), which results from the stack of 3–5 graphene layers that is created during the heat reduction process. The RGO sheet possesses nanocavities with single layer graphene ~ 0.6 nm in thickness (G-L). It is found that the defects and single layer graphene coexist in the RGO host, with a thickness of ~0.8 nm for the small RGO sheet (E-F) Fig.1(c).

Fig.1-FESEM images of RGO (a) at low magnification (5 K) (b) at high magnification (70 K). (c) AFM image and profiles of RGO along the indicated lines in different locations.

The X-ray diffraction (XRD) patterns of RGO and GO are shown in Fig. 2(a). It is found that the characteristic diffraction peak of GO at $\sim 10^\circ$ disappears in RGO, which demonstrates that the GO was reduced to RGO during the heat-treatment. The RGO XRD pattern consists basically of two broadened peaks located at around 26° and 43° , corresponding to the (002) diffraction of the graphitic layered structure and the (100) diffraction for graphite, respectively [17]. The XRD pattern in Fig. 2(a) is typical of non-graphitic carbon materials with a highly disordered nanocrystalline structure. In addition, the

samples show a low signal-to-background ratio, which is probably attributable to incoherent scattering from non-crystalline materials. It is unavoidable that large amounts of hydrocarbons, impurities, and heteroatoms are formed on the graphene surfaces during the oxidative process in strong acid in the modified Hummers' method [19]. Thus, the XRD results suggest that RGO is composed of disordered graphite nanocrystallites with stacked layers of graphene sheets, in agreement with the SEM and AFM observations in Fig. 1. The Raman spectra (Fig. 2(b)) of RGO exhibit two peaks at about 1334.8 cm^{-1} and 1603.4 cm^{-1} , corresponding to the typical D band and G band for carbon material [21]. The D and G band positions are very sensitive to the microstructure of carbon materials, including defects, disorder, edges, and carbon grain size [22]. The intensity ratio of the D band to the G band (I_D/I_G) could reflect the degree of disorder of RGO. Large I_D/I_G values (1.22), a prominent D band, and a wide G band indicate the loss of long-range ordering between the graphene sheets, which is consistent with the XRD results. This is probably because a high density of cavities and/or holes and/or defects are present in the graphene nanosheets in the RGO host. In addition, surface area measurements of the RGO via nitrogen gas absorption yield a large Brunauer-Emmett-Teller (BET) value of $330.9\text{ m}^2\text{ g}^{-1}$, further confirming this conclusion. However, RGO anode shows a very low initial Coulombic efficiency mainly owing to the high surface area. The X-ray photoelectron spectra (XPS) shown in Fig. 2(c) and (d) were collected to estimate the functionalization of the RGO. Three peaks are obtained from XPS spectra in the C1s region: The main peak is located at 284.4 eV, with a peak area proportion of 52.6 %, corresponding to C-C bonding (sp^2 carbon) in defect-free graphite lattice. The peaks at 285.5 eV and 288.1 eV with peak area proportions of 31.1 % and 16.3 % are attributed to C-OH and/or C-C bonding in defective graphite lattice and C=O bonding, respectively. The low proportion of C=O indicates that most of the carboxyl and hydroxyl functional groups were reduced. The O1s spectrum of RGO (Fig. 2(d)) shows two peaks

located at 533.1 eV and 530.3 eV, assigned to the C-OH and C=O species, respectively [20-21]. Therefore, the XRD, Raman, and XPS spectra clearly demonstrate that RGO was successfully synthesized by simple heating of GO in a H₂/Ar mixed gas atmosphere.

Fig.2-XRD patterns of GO and RGO (a), Raman spectrum of RGO (b), and XPS survey scan of C 1s (c) and O 1s (d) photoelectron spectra of RGO.

3.2 Electrochemical performances

The Na-ion storage behavior of RGO is revealed by the cyclic voltammograms and charge-discharge profiles in Fig 3. The Na-ion storage behavior of RGO is similar to that of its Li counterpart [23]. The CV curve of first cycle at 1 C is shown in Fig 3a. The RGO anode shows a large irreversible oxidation reaction at about 0.75 V-0.02 V at the first cycle, which is consistent with a large initial irreversible capacity during discharge/charge processes (Fig

3b). It is well known that the decomposition voltage of propylene carbonate (PC) is at ~0.7 V in LIBs [24,25], which should be much smaller for SIBs due to the standard electrode potential difference ($E^\circ_{\text{Li/Li}^+} - E^\circ_{\text{Na/Na}^+} = 0.33 \text{ V}$). A sharp cathodic peak shows up at 0.26 V versus Na/Na^+ , which is likely to be assigned to the PC decomposition therefore forming a solid electrolyte interphase (SEI) film on the electrode surface. Tang et al. reported a similar result that a PC decompose at 0.36 V in SIBs with hollow carbon nanospheres anode [17]. Similarly, a large irreversible plateau between 0.58 V and 0.75 V is observed in the charge/discharge curve during the first Na-storage. By analogy, it could have originated from the formation of the solid electrolyte interphase (SEI) film on the electrode surface and the reaction of sodium ions with residual-oxygen-containing functional groups. In the following cycles (Fig 3c), the CV curves showed good repeatability, indicating that the sodium ions could reversibly reacted with the RGO and leading to good cycling stability for long cycles. A pronounced cathodic peak is observed at near 0.01 V, in analogy to lithium ion insertion in carbonaceous materials for LIBs [28], while there is no anodic peak occurs in the reverse cycle. It indicates that the mechanisms of Na in this low-voltage area could be envisaged to the sodium adsorption on the graphene sheets and/or active sites. A pair of small cathodic and anodic peaks can be detected at 0.8 V and 1.57 V, respectively, which gradually disappear in the prolonged cycles. It likely originates from interaction between sodium ion and impurity atoms in RGO. As illustrated in Fig. 3(d), the charge/discharge profiles of subsequent cycles show sloping curves and large voltage hysteresis between discharge and charge curves, and the reversible capacities decrease slightly over prolonged cycling. The charge/discharge profiles indicate that the reaction between sodium ions and graphene layer resembles capacitive behavior. The discharge capacities of RGO after the 2nd, 10th, 50th, 100th, 200th, and 250th cycles are 177.0, 136, 123.7, 110.3, 97.6, and 94.3 mAh g⁻¹ at 1 C, respectively. From those CV and charge/discharge curves, it could be speculated that the Na-storage mechanism

of RGO is similar to that of its Li equivalent, including adsorption on the graphene sheets or interaction with impurity atoms [15,29]. The major contribution will be the capacitive behavior.

Fig. 3-Cyclic voltammograms of RGO in a coin cell at scan rate 0.01 mV s⁻¹ for (a) first cycle and (c) subsequent cycles with zoom-in area (inset). Charge/discharge profiles of RGO in a coin cell at 1 C for (b) first cycle and (d) subsequent cycles.

It can be expected that RGO could show good cycling performance and rate capability due to its capacitive mechanism. The outstanding cycling performance of RGO is shown in Fig. 4a. The electrochemical performance was tested at 0.2 C (40 mAh g⁻¹) and 1 C (200 mAh g⁻¹), respectively. The RGO anode shows similar trends at different current densities: high capacity loss for the first cycle, then good stability over prolonged cycling. After 250 cycles,

the electrode exhibits a reversible capacity of 174.3 mAh g⁻¹ at 0.2 C and 93.3 mAh g⁻¹ at 1 C. It should be noted that RGO exhibits an excellent cycling performance (Fig 4b), remaining the capacity of 141 mAh g⁻¹ at 0.2 C over 1000 cycles with a capacity retention ratio of 45.0 %. To the best of our knowledge, it is the best electrochemical performance with long cycling life for carbon anode in SIBs compared with the reported results [11-18].

Fig. 4-(a) Cycling performance of RGO at 0.2 C and 1 C for 250 cycles (b) cycling performance of RGO at 1 C for 1000 cycles.

The rate performance of RGO is presented in Fig. 5a. The average charge capacities are 217.2, 176.4, 150.9, 118.7, and 95.6 mAh g⁻¹ at the different current densities of 0.2 C, 0.4 C, 1 C, 2 C, and 5 C, respectively. When the current is finally directly reduced back to 0.2 C, the average capacity can recover to 180.9 mAh g⁻¹. RGO shows a superior rate capability presenting capacity decrease of 0.4 times with applied current rate increase of 8 times. Finally, the rate performance of the RGO is compared with the two best results for carboneous anodes of SIBs, hollow carbon nanospheres [17] and hollow carbon nanowires [18] (Fig 5b). It is obvious that the hollow carbon naospheres show a relatively low capacity for low current density (< 200 mA g⁻¹). Nevertheless, it show the slightest capacity decay even for applied

current of up to 5 A g^{-1} . The hollow carbon nanowires show the highest capacity for the similar lower current density while did not show the rate capability for higher current density ($> 500 \text{ mA g}^{-1}$). The RGO, on the contrary, could provide a medium performance, which provides a higher capacity in lower current density. Moreover, it offers a slower capacity decay for an applied higher current density as well. The excellent electrochemical performance in terms of Na-ion storage is due to the superior structure of RGO, in which the graphene nanosheets in the RGO host are interconnected so as to minimize the diffusion lengths of Na-ions within the electrode. Furthermore, a large number of surface defects, heteroatoms, and hydrocarbons are introduced onto the graphene films by an oxidative process that can play a role in sodium incorporation even though leading to large initial irreversible Coulombic efficiency as well. More importantly, the graphene nanosheets overlap each other and show a thin wrinkled structure, due to the formation of the nanocavities and/or holes and/or defects, which is favorable to insertion of the relatively large Na ions. It is noteworthy that all of those results show the morphology such as porosity, size of graphene stacks, purity and so on of carbon anodes plays a key role in improving the electrochemical performances of sodium ion batteries, therefore, modification of the nanostructure of material is a significant strategy to optimize electrochemical properties of electrode. The exact effect of the carbon nanostructure is hard to confirmed and is subject to further experimental studies.

Fig. 5-(a) Rate capability of RGO at variant current rates. (b) Comparison of rate capability of RGO with hollow carbon nanospheres from ref. [17] and hollow carbon nanowires from ref. [18].

4. Conclusions

In this report, RGO anode material for sodium ion batteries was obtained in large quantities by a facile method. We demonstrated that the prepared RGO anode shows Na-ion insertion properties at room temperature, with excellent cycling stability and rate capability. It should be noted that the large irreversible loss at the first cycle could be reduced in the future by reducing the surface area. The experimental results clearly show the significant Na-storage capability of RGO, proving its feasibility as an anode for the sodium ion battery. The detailed reaction mechanisms need more experimental research into various nanostructured non-graphitic carbon materials, in particular those with complex nanostructures and activated sites.

Acknowledgements

This work was financially supported by the Australian Research Council through a Discovery Project (DP110103909). The authors would like to also thank Dr Tania Silver for critical reading of the manuscript.

References

- [1] Slater M D, Kim D, Lee E, and Johnson CS. Sodium-ion batteries. *Adv Funct Mater*
DOI: 10.1002/adfm.201200691.
- [2] Qiao J, Chen Y, Wu L, Cao Y, Ai X and Yang H. High capacity Na-storage and superior cyclability of nanocomposite Sb/C anode for Na-ion batteries. *Chem Commun* 2012;48:7070-2.
- [3] Komaba S, Matsuura Y, Ishikawa T, Yabuuchi N, Murata W, Kuze S. Redox reaction of Sn-polyacrylate electrodes in aprotic Na cell. *Electrochem Commun* 2012;21:65-8.
- [4] Park Y, Shin D-S, Woo SH, Choi NS, Shin KH, Oh SM, Lee KT, and Hong SY. Sodium terephthalate as an organic anode material for sodium ion batteries. *Adv Mater* 2012;24(26):3562-7.
- [5] Senguttuvan P, Rousse G, Seznec V, Tarascon J-M, and Palacin MR. *Chem Mater* Na₂Ti₃O₇: Lowest voltage ever reported oxide insertion electrode for sodium ion batteries. 2011; 23: 4109-11.
- [6] Kim H, Kim DJ, Seo D-H, Yeom MS, Kang K, Kim DK, and Jung Y. Ab initio study of the sodium intercalation and intermediate phases in Na_{0.44}MnO₂ for sodium-ion battery. *Chem Mater* 2012; 24(6): 1205-11.
- [7] Kang J, Baek S, Mathew V, Gim J, Song J, Park H, Chae E, Rai AK, Kim J. High rate performance of a Na₃V₂(PO₄)₃/C cathode prepared by pyro-synthesis for sodium-ion

batteries. J Mater Chem 2012; 22(39): 20857-60.

[8] Kim D, Lee E, Slater M, Lu WQ, Rood S, Johnson CS. Layered $\text{Na}[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathodes for Na-ion battery application. Electrochem Commun 2012;18:66-9.

[9] Zhu L, Niu Y, Cao Y, Lei A, Ai X, Yang, H. n-type redox behaviours of polybithiophene and its implications for anodic Li and Na storage materials. Electrochimica Acta 2012; 78:27- 31.

[10] Ge P, Fouletier M. Electrochemical intercalation of sodium in graphite. Solid State Ionics 1988;28–30:1172-5.

[11] Joncourt L, Mermoux M, Touzain P, Bonnetain L, Dumas D, Allard B. Sodium reactivity with carbons. J Phys Chem Solids 1996;57:877-82.

[12] Alcantara R, Fernandez Madrigal FJ, Lavela P, Tirado JL, Jimenez Mateos JM, Gomez de Salazar C, Stoyanova R, and Zhecheva E. Characterisation of mesocarbon microbeads (MCMB) as active electrode material in lithium and sodium cells. Carbon 2000;38:1031-41.

[13] Stevens DA and Dahn JR. High capacity anode materials for rechargeable sodium-ion batteries. J Electrochem Soc 2000;147:1271-3.

[14] Alcantara R, Jimenez Mateos JM, and Tirado JL. Negative electrodes for lithium- and sodium-ion batteries obtained by heat-treatment of petroleum cokes below 1000°C. J Electrochem Soc 2002; 149 (2) A201-A205.

- [15] Thomas P and Billaud D. Electrochemical insertion of sodium into hard carbons.

Electrochimica Acta 2002;47:3303-7.
- [16] Alcantara R, Lavela P, Ortiz GF, and Tirado JL. Carbon microspheres obtained from resorcinol-formaldehyde as high-capacity electrodes for sodium-ion batteries.

Electrochem Solid-State Lett 2005;8(4):A222-5.
- [17] Tang K, Fu L, White RJ, Yu L, Titirici M-M, Antonietti M, and Maier J. Hollow carbon nanospheres with superior rate capability for sodium-ion batteries. Adv Energy Mater 2012; 2:873-7.
- [18] Cao Y, Xiao L, Sushko ML, Wang W, Schwenzer B, Xiao J, Nie Z, Saraf LV, Yang Z, and Liu J. Sodium ion insertion in hollow carbon nanowires for battery applications.

Nano Lett 2012;12(7):3783-7.
- [19] Hummers W, Offeman R. Preparation of graphitic oxide. J Am Chem Soc 1958; 80:1339.
- [20] Yang D, Velamakanni A, Bozoklu G, Park S, Stoller M, Piner RD, Stankovich S, Jung I, Field DA, Ventrice, Jr., CA, and Ruoff RS. Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy. Carbon 2009; 47:145-52.
- [21] Tang L, Wang Y, Li Y, Feng H, Lu J and Li J. Preparation, structure, and electrochemical properties of reduced graphene sheet films. Adv Funct Mater

2009;19(17):2782-9.

- [22] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, and Ruoff RS. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 2007;45:1558-65.
- [23] Wang C, Li D, Too CO, and Wallace GG. Electrochemical properties of graphene paper electrodes used in lithium batteries. *Chem Mater* 2009;21(13):2604-6.
- [24] Arakawa M, Yamaki JJ. The cathodic decomposition of propylene carbonate in lithium batteries. *J Electroanal Chem* 1987;219:273-280.
- [25] Li JT, Maurice V, Swiatowska-Mrowiecka J, Seyeux A, Zanna S, Klein L, Sun SG, Marcus P. XPS, time-of-flight-SIMS and polarization modulation IRRAS study of Cr_2O_3 thin film materials as anode for lithium ion battery. *Electrochim Acta* 2009;54:3700–3707.
- [26] Wenzel S, Hara T, Janek J and Adelhelm P. Room-temperature sodium-ion batteries: improve the rate capability of carbon anode materials by templating strategies. *Energy Environ Sci* 2011;4:3342-3345.
- [27] Winter M, Moeller KC, Besenhard JO. Carbonaceous and graphitic anodes in lithium batteries. *Science and Technology*, Springer, 2003.
- [28] Dahn JR, Zheng T, Liu Y, Xue JS. Mechanisms for lithium insertion in carbonaceous materials. *Science* 270;1995:590-593.

[29] Stevens DA, Dahn JR. The mechanisms of lithium and sodium insertion in carbon materials. *J Electrochem Soc* 2001;148:A803-11.