Energy storage applications of graphene-based materials

Lai, Linfei

2013

Lai, L. (2013). Energy storage applications of graphene-based materials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54849>

<https://doi.org/10.32657/10356/54849>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**ENERGY STORAGE APPLICATIONS OF GRAPHENE-BASED
MATERIALS**

LAI LINFEI

**LAI LINFEI
SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
2013**

**ENERGY STORAGE APPLICATIONS OF
GRAPHENE-BASED MATERIALS**

2013

ENERGY STORAGE APPLICATIONS OF GRAPHENE- BASED MATERIALS

LAI LINFEI

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

ACKNOWLEDGEMENTS

“The real glory is being knocked to your knees and then coming back. That’s real glory. That’s the essence of it.”

-----Vince Lombardi

My heartfelt thanks go to my supervisor, Prof. Shen Zexiang, who encourages, supports and guides me throughout my studying of the whole projects. I learnt from him not only the knowledge of science, but also the decent personality.

I own my deepest gratitude to my co-supervisor Prof. Lin Jianyi. He always supported me on research difficulties, spent an incalculable amount of time guiding me with all my experiments, and carefully revised all my drafted manuscripts. He is a professor of profound learning, and his diligence has always encouraged me.

It is my distinct opportunity to recognize Prof. Rodney S. Ruoff, who offered me the valuable opportunity to study in University of Texas at Austin (UT Austin). His encouragements and unwavering support have sustained me throughout my studies at UT Austin.

I would like to show my gratitude to my colleagues in Prof. Shen’s group, who helped me in my projects and shared the happy hours together. They are Dr. Zhan Da, Mr. Wang Liang, Dr. Liu Xiaoxu, Ms. Sun Li, Dr. Luo Zhiqiang, Miss Cai Xiaoyi, Mr. Sun Linfeng, Mr. Liu Jilei, Mr. Yan Jiaxu, Dr. Ni Zhenhua, Dr. You Yumeng, Dr. Wang Yingying, Dr. Ma Yun, Dr. Hu Hailong, Dr. Li Dongfei, Dr. Cong Chunxiao, Dr. Yang Huanping, Mr. Zhang Zhifeng.

As an attachment student in Institute of Chemical Engineering Science (ICES), Agency for Science, Technology and Research (A*STAR), I carried out most of my experiments in ICES. I would like to express my sincere thanks to team members of

Prof. Lin group: Dr. Lim San Hua, Mr. Poh Chee Kok, Dr. Chen Luwei, Dr. Tian Zhiqun, Ms. Wang Zhan, Ms. Jaclyn Teo Seok, Ms. Karine Koh Boon and Ms. Catherine Choong Kai Shin, who helped me in one way or another. I would also like to express my sincere appreciation and thanks to my groupmates at UT Austin. They are Dr. Jeff. Potts, Dr. Zhang Lili, Dr. Ji Hengxing, Mr. Bai Xin, Dr. Li Huifeng, Dr. Hao Yufeng, Dr. Wu Yaping, Dr. Meng Lingjie, Ms. Zhao Xin and Mr. Ji Junyi.

I owe a debt of gratitude to my wonderful and loving husband, Mr. Li Zhenggang, for his help and support in both my work and life. I would like to give my thanks to my sister and parents who always support me from spiritual and love me with heart.

Table of Contents

ACKNOWLEDGEMENTS	I
Summary.....	V
Publications.....	VIII
Chapter 1 Introduction of Graphene Based Energy Storage Materials	1
1.1 Energy Storage/Conversion Systems.....	1
1.1.1 Supercapacitor	2
1.1.2 Catalyst for Oxygen Reduction Reaction (ORR)	7
1.1.3 Carbon Composite for Li-ion Battery.....	8
1.2 Introduction to Graphene	11
1.2.1 Graphite oxide (GO) and graphene oxide (G-O)	12
1.2.2 Reduced G-O (rG-O)	14
1.3 Applications of Graphene in Energy Storage/ Conversion Systems	17
1.3.1 Graphene Based Supercapacitors.....	17
1.3.2 Graphene Composite for Oxygen Reduction Reaction	21
1.3.3 Graphene Composite for Li-ion Storage	22
1.4 The motivation and organization of this thesis.....	27
Chapter 2 Synthesis of NH₂-Graphene and Its Electrochemical Properties.....	30
2.1 The importance of introducing –NH ₂	30
2.2 Experiment and characterization.....	31
2.2 Results and Discussion.....	33
2.4 Performance of –NH ₂ -G as Supercapacitor Electrode.....	41
2.5 Conclusions	43
Chapter 3 Polyaniline/graphene composite as supercapacitor electrodes.....	45
3.1 Significance of Prepare Polyaniline/Graphene Electrodes.....	45
3.2 Experiment and Characterization	48
3.3 Results and Discussion.....	49
3.4 Conclusions	66
Chapter 4 Graphene/Polypyrrole as Supercapacitor Electrodes	68
4.1 The PPy and PPy Composite.....	68
4.2 Experiment and Characterization	69
4.3 Results and Discussion.....	70
4.4 Conclusion	80
Chapter 5 Active Center Structure of Nitrogen-doped Graphene-based Catalysts for ORR	82
5.1 Introduction.....	82

5.2 Experiment and Characterization.....	83
5.3 Results and Discussion	86
5.5 Conclusion.....	98
Chapter 6 Active Center and Catalytic Mechanism of Graphene-Supported Non-precious Metal Electrocatalysts.....	99
6.1 Introduction.....	99
6.2 Experiment and Characterization.....	100
6.3 Results and Discussion	101
6.5 Conclusion.....	111
Chapter 7 Transition Metal Nitride/oxide Based Anode Materials for Li-ion Battery	112
7.1 Transition Metal Nitride/rG-O Based Anode.....	112
7.1.1 Introduction	112
7.1.2 Experiment and Characterization	114
7.1.3 Results and Discussion	115
7.2 Transition Metal Oxide/Graphene Anode.....	123
7.2.1 Introduction	123
7.2.2 Experiment and Characterization	126
7.2.3 Results and Discussion	127
7.2.4 Conclusion	136
Chapter 8 Conclusions and Future Work.....	137
8.1 Conclusions.....	137
8.2 Future Work.....	139
References	141

Summary

This thesis focuses on the investigation of chemically prepared graphene/ graphene composites and their application as new energy storage materials. This thesis is divided into four parts.

The first part (Chapter 1) introduces three energy storage and conversion systems, i.e. supercapacitors, Li-ion battery, and PEM fuel cell. It also reviews the progress on the preparation, physical and chemical properties, and energy applications of graphene and graphene composites.

The second part (Chapter 2-4) reports on the investigation of graphene surface modifications and the effect of graphene surface chemistry on the electrochemical performance of graphene/polyaniline, graphene/polypyrrole composites as supercapacitor electrodes. Graphene oxide (G-O) prepared from oxidation of graphite by chemical method has abundant oxygen-containing groups and is insulating. Hence it should be reduced by thermal annealing or chemical reduction in order to improve its conductivity when graphene is used as electrode materials. Reduced G-O (rG-O) shows low hydrophobicity and further modification is particularly important to improve the solubility, processability, and the reactivity with metal ions or monomers. In Chapter 2, a novel solvothermal process is presented to achieve both the reducing of G-O and the introducing of -NH_2 to graphene in one step. The NH_2 -Graphene ($\text{NH}_2\text{-G}$) is an exceptional supercapacitor electrode material with high specific capacitance (up to 217.8 F g^{-1}), superior over commercially available G-O, activated carbon, chemically reduced G-O, and carbon nanotubes (CNTs). Chapters 3 and 4 on graphene/polyaniline and graphene/polypyrrole demonstrate how the synergistic effect between conducting polymer and functionalized graphene greatly enhance the electrochemical performance. 8-fold capacitance increase (up to 500 F g^{-1}), excellent cycle stability after polyaniline

(PANi) loading and graphene surface functionalization are recorded, showing great opportunities for the exploration of novel materials with greatly improved performance as supercapacitors electrodes.

In the third part (Chapters 5 and 6), graphene based non-noble metal catalysts are prepared and studied for the oxygen reduction reaction (ORR). The N-doped graphene has pronounced ORR activity in alkaline electrolyte. However the development of non-noble metal catalysts for acidic environments remains challenging. In chapter 5 graphitic N is found to greatly increase the current density while pyridinic N species may convert the ORR reaction mechanism from $2e^-$ dominated process to $4e^-$ dominated process. A simple but effective one-step pyrolysis method is employed to prepare transition metal nitride (MeN) / N-modified graphene (N-G) composite from graphene oxide (G-O). These MeN-N-G composites show considerably higher ORR catalytic activity in acidic electrolytes than MeN-N-C, where C represents activated carbon or graphite. This is the first report on the preparation of MeN on graphene supports for ORR catalysts in acidic electrolytes. There are numerous reports of N doped carbon and various MeN which exhibit ORR activities, but the nature of catalytic active center is still not clear. Based on X-ray diffraction (XRD) and ultraviolet photoelectron spectroscopy (UPS) data, the ORR mechanism and the nature of the active center of MeN based catalyst are rationalized in Chapter 6. An active center is proposed, where the pyridinic N serves as the active site and donates its π electrons to the O_2 anti-bonding orbitals. The transition metal not only accepts back-donation of electrons from O_2 , facilitating the weakening and cleavage of the O-O bond, but also transfers its electrons to the pyridinic N. The synergistic effects between N and transition metal mean that non-precious metal catalysts can be effective for ORR.

The fourth part (Chapter 7) is contributed to the study of MeN/graphene and Me_xO_y/graphene composites as the anode material of Li-ion battery. The MeN/graphene has shown rather high rate capacity and stability, far more superior over the conventional graphite anode. Nanostructured Co₃O₄ supported on N-doped graphene (NMEG) is successfully synthesized and selected as model metal oxide to investigate the effect of metal oxide weight ratio on the Li ion storage behaviour of Me_xO_y/graphene composites. 70%Co₃O₄/NMEG composite delivers a reversible capacity of 640 mAh g⁻¹ at a current density of 625 mA g⁻¹, which is 10 folds larger than that of bare Co₃O₄ (52±3 mAhg⁻¹). In this system NMEG is referred as N-doped microwave exfoliated graphene. N functionalities are helpful for the Co₃O₄ growth and uniform dispersion at the edge as well as on basal plane of NMEG sheets.

Publications

1. **Lai LF**, Potts JR, Zhan D, Wang L, Poh CK, Tang CH, Gong H, Shen ZX, Lin JY & Ruoff RS. Exploration of the active center structure of nitrogen-doped graphene-based catalysts for oxygen reduction reaction. *Energy Environmental Science* 5, 7936, 2012.
2. **Lai LF**, Yang HP, Wang L, Teh BK, Zhong JQ, Chou H, Chen LW, Chen W, Shen ZX, Ruoff RS & Lin JY. Preparation of Supercapacitor Electrodes through Selection of Graphene Surface Functionalities. *ACS Nano*, 6, 5941, 2012.
3. **Lai LF**, Wang L, Yang HP, Sahoo NG, Tam QX, Liu JL, Poh CK, Lim SH, Shen ZX & Lin JY. Tuning graphene surface chemistry to prepare graphene/polypyrrole supercapacitors with improved performance. *Nano Energy*, 1, 723, 2012.
4. **Lai LF**, Chen LW, Zhan D, Sun L, Liu JP, Lim SH, Poh CK, Shen ZX & Lin JY. One-Step Synthesis of NH₂-Graphene from In-situ Graphene-Oxide Reduction and Its Improved Electrochemical Properties. *Carbon*, **49**, 3250, 2011.
5. **Lai LF**, Li ZG, Zhen YD, Potts JR, Zhan D, Poh CK, Yan JX, Lam YM, Lin JY, Shen ZX & Ruoff RS. Graphene-Supported Non-precious Metal Electrocatalysts for Oxygen Reduction Reactions: the Active Center and Catalytic Mechanism. Submitted to *ChemSusChem*.
6. **Lai LF**, Zhu JX, Yu YW, Wang L, Liu XX, Liu JL, Jiang SR, Yan QY, Shen ZX & Lin JY. Co₃O₄/NEMG electrode as Li-Ion anode with high reversible capacity and improved initial cycle performance. Accepted by *Nano Energy*.
7. **Lai LF**, Ji HX, Potts JR, Shen ZX, Lin JY & Ruoff RS. One novel and universal method to prepare transition metal nitrides / N- modified graphene anodes with high cycleability for Li-ion battery. To be submitted.
8. **Lai LF**, Cai XY, Zhan D, Asymmetrical supercapacitors with pseudocapacitive positive and negative electrodes. To be submitted.
9. Zhan D, Ni ZH, Chen W, Sun L, Luo ZQ, **Lai LF**, Yu T, Wee ATS & Shen ZX. Electronic

- structure of graphite oxide and thermally reduced graphite oxide. *Carbon*, **49**, 1362, 2011.
10. Zhan D, Yan JX, Lai LF, Ni ZH, Liu L & Shen ZX. Engineering the electronic structure of graphene, *Advanced Materials*, 24, 4055, 2012.
 11. Lim SH, Li ZT, Poh CK, Lai LF & Lin JY. Highly active non-precious metal catalyst based on poly(vinylpyrrolidone)-wrapped carbon nanotubes complexed with iron-cobalt metal ions for oxygen reduction reaction. *Journal of Power Sources*. 214, 15, 2012.
 12. Zhang LL, Zhao X, Ji HX, Stoller MD, Lai LF, Murali S, McDonnell S, Cleveger B, Wallace RM & Ruoff RS. Nitrogen doping of graphene and its effect on quantum capacitance, and a new insight on the enhanced capacitance of N-doped carbon. *Energy Environmental Science*, 5, 9618, 2012.
 13. Liu JL, Lai LF, Sahoo NG, Zhou WJ, Shen ZX & Chan SH. Carbon Nanotube-Based Materials for Fuel Cell Applications. *Australian Journal of Chemistry*, 65, 1213, 2012.
 14. Luo ZQ, Lim SH, Tian ZQ, Shang JZ, Lai LF, Macdonald B, Fu C, Shen ZX, Yu T & Lin JY. Pyridinic N doped graphene: synthesis, electronic structure, and electrocatalytic property. *Journal of Materials Chemistry*, 21, 8038, 21, 2011.

Conference Presentation

1. **Lai LF**, Sun L, Zhan D, Shen ZX, Lin JY, “Facile synthesis of new amino groups functionalized graphene as electrochemical supercapacitors”, Recent advances in graphene and related materials, Aug 1-6, 2010, **Singapore**
2. **Lai LF**, ZX Shen, Lin JY, “Nitrogen doped graphene oxide as Pt-free electrocatalyst for oxygen reduction in fuel cells”, Recent advances in graphene and related materials, Aug 1-6, 2010, **Singapore**
3. **Lai LF**, Tam QX, Teh BK, Sun L, Poh CK, Gu ST, Chen LW, Shen ZX, Lin JY, “Graphene/conducting polymer composite and their enhanced electrochemical properties. International Conference on Materials for Advanced Technologies (ICMAT), June 27- July 1, 2011, **Singapore**.
4. **Lai LF**, Gu ST, Poh CK, Tian ZQ, Sun L, Zhan D, Chen LW, Lin JY, Shen ZX, “Non-precious metal catalyst for oxygen reduction reaction in PEM fuel cells: catalyst carrier effect on activity and selectivity” International Conference on Materials for Advanced Technologies (ICMAT), June 27- July 1, 2011, **Singapore**.
5. **Lai LF**, Shen ZX, Lin JY, “Influence of graphene surface chemistry on the performance of graphene/conducting polymer electrochemical supercapacitors” 2011 MRS fall meeting & exhibit, Nov. 28 – Dec. 2. The United States of America.

Chapter 1

Introduction of Graphene Based Energy Storage Materials

1.1 Energy Storage/Conversion Systems

The consumption of fossil fuels is forecasted to have severe future impact on world economics and environment. Development of low cost and ecological friendly new energy sources and energy storage systems are needed urgently in response to the modern society development and emerging environmental concerns. Electrochemical energy storage/conversion systems are under serious considerations, including rechargeable batteries, fuel cells, and electrochemical capacitors. These three systems show different energy storage/conversion mechanisms, but all exhibit “electrochemical similarities”. For example, all of these three systems have a cell configuration of two electrodes in contact with electrolyte, and their energy generation process occurs at the electrode and electrolyte interface. Therefore, the requirements for electrode materials, such as good charge conductivities, electrochemical and chemical stabilities are valid for all the three systems.

Carbon plays significant role as the active material for one or both of the electrodes in the three systems, such as anode in Li ion battery (LIB), anode and/or cathode in electrochemical double layer capacitor (EDLC), Pt support in low temperature polymer electrolyte membrane fuel cell (PEMFC). The structural and electrochemical properties of carbon materials are crucial in determining and improving the performance of energy conversion/storage devices. In this thesis, graphene and graphene-composites are synthesized and studies in depth for their applications in supercapacitors, LIBs and PEMFCs. Graphene is a new carbon

allotrope with extraordinarily high crystal and electronic quality as well as excellent structural and chemical properties which could be distinctly different from other carbon allotropes. My thesis will show how we achieve high performance of supercapacitors, Li ion batteries and PEM fuel cells using graphene and its composites in place of carbon materials in these energy conversion/storage systems.

1.1.1 Supercapacitor

Electrochemical capacitors, also known as supercapacitor, or ultracapacitors are a class of electrochemical energy storage devices for rapid, reversible storing and releasing electrical energy.[1] The specific energy of supercapacitors is several orders of magnitude higher than that of conventional capacitors. A high performance supercapacitor should have high energy density ($1\sim 10 \text{ Whkg}^{-1}$, verified by specific capacitance value and potential window), high power density ($10^3\sim 10^5 \text{ Wkg}^{-1}$, determined by its internal resistance and voltage), and high cycle stability (> 100000 cycles depending on the electrode active materials selected).[2] The specific energy and power densities of supercapacitor cells could cover the gap between batteries and conventional capacitors, as shown in Fig. 1.1, and have great potential for a wide range of applications in electronic devices, hybrid electric vehicles, pulse laser equipment, and industrial power management systems.

For conventional capacitor, the energy is stored by transfer of charge carriers from one metal plate to another. The separated charge could be harvested by applying an external circuit. For electrochemical double layer supercapacitors, which consist of positive and negative electrodes, separator and electrolyte (see Figure 1.2), an electrochemical double layer is reversibly created at the electrode/electrolyte interfaces by anion and cation species from the electrolyte. A voltage potential applied on the

positive electrode draws the negative ions from the electrolyte (e.g. aqueous KOH, H₂SO₄, (NH₄)₂SO₄ or ion liquids), while the negative electrode attracts the positive ions.

Figure 1. 1 Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion/storage systems compared to an internal combustion engine and conventional capacitors. Reprinted with permission from ref.[3]

The charge moving between the two electrodes is prevented by a porous dielectric separator assembled between the two electrodes. The capacitance of a double layer capacitor, C could be calculated by the model described by Helmholtz in 1853:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad \text{eq. 1.1}$$

where ϵ_r is the dielectric constant of the electrolyte, ϵ_0 is the permittivity of vacuum, d is the effective thickness of the double layer, and A is the surface area of electrode. The double layer capacitance of carbon based electrodes is usually between 5 to 20 μFcm^{-2} due to the high surface area created by the porous structure and the small charge separation ($\sim 1\text{nm}$) created by the double-layer around the particles in the electrodes.[4] For a typical EDLC with a high surface area of 1000 m^2/g , and a double

layer capacitance of $10 \mu\text{F}/\text{cm}^2$, specific capacitance (SC) of 100 F/g can be achieved, which is thousands times higher than that of conventional capacitors.

The energy stored in a supercapacitor, W can be calculated using Equation 1.2:

$$W = \frac{1}{2} CV^2 \quad \text{eq. 1.2}$$

where V is the voltage potential cross the electrodes. V could be ~ 1 or 3V depending on the electrolyte (aqueous or organic) used.

Figure 1. 2 Schematic of an electrochemical double layer capacitor.

The supercapacitors can be divided in two types based on the energy storage mechanism: 1) classical electrochemical double layer capacitors (EDLCs) which store energy by adsorption or desorption of ions from electrolyte; and 2) pseudocapacitors which store energy by reversible surface redox reactions.[5] EDLCs are non-Faradaic ultracapacitors, with performance strictly relying on the double-layer capacitance.

Carbon materials are widely used as supercapacitor electrodes due to their low cost, chemical stability, accessibility, adaptable porosity, as well as versatile existing structures, such as nanotubes, nanofibers, monoliths, and aerogel particles.[2, 4] High

surface area and pores adapted to the size of ions are crucial for supercapacitor performance. In order to achieve a high double layer capacitance, EDLCs require electrode carbon materials with high specific surface area and defined pore structures to ensure the availability of electrolyte ions to the surface charges.[6] High performance supercapacitors also require electrode materials to have high thermal and mechanical stabilities, and high conductivity. Therefore, porous carbon prepared by various methods, such as CO_2 [7] or KOH activation,[8-10] self-assemble polymerization and carbonization,[11] and template guided synthesis[12] are vastly reported.

Pseudocapacitors utilize conducting polymers (such as, polyacetylene, polypyrrole, and polyaniline) or metal oxides (such as NiO , RuO_2 and Co_3O_4) as electrode materials. They store electrical energy by fast faradic reactions, which generate a charge transfer process between electrode and electrolyte, and involve oxidation-reduction reactions of electrochemically active species at the electrode surface at certain potential.[13, 14] Pseudocapacitors are expected to show higher specific capacitance than EDLC, ranging from 100 ~ 600 F/g for conducting polymers and 700 ~ 1100 F/g for metal oxides/hydroxides. However, the value is often not as high as expected due to the poor conductivity of pseudocapacitive electrodes.[13] Therefore, porous carbon is often used as additive and/or support [15-17].

There exist two kinds of supercapacitor configurations: 1) the symmetric supercapacitors with both electrodes built from the same material, and 2) the asymmetric supercapacitor with positive and negative electrodes constituted from different materials. For an asymmetric supercapacitor, different capacitances C_1 and C_2 are assigned for the two electrodes, and the total capacitance can be calculated as following:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad \text{eq. 1.3}$$

Therefore, the total capacitance of a supercapacitor device is controlled by the electrode with the smallest capacitance value. In account with the doubled weight, the specific capacitance (CS) for two-electrodes device is a factor of four compared with that of single electrode capacitance measured in 3-electrode system. The maximum energy stored in such a capacitor can be calculated by eq. 1.2.

The maximum power of the supercapacitor depends on the internal resistant R_s :

$$P = \frac{U^2}{4R_s} \quad \text{eq. 1.4}$$

A significant enhancement of power density and energy density can be achieved by an increase of capacitor voltage (U_0). Nonaqueous electrolyte, e.g. organic salt (TEABF_4) dissolved in acetonitrile or ionic liquid allows the capacitor to be charge/discharged up to 2.0-2.7 V, favouring the increase of the energy and power densities.

Activated carbon (AC) was the first material chosen for EDLC electrodes. AC is composed of extremely but 'rough' particles with size of 1-20 nm, and has huge surface area of roughly 1000 to 3000 m^2/g . [18] In an activated carbon electrode with a surface area of 1000 m^2/g , only less than 1/3 of the surface area is available for the formation of ionic double layer. [19] Unlike other type of carbon electrodes containing micropores including dead end pores and slit, the CNTs has open structure enabling almost all the surface area accessible to the electrolyte. [19] Graphene, a planar sheet of sp^2 -bond carbon atoms could also contribute most of its surface area for charge storage. Graphene oxide prepared from chemical oxidation of graphite has abundant O-containing functional groups. These functional groups endowed graphene stronger affinity with pseudocapacitive materials, compared with those pure activated carbon,

or carbon nanofibers. Therefore, graphene may function as a good carrier to load pseudocapacitive materials to prepare supercapacitor electrodes with high capacitance value and improved cyclability.

1.1.2 Catalyst for Oxygen Reduction Reaction (ORR)

Polymer electrolyte membrane fuel cells (PEMFCs), also known as proton exchange membrane fuel cells, are currently one of the most effective and non-polluting power generators. PEMFCs convert chemical energy stored in the fuel to electrical energy through two electrochemical reactions: the reduction of oxygen at cathode and oxidation of hydrogen at anode.[20, 21] The heart of PEMFC is membrane electrode assembly (MEA), which consists of two gas diffusion layers, two catalyst layers that sandwich the polymer electrolyte membrane in the middle (see Fig. 1.3). Hydrogen fed into the cell diffuses to the anode catalyst layer and could be catalyzed to form protons and electrons. Electrons form a current in an external circuit, while the protons migrate through the membrane. Meanwhile, oxygen (blue) fed into the cell diffuses to the cathode catalyst layer, which further reacts with protons that have transported through the proton conductive membrane and electrons arriving from the circuit, to form water:

Figure 1. 3 Polymer electrolyte membrane fuel cells (PEMFCs) components.

This reaction is well known as oxygen reduction reaction (ORR). The rate of ORR at the cathode is significantly lower than that of the counterpart reaction at the anode. Many research efforts have been targeted to the cathode development. At present, the most commonly used catalysts for these reactions are platinum (Pt) or Pt alloys supported on amorphous carbon,[22-24] with Pt loading weight ratio ranging from 10% to 90%. Except for the prohibitive production cost of Pt-based electrocatalysts, the low reaction rate of ORR of Pt at cathode is the main problem.[25] Thus, the development of lower cost high performance catalysts to replace Pt is highly desirable, especially at the cathode, where the sluggish ORR calls for much higher loadings of Pt compared to the speedy hydrogen oxidation reaction at the anode. The most promising fuel cell catalyst should exhibit optimum catalytic activity for ORR by having a great density of active sites, low Pt loading, and long operating life. This forms the second target of my thesis study. A series of novel graphene-based non-precious metal catalysts such as graphene/transition-metal-nitride have been successfully synthesized, showing compatible ORR performance with conventional Pt/C catalysts. The ORR reaction mechanism and the structure of the active centers are well understood *via* detailed characterization and in-depth analysis.

1.1.3 Carbon Composite for Li-ion Battery

Among various power and energy storage systems, rechargeable lithium-ion batteries (LIB) are promising compared with other electrochemical energy storage and conversion systems such as lead acid, Ni-Cd and Ni metal hydride batteries, due to higher specific energy density, no memory effect, slow loss of discharge and longer

cycle life time. The worldwide market for rechargeable lithium ion batteries was estimated to be higher than 10 billion per year in 2005 and still growing.[26]

The typical rechargeable lithium battery consists of an anode, a non-aqueous liquid electrolyte, and a cathode. On charging, lithium ions are delithinated from the cathode, diffuse through the electrolyte, and intercalated / lithinated to anode while electrons are passing through the external circuit, as shown in Fig. 1.4. The Li ions are released by the anode and further inserted into the cathode upon discharge. The positive electrode half-cell reaction with LiCoO_2 as the active material is given as follows

Carbon is routinely used as the anode active material and the half-cell reaction is given as:

Figure 1. 4 Schematic representation of a lithium-ion battery. Negative electrode (graphite) and positive electrode (LiCoO_2) are separated by a non-aqueous liquid electrolyte (adapted from ref. [27]).

Graphite is the commercialized anode material with excellent cycle performance and high coulombic efficiency. However, the specific capacity of graphite is 372 mAhg^{-1} only and it has a key drawback of low power density caused by the high polarization, especially at high charge/discharge rates. Poor charge carrier conductivity

at high charge/discharge rates are the main cause for high polarization. Thus, LIB at current status cannot meet the demands of rechargeable batteries with both high power and energy densities for the applications in EVs, HEVs, and high-speed telecommunication devices.[28-30] In order to improve the performance of LIBs, advanced anode materials are required with specific capacity higher than that of graphite, high electronic/thermal conduction, large surface area, and well-developed porous structure which offers short diffusion path for ionic transport.[31] A variety of carbon nanomaterials, such as CNTs,[32] mesoporous carbon,[33] fullerenes,[34] and graphene [35] have been explored for this purpose. Apart from carbon nanomaterials, metal alloys (Si, Sn etc), metal oxides (TiO_2 , Fe_3O_4 , Co_3O_4 and V_2O_5 etc),[36] and metal nitrides (CoN , FeN , NiN and CuN etc) [37] have been also studied for replacing graphite as superior anode materials for LIBs.

Graphene, which has large surface area, superior electrical and thermal conductivities, and suitable porous structure, is expected to be a superior candidate as electrode material with a high power and energy density. In graphene based anodes, the Li-ions will be adsorbed on the two sides of the sheet and along the edges, with a theoretical capacity of 744 mAh/g.[38] Graphene has a theoretical surface area of over 2600 m^2/g . Graphene powders are truly disordered, so the sheets are randomly oriented making it isotropic in all directions. Thus the storage of the Li-ion will be isotropic, again enhancing the capacity of the anode. The disordered nature of the graphene based anode will overcome any kinds of ‘pulverization’ effects that are faced by recent high density intermetallic anodes, thereby expected to show improved rate capabilities. In this thesis graphene and graphene-based composites (nanostructured metal oxides, nitrides) have been explored, with great successes, as anode electrodes,

showing significant improvements as compared to commercially available graphite anode.

In conclusion, PEM fuel cells, supercapacitors, and Li-ion batteries are studied in this thesis as three important energy conversion/storage systems. The performance of these energy conversion/storage systems directly relies on the properties of electrode materials. Carbon is of great importance in these studies as indispensable component, such as ORR catalyst support in PEMFC, both cathode and anode in electrochemical double layer capacitor, and LIBs anode. Among various available carbon allotropes, graphene has become the centre of attention with growing amount of research carried out in the field of clean energy devices due to the beneficial combinations of exceptional mechanical and electrical properties, and high surface area. The application of graphene and graphene-composites in these three systems is the main focus of the thesis. Therefore, the synthesis of graphene from graphite, reduction of G-O/GO and their structural, chemical properties will be introduced in the following section.

1.2 Introduction to Graphene

Andre Geim and Konstantin Novoselov at the University of Manchester were awarded with Nobel Prize in Physics in 2010 for their revolutionary experiments about single layer graphene from bulk graphite. Graphene is one atom thick sheet of sp^2 -bonded carbon atoms arranged in a regular hexagonal pattern. As the building block for many other carbon allotropes, graphene has unique properties,[43] including ballistic conduction of charge carriers,[39] ambipolar electric field effect, high mechanical properties,[40] quantum Hall effect at room temperature,[41, 42] tunable band gap,[43, 44] and extra-high theoretical surface area. These are distinctly different from other carbon allotropes, for example, carbon nanotubes, fullerenes and graphite,

making graphene a hot research topic in the fields of microelectronics,[42, 45, 46] energy storage,[47-49] condensed-matter physics and materials science, with many new potential applications.[50-52]

1.2.1 Graphite oxide (GO) and graphene oxide (G-O)

The well-known scotch tape method first reported the discovery of graphene,[41, 46, 53] in which single layer graphene could be detached from highly ordered pyrolytic graphite (HOPG) by using adhesive scotch tape. Up to now, a variety of methods have been developed for the growth, fabrication, and synthesis of graphene and its derivatives, such as chemical exfoliation techniques, epitaxial growth *via* chemical vapour deposition, and growth from metal-carbon melts and graphite oxide reduction.

Wet chemical preparation of graphene *via* graphite oxide reduction was probably historically the most commonly used method for the synthesis of graphene. Since 1962 researchers intentionally tried to obtain thin graphite oxide (GO) flakes from graphite by using several kinds of oxidants with different treatment procedures.[54-56] Typically, GO is derived from a process called “Hummers method” or “modified Hummer’s method”,[57] in which graphite is oxidized by concentrated H_2SO_4 with NaNO_3 and/or KMnO_4 . H_2O_2 is then used to react with excess KMnO_4 , resulting in water soluble MnSO_4 , which can be washed out by rinsing.

GO is a compound of hydrogen, oxygen, and carbon in variable ratios, with C to O atomic ratio of 1.7 or higher,[58] depending on particular synthesis method and degree of oxidation. It maintains the layer structure of the parent graphite, but the layers are buckled or holded, with the interlayer spacing of about two times larger (~ 0.7 nm) than that of graphite. GO may be simply regard as stacked graphene oxide (G-O) sheets with interlayer distance larger than that of graphite. The dispersion of bulk GO

material in water or organic solvents can yield monomolecular sheets, known as graphene oxide (G-O). G-O layers are about 1.1 ± 0.2 nm thick as measured by atomic force microscopy (AFM).[16, 59] G-O carbon basal planes are decorated with epoxy bridges and hydroxyl groups, in addition to carboxyl and carbonyl groups located probably predominantly at the edges (Fig. 1.5).[60] There also exist various O-containing groups on both sides of G-O platelets. Usually water molecules are contained in GO, intercalating into the interlayer spaces of G-O component sheets (Fig. 1.6). [61, 62]

Figure 1. 5 Structural model for G-O sheet prepared by oxidation with $\text{KMnO}_4/\text{H}_2\text{SO}_4$. The model only indicates the chemical connectivity but not the exact spatial distribution of functional groups. $-\text{OH}$ groups are perpendicular to the graphene carbon plane, and the interplanar spaces also contain water molecules(Adapted from Ref.[62])

Figure 1. 6 Proposed hydrogen bonding network formed between epoxide and hydroxyl groups on GO and water (adapted from ref. [63]).

Thermal or mechanical treatment (sonication or magnetic stirring) of GO could obtain homogeneous colloidal suspension of G-O sheets in organic or aqueous

solutions.[64] Sonicating of GO in water is the most common method for quick exfoliation of GO, but may cause structural damage to the G-O platelets by reducing the dimension of G-O and producing more defects/edges. Mechanical stirring or thermal exfoliation are relatively mild, but long duration and drying process are required, respectively, to obtain graphene sheets with comparatively larger size. G-O can be well dispersed in water with high stability at a concentration up to 3mg/mL with colour of dark brown suspensions.

1.2.2 Reduced G-O (rG-O)

G-O can be partly reduced to graphene-like sheets by eliminating the oxygen-containing functional groups with the recovery of a sp^2 hybridized structure. By nature, GO and rG-O are both electrically insulating, due to the existence of large amount of O-containing functional groups. The reduced GO (rG-O) sheets have relatively high conductivity. With residual oxygen functional sites, DC conductivities of rG-O could still reach 1×10^3 to $2.3 \times 10^3 \text{ Sm}^{-1}$, comparable to that of compressed graphite monoliths.[59] Therefore, when graphene-derived materials are used as active materials in conductive electrodes for energy storage and conversion, GO reduction to rG-O is usually required. Chemical, thermal,[65-67] and hydro/solvothermal reduction[68, 69] are regarded as effective approaches for GO reduction.

GO is thermally unstable, which easily undergoes pyrolysis at elevated temperatures, resulting in expansion/exfoliation of G-O sheets as well as partly removal of O-containing groups. The exfoliation of GO happens when the decomposition rate of hydroxyl and epoxy groups and the evaporation rate of the intercalated water molecules surpass the diffusion rate of the as-evolved gas, thus yielding a pressure that exceeds Van der Waals forces that hold G-O sheets together (Fig. 1.7).[70] The BET surface area of thermally exfoliated/reduced GO ranges from

400 to 900 m²g⁻¹,[70] larger than that of chemically reduced GO sheets (466 m²g⁻¹).[61]

Zhu et al. reported the exfoliation together with reduction of GO by microwave treatments. The obtained microwave exfoliated GO (MEGO) powders had surface area of 463 m²g⁻¹. [71] The C/O ratios of 2.75 for MEGO is higher than that for GO powders (~1.7),[71] but still lower than that of thermally expanded GO (~10.0).

Figure 1. 7 Illustration of the expanded GO by thermal treatment (adapted from ref [72]).

It is worth to note that thermal exfoliation/reduction causes a severe structural damage and weight loss due to the release of CO₂. 30% of the GO mass is lost during the thermal treatment, leaving topological defects and vacancies in the 2D plane of the rG-O.[70] These defects would inevitably affect the mechanical, electronic properties of the rG-O.[70]

The chemical methods using reducing agents such as hydrazine monohydrate,[61] sodium borohydride (NaBH₄),[73] hydroquinone,[74] dimethylhydrazine[75] to reduce G-O. Compared with thermal exfoliation/reduction, chemical reduction does not involve exfoliation process. Therefore, GO has to be mechanically exfoliated by magnetic stirring or ultrasonication to form G-O before chemical reduction is applied.

Hydrazine is the most widely used reductant in rG-O or rGO preparation.[61] It can selectively reduce alkenes through *syn-addition* of H₂ across the alkene, which is accompanied with the release of N₂ as by-product. The rG-O black powder obtained from G-O reduction with hydrazine exhibits high conductivity of $\sim 2400 \pm 200 \text{ S m}^{-1}$, compatible to $2500 \pm 20 \text{ S m}^{-1}$ for graphite but much higher than $0.021 \pm 0.002 \text{ S m}^{-1}$ for GO.[61] The BET surface area of the hydrazine-reduced G-O was measured to be $466 \text{ m}^2 \text{ g}^{-1}$, although far below the theoretical value of pristine graphene ($2620 \text{ m}^2 \text{ g}^{-1}$), but still higher than that of dried down GO. Hydrazine induces N heteroatom to rG-O, in which N exists in the form of amines, hydrazine, aziridines or other similar structure, with a C/N atomic ratio lower than ~ 16.0 . [76] Raman spectra of amorphous carbon show strong peak located at 1340 cm^{-1} could be assigned to D band activated by defects *via* an intervalley double-resonance Raman process.[20] Carbon with high graphitization has a characteristic peak at $\sim 1580 \text{ cm}^{-1}$, and $\sim 2670 \text{ cm}^{-1}$, which could be assigned to the G band, in plane vibrational mode (E_{2g} phonon at the Brillouin zone center), and the 2D band, intervalley double resonance scattering of two TO phonons around the K-point of the Brillouin zone. [21, 22] Commonly the intensity ratio of D band to G band (I_D/I_G) has been used to evaluate the defect intensity in graphene. The increase of disorder associated with the introduction of N can be demonstrated by using Raman spectroscopy, which shows increase in graphite I_D/I_G band ratio due to the decrease of the sp^2 spatial dimensions of graphene network.[76]

NaBH_4 is another widely used reducing agent, which is effective in removing C=O bonds, but has mild efficiency in reducing of epoxides and carboxylic acids. However, NaBH_4 is beneficial to produce rG-O with low sheet resistance when developing rG-O as electroconductive membrane. The rG-O reduced with NaBH_4 was shown to have

much lower sheet resistance ($59 \text{ k}\Omega \text{ sq}^{-1}$) than that ($780 \text{ k}\Omega \text{ sq}^{-1}$) using hydrazine as the reducing agent.[76]

Other reducing agents like hydroquinone,[74] hydrogen gas,[77] strong alkaline solution,[78] and ammonia water[79] have also been used for chemical formation of rG-O. Hydrogen gas coupled with thermal reduction is proved to be effective G-O reduction protocol with C/O atomic ratio of 10.9-14.8. Alkaline is inferior reductants than hydrazine or NaBH_4 , while acid only facilitate dehydration of the graphene surface.

Electrochemical method can also be used in reducing of GO films on a variety of substrates (ITO, glassy carbon etc.), in which linear sweep voltammetry is applied to the electrodes in sodium phosphate buffer. The reduction started at a voltage of -0.6V and finished in 2000 seconds. A C/O atomic ratio of 23.9:1, and conductivity of 8500 S m^{-1} was achieved for electrochemically reduced G-O electrode.[80] Although the reduction mechanism is still not clear, the mild reaction conditions preclude the using of hazardous chemical reactants.

In conclusion, graphene can be prepared in large scale by reducing the chemically oxidized graphite. Thermal and chemical reducing methods are well-recognized approaches to prepare rG-O with high conductivity. The thermal reducing process also involves a notable exfoliation effect, which is noteworthy when the as-prepared rG-O is applied for energy storage materials.

1.3 Applications of Graphene in Energy Storage/ Conversion Systems

1.3.1 Graphene Based Supercapacitors

Supercapacitors require electrode materials with high specific surface area and defined pore structures to ensure the availability of electrolyte ions to the surface charges.[6]

The specific capacitance (SC) of graphene (F/g) is higher than that of CNT and activated carbon in most recent reports, which may be due to the following reasons: 1) Although graphene itself is non-porous, graphene-based materials have 3D structure with large surface area over $400 \text{ m}^2\text{g}^{-1}$ and accessible pore structures (due to sheet holding); 2) Graphene has excellent electron mobility so that graphene based EDLC cells show an ultrafast frequency response.[10]

Figure 1. 8 (a) SEM image of chemically derived graphene surface, (b) TEM image showing graphene sheets expanding from chemically derived graphene surface, (c) low and high (inst) magnification SEM images of graphene particle electrode surface, and (d) schematic of test cell assembly. Reprinted with permission from ref.[81].

Ruoff and co-workers first reported the chemical reduction of GO to rG-O sheets in aqueous dispersion[61] and the application of rG-O as ultracapacitor electrode materials.[81] This rG-O had specific surface area of over $705 \text{ m}^2\text{g}^{-1}$, and large SC of 135 and 99 Fg^{-1} in aqueous and organic electrolyte respectively (see Fig. 1.8 for morphology characterization and cell setup).[81] The graphene based supercapacitor prepared by Wang et al. has a maximum SC of 205 Fg^{-1} , power density of 10 kWkg^{-1} when the energy density is 28.5, and 90% SC retention after 1200 cycles (Table

1.1).[82] Vivekchand et al. reported that thermal expanded GO in ionic liquid electrolyte enabled the operation voltage to be expanded up to 3.5 V, exhibited a SC and energy density of $\sim 75 \text{ Fg}^{-1}$ and 31.9 Whkg^{-1} respectively, compared with the SCs of single wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs), which were 64 and 14 Fg^{-1} respectively.[83] These results suggest the potential of graphene based supercapacitors to be fabricated and commercialized, once the improved scalability and reduced cost are reached. Commercially available supercapacitor use tetraethyl-ammonium tetrafluoroborate (TEA BF_4) in propylene carbonate (PC) as electrolyte. The TEA BF_4 could be also added to the PC/rG-O suspension to fabricate supercapacitor device, and a specific capacitance (SC) value of 112 Fg^{-1} was achieved.[84]

Table 1. 1 Electrochemical performance of graphene composites based supercapacitors electrodes

Electrode material	Performance parameter		Cycle stability	Testing system	Ref.
	SC (Fg^{-1})	Power density (kW kg^{-1})			
CNT/PANi	780	NT	67% after 1000 cycles	CV at 1 mV s^{-1} scan rate	[85]
GNS	150	NT		SC maintained with the current of 0.1 A g^{-1} for 500 cycles	[86]
GNS	38.9	2.5	NT	CV at 50 mV s^{-1}	[87]
GNS- $\text{Co}(\text{OH})_2$	972.5	NT	NT	N/A	[88]
GNS/CNT/PANi	1035	NT	96% after 1000 cycles	CV at 1 mV s^{-1}	[85]
GNS/PANi	1046	$70@39 \text{ Whkg}^{-1}$		SC measured at 1 mV s^{-1}	[89]
GNS	205	$10@28.5 \text{ Whkg}^{-1}$	90% after 1200 cycles	GNS prepared from GO	[82]
GNS/PANi	531	NT		Mass ratio of PANI/GNS of 100:1	[90]
AC	80-125	NT	NT	2-electrode system	[23]

Key: CNT- carbon nanotube; PANi- polyaniline; GNS- graphene nanosheet; SC- specific capacitance; AC- activated carbon, NT-data not given.

Pseudocapacitors store electrical energy by the Faradaic reactions generated charge transfer between electrode and electrolyte. Transition metal oxides/hydroxides

(MnO_2 , [91] RuO_2 , [92, 93] Co_3O_4 , [94] NiO , [95, 96] etc.) and polymers (polyaniline, [14, 97] polypyrrole, [98, 99] polythiophene, [100] etc.) are commonly used materials for pseudocapacitors. However, generally speaking, the specific capacitance value of pseudocapacitor is not as high as anticipated due to the chemical and physical properties of the electrode materials. In particular unsatisfactory conductivity usually limits their use in high performance supercapacitors. The addition of highly conductive carbon into pseudocapacitive electrode can generally promote the electrochemical capacitance of electrode materials and improve its cycling performance as well. There are vast reports of loading pseudocapacitive materials onto carbon nanomaterials to prepare supercapacitor electrodes or devices. [5, 96, 99, 101] In these reports, both the large specific surface area of carbon and the “synergistic effects” arising from the interaction of pseudocapacitive and carbon materials are widely stated. [89, 90, 102] For example, graphene have high conductivity, which functions as a conductor for electrons when polyaniline (PANi) is fully charge or discharge in an insulating form of leucoemeraldine or pernigraniline. In addition, rG-O with high surface area also induces electric double layer charging-discharging mechanism. Wang et al. reported the preparation of electrode material with high performance based on PANi doped G-O sheets. [90] A specific capacitance of 531 Fg^{-1} was achieved when the mass ratio of PANi/graphene was 100:1, significantly higher than that of pure PANi (216 Fg^{-1}). [90] The unique 3D structure of graphene, together with the O-containing groups, the wrinkles, edges, defects help the adsorption and attachment of monomers/ metal ion precursors, which further induced the uniform distribution of pseudocapacitive materials to graphene sheets. The combination of graphene, which has high surface area and layered structure, with pseudocapacitive materials is promising for high performance supercapacitor application.

1.3.2 Graphene Composite for Oxygen Reduction Reaction

Due to the distinctive electronic properties, graphene has attracted strong interest both from the theoretical scientific and experimental fields during the past few years. Various strategies have been selected to tailor the electronic properties of graphene *via* physical or chemical methods.[103, 104] With the recent interest in reducing Pt loading or replacing Pt based catalyst in fuel cells, nitrogen doped carbon materials and/or organic macrocyclic complex related materials are proven to be effective as noble-metal-free electrocatalyst for oxygen reduction reaction (ORR).

Figure 1. 9 Rotating ring-disk electrode voltammograms for the ORR at the graphene, Pt/C, and N-graphene electrode (rotating rate: 1000 rpm) in air-saturated 0.1 M KOH. (b) Current density (j)-time (t) chronoamperometric responses of the Pt/C and N-graphene electrodes at -0.4 V in air saturated 0.1 M KOH. The arrow indicates the addition of 2% (w/w) methanol into the air-saturated electrochemical cell. Reprinted with permission from ref[105].

Recently, several groups reported surprisingly high ORR activities in graphene that were doped with N.[105, 106] Various techniques have been utilized for the synthesis of N-doped graphene sheets, such as arc-discharge,[107] hydrazine reduction,[108] NH₃ treatment of GO[109] and *in-situ* growth by chemical vapour deposition (CVD) method.[110] Geng and co-workers used blended ammonia/argon gas to anneal GO to prepare N-doped graphene (N-rG-O).[106] They found that the optimum temperature to obtain N-rG-O with high ORR performance was 900 °C. The catalyst had a ORR activity comparable to or better than commercialized Pt/C (loading: 4.85_{μgpt} cm⁻²) in

oxygen saturated 0.1 M KOH.[106] They found the quaternary N played the most important role for ORR. N-doping introduces an extra unpaired electron in each N atom and causes localized distribution of the electron density. The nearby carbon with highest spin density are the electrocatalytic active sites, while if the negative value of spin density is small, the carbon atoms with large positive atomic charge density are the active sites.[111] Qu and co-workers synthesized N-doped graphene (mainly pyridinic N) by the CVD method, and they found the N-graphene had 3 times higher activity than that of Pt/C electrode over a potential from -0.2 to -1 V (Fig. 1.9). N-graphene has long-term stability, tolerance to methanol crossover, which are superior than Pt/C.[105] These information suggest tuning of the catalytic performance of N-doped graphene catalysts require a rational design, and detailed atomistic insight into the N-dopant structure in the graphene network.

1.3.3 Graphene Composite for Li-ion Storage

Li-ion battery (LIB) has a major drawback of low power density due to the large polarization, especially at high charge/discharge rates. The poor thermal and electrical conductions of electrodes, and a slow Li ion diffusion rates across the electrolyte and electrode interface are the main causes for high polarization. Therefore, it is of great importance to develop new electrode materials with high electronic/thermal conductivity, large surface area, well-developed porous structure, which offer short diffusion path for ionic transportation. Graphite is the commercialized anode material with excellent cycle performance and high columbic efficiency. Li ions intercalated to graphite during charging and form a compound of LiC_6 . However, the specific capacity of graphite is only 372 mAhg^{-1} . In order to improve the performance of LIBs, anode materials with high specific capacity are required. A variety of carbon nanomaterials, such as CNTs,[32] mesoporous carbon,[33] fullerenes[34] have been

explored for this purpose. Apart from carbon nanomaterials, metals, metal oxides and metal nitrides were also studied for the replacement of graphite as superior anode materials for LIB application.[26, 112] Graphene which has large surface area, superior electrical and thermal conductivity, and porous structure is expected to be a good anode material for high-energy and high-power energy storage. Additionally, graphene has also been used, with great successes, as additives for both cathode [113] and anode[38].

The Li storage on graphene sheets was first reported by Kudo and co-workers.[114] The authors found that the incorporation of CNT and C₆₀ into rG-O could increase specific capacity from 540 mAhg⁻¹ for rG-O to 730 and 784 mAhg⁻¹. [114] The electron affinity of CNT and C₆₀ causes an electronic charges in graphene materials and the *d*-spacing increase from 0.37 nm of rG-O to 0.40 and 0.43 nm of CNT and C₆₀ respectively, both of which facilitate Li ion intercalation. Pollak et al. used *in-situ* Raman to investigate the interaction of Li⁺ with single and few layered graphene. They found that the interaction of Li⁺ with few-layered graphene was similar to that for bulk graphite, while radically different from that of single layer graphene.[115] High surface area and high concentration of carbon edges of graphene provide high capacity,[116] however, also induce severe irreversible capacity loss during the first several cycles.[117] Pan and co-workers found that highly disordered graphene sheets were promising as high-capacity Li ion batteries anode, and high reversible capacities of 794-1054 mAhg⁻¹ were achieved.[35] Wang and co-workers investigated the lithium storage properties of graphene by first principles calculations.[38] Their results showed that lithium could be stably stored on both sides of graphene sheets (LiC₃) with a theoretical capacity of 744 mAhg⁻¹. [38] Their experimental data also showed Sn/Graphene had a reversible capacity of 795 mAhg⁻¹

in the second cycle, and the capacity maintained at 508 mAhg^{-1} after 100^{th} cycle.[38] Sato and co-workers proposed a Li_2 covalent molecule model for Li interaction with highly disordered carbon.[118] If the graphene active defects such as edges and vacancies can accommodate additional Li, the defects and structural disorder in rG-O due to the oxidation and reduction processes will turn to be an advantage for its application as an anode material.

It is also noteworthy that the low electrical conductivity of partially reduced G-O (under low reducing temperature, or weak reducing agent) may induce severe polarization during rapid charging and discharging processes, which will make rG-O at high potential platform prevails. Unlike graphite anode, which has a flat discharge plateaus below 0.7V, rG-O does not give potential plateaus, indicating the Li-ion batteries with rG-O as anode cannot provide stable potential outputs. As seen from Fig.1.10, rG-O electrode has to be charged to 3.5 V to achieve a capacity of 800 mAhg^{-1} . If the rG-O is used in a full cell, the overall potential of the full-cell may drop as the cathode of LiFePO_4 still remains at 3.4 V. rG-O has high surface area, and the irreversible capacity in the first discharge owing to the formation of solid electrolyte interface (SEI) is also large. Therefore, for pure rG-O material prepared from chemical method without special treatment or modification, the first cycle efficiency is less than 50%. This kind of pure rG-O itself may not be suitable for LIB anode, but would be promising after modified or combined with other nanomaterials to encounter the aforementioned problems.

Figure 1. 10 Charge/discharge profiles of (a) graphite, (b) graphene, (c) graphene with CNT, and (d) graphene with C_{60} at a current density of 50mA g^{-1} . Reprinted with permission from ref[114].

Many metals or metal oxides are promising anode materials for Li-ion batteries because of their high both theoretical and experimental Li-ion storage capacities compared with graphite. However, the main drawbacks of these materials when used for anode are their huge volume expansion during lithium insertion/extraction process, which further cause the pulverization of the whole electrode. Thus, graphene blended with metal oxides to form graphene composite is vastly reported (table 1.2).

G-O itself is decorated with oxygen containing functional groups, which provide abundant adsorption sites for metal or metal oxide growth. Therefore, compared with CNT or fullerene, G-O or rG-O is a promising candidate as carrier to load metals or metal oxides to prepare Li ion storage active materials. Although silicon has a theoretical capacity of 3579 mAhg^{-1} , the large volume expansion (270% for $\text{Li}_{3.75}\text{Si}$ phase) and structural deformation during lithium insertion/extraction result in severe capacity degradation. After combined with graphene, Si/graphene composite shows a reversible capacity of 1168 mAhg^{-1} up to 30 cycles, compared with silicon nanoparticles which dropped from 3000 to 346 mAhg^{-1} after 30 cycle. The authors found that the adding of graphene reduced the resistance of silicon, implying the

enhanced conductivity of the composite, compared with silicon.[119] Graphene has conductive 3D network which could served as a structural scaffold to anchor metal or metal oxide nanoparticles, but also enhance the electrical conductivity of the composite. In vast publications, the authors believed that the porous structure and high surface area of graphene facilitate the electrolyte penetration, as well as function as buffer layer to resist the electrode volume change. Other options for anode materials of Li-ion batteries are transition metal oxides, such as Co_3O_4 , Fe_2O_3 , SnO_2 , etc. These nanoparticles are introduced during the chemical reduction of G-O, or loaded onto rG-O. For example, Wang et al., prepared a $\text{SnO}_2/\text{rG-O}$ composite by reducing G-O in the presence of SnCl_2 at 120°C . [120] This composite exhibited a reversible discharge capacity of 765 mAhg^{-1} , and first cycle efficiency of 54%. Co_3O_4 is another anode material with high theoretical capacity of 890 mAhg^{-1} . It also suffers from large volume change during charge/discharge process. Co_3O_4 can be introduced into graphene sheets by hydrolysis of Co^{2+} salt in alkaline medium with G-O, and then calcinate the resulted $\text{Co}(\text{OH})_2/\text{G-O}$ at 450°C . A specific capacity up to 800 mAhg^{-1} is achieved for the $\text{Co}_3\text{O}_4/\text{rG-O}$ in the first cycle, and then increased to 935 mAhg^{-1} after 30 cycles. However, the capacity of rG-O or bare Co_3O_4 decreased from 955 to 638 mAhg^{-1} , or from 817 to 184 mAhg^{-1} after 30 cycles.[121]

Table 1. 2 Performance of rG-O and rG-O/composite for Li-ion anodes

Materials	1 st discharge capacity (mAhg^{-1})	Initial reversible capacity (mAhg^{-1})	1 st cycle efficiency	N th -cycle charge capacity (mAhg^{-1})	Number of cycles	Rate performance	Ref.
rG-O	2200	1050	47 %	650	30	--	[121]
rG-O/MnO	1380	735	57%	495	40	208 mAh/g at 1.6A/g	[122]
rG-O/NiO	1030	700	68%	646	30	368 mAh/g at 0.8A/g	[123]
rG-O/TiN	860	650	76%		35	325 mAh/g at 2A/g	[124]
rG-O/ SnO_2	1700	1125	66%	820	30	270 mAh/g at 1A/g	[125]
rG-O/ Fe_3O_4	1450	900	62%	580	100	580 mAh/g at 1.7A/g	[126]
rG-O/ Co_3O_4	1100	800	72%	800	50	500 mAh/g at 0.5A/g	[121]

1.4 The motivation and organization of this thesis

This thesis presents the study of graphene and graphene composites for energy storage and conversion applications. The thesis includes four major parts:

Motivation for part 1 (Chapter 1): Part 1 is the introduction chapter, briefly introducing the preparation methods of graphene, graphene oxide and reduced graphene oxide, and their applications in fuel cells, supercapacitors, and lithium ion batteries.

Motivation for part 2 (Chapters 2-4): Part 2 presents the study of functionalized graphene (NH₂-graphene) and conducting-polymer/graphene composites (polyaniline/graphene and polypyrrole/graphene) and their application in supercapacitors. Nitrogen is a common heteroatom which can be introduced into carbon network by thermal treatment of carbon together with nitrogen containing molecules or *via in-situ* growth by the CVD method. Primary amine can be introduced into graphene sheets as ionizable functional groups *via* carboxylic group activation and amidation. In Chapter 2, a novel solvothermal process is carried out to achieve GO reduction and the introduction of -NH₂ to carbon edges in one step. The resulting primary-amine-modified-graphene (NH₂-G) is an exceptional electrode material for supercapacitor application, and up to 217.8 F g⁻¹ high specific capacitance was measured, better than commercial GO, activated carbon, chemically reduced GO, and CNTs. Chapters 3 and 4 report on graphene/conducting-polymer composites as supercapacitor electrodes. The largest synergistic effect has been observed on polyaniline (PANi)/NH₂-G hybrid system in 1M H₂SO₄ electrolyte. 8-fold capacitance increase (up to 500 F g⁻¹) and excellent cycle stability after PANi loading and graphene surface modification are

recorded, showing an prospect for the design of suitable materials with considerably enhanced performance as supercapacitors.

Motivation for part 3 (Chapters 5 and 6): Part 3 is focused onto N-doped graphene as a promising catalyst for ORR. There are numerous reports of N doped carbon which exhibit ORR activities, but the nature of catalytic active center was still not clear. Therefore, I investigated the N bonding state and its effect on the selectivity and catalytic activity for ORR. A simple but effective one-step pyrolysis method was employed to prepare transition metal nitride (MeN)/N-modified graphene (N-G) composite from G-O. These MeN-N-G composites show considerably higher ORR catalytic activity in acidic electrolytes than MeN-N-C, where C represents active carbon or graphite. This is the first report on the preparation of MeN on graphene supports for ORR catalysts in acidic electrolytes. Based on XRD and UPS data the ORR mechanism and the nature of the active center can be rationalized. The pyridinic N serves as the active center and donates its π electrons to the O_2 anti-bonding orbitals. The metal core not only accepts back-donation of electrons from O_2 , facilitating the weakening and cleavage of the O-O bond, but also transfers its electrons to the pyridinic N. The synergistic effects between N and transition metal mean that non-precious metal catalysts can be effective for ORR.

Motivation for part 4 (Chapter 7): In part 4 (Chapter 7), the preparation of MeN/graphene and Co_3O_4 /graphene composites are reported and their significantly enhanced performance as LIB anode show the advantage of using graphene as the support to stabilize the nanostructural active materials for energy storage. The FeN-rG-O delivers a capacity over 510 mAhg^{-1} at a current density of 100 mA g^{-1} , and remains stable for more than 100 cycles which is two times as high as that of conventional graphite anode.

Chapter 2

Synthesis of NH₂-Graphene and Its Electrochemical Properties

2.1 The importance of introducing –NH₂

As a common heteroatom, nitrogen is reported being introduced into carbon nanomaterials by in-situ growth, chemical vapor deposition [127, 128] or thermal annealing of carbon together with nitrogen precursors.[127, 129, 130] The nitrogen doped (N-doped) carbons with enhanced catalytic and electrochemical performance are vastly reported [127-133]. However, treatment of carbon together with N-containing molecules under high temperature are required, and only thermally stable quaternary, pyridinic, pyrrolic, and pyridinic-N-oxides N atoms were obtained [130, 132, 134]. Substituted nitrogen has poor chemical reactivity and wettability, which need to be improved before various applications.

Different from substituted N, primary amine (-NH₂) can be introduced into carbon sheets as ionizable functional groups, which could not only improve graphene solubility, but also assist graphene easily to react with other polymers, organic molecules, and biological systems. The conventional method requires carboxylic acid group activation and amidation to obtain –NH₂ functionalization. Carboxylic acid groups on the carbon surface need to be activated with SOCl₂, or carbodiimides in organic solvents,[135] and then react with amine precursors to realize the introduction of covalent –NH₂ modification. There is no report on modification of graphene with –NH₂ in one-step process. We present here a one-step solvothermal process to achieve

the reduction of G-O and the introduction of -NH_2 to graphene for the first time. The electrochemical performance of $\text{NH}_2\text{-G}$ as supercapacitor electrodes is also investigated and compared with that of G-O.

2.2 Experiment and characterization

Graphene oxide (G-O) was prepared from natural flake graphite powder as reported elsewhere.[57] 5 g of graphite and 3.5 g of NaNO_3 were placed in a flask. 350 mL of H_2SO_4 were slowly added with stirring in ice-bath environment, 10 g of KMnO_4 were added with vigorously stirring for 2 hours and keep for 6 days at room temperature. The mixture was added with 200 mL of 5 wt% H_2SO_4 and temperature was kept at 98 °C under fluxing for 2 hours. 10 mL of H_2O_2 (30 wt% aqueous solution) was added to terminate the reaction when temperature was reduced to 50 °C. The resultant mixture was purified by repeating following procedures: washing with 1 L of 3 wt% H_2SO_4 / ultrasonication for 30 min at 140 W/ centrifugation at 6000 rpm for 30 min, until the supernatant is colourless. The product was then collected and freeze dried for 2 days.

100 mg of G-O was added to 40 mL of ethylene glycol under ultrasonication, 1 mL of ammonia water was further added. The as-obtained solution was transferred to a Teflon lined autoclave for solvothermal reaction at 180 °C for 10 hours. After reaction, the precipitate was filtered and washed repeatedly with distilled water and dried at 60 °C for 24 h for further usage. The samples used for electrochemical characterization were prepared following this procedure, except for further declare.

The effect of ammonia amount on the nitrogen concentration of $\text{NH}_2\text{-G}$ was investigated by adding different weight ratio of ammonia from 1.82 : 1 ~ 10.90 : 1 (ammonia : G-O) was processed. The details of the reaction procedures and post-treatments of product were the same as the procedures mentioned above.

SEM (scanning electron microscope) characterization was carried out with a field-emission scanning electron microscope (FESEM, JEOL JSM-6700F). The crystal structure of the graphene was investigated by a Bruker D/MAX 2500 X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The surface area was determined by Brunauer-Emmett-Teller (BET) method measuring the adsorption of N $_2$ using a ASAP2020 volumetric adsorption analyzer (Micromeritics, U.S.A.). The pore size distribution plot of the samples was determined by Barrett-Joyner-Halenda (BJH) method using desorption branch of the N $_2$ isotherms. The surface chemical composition of the samples was calculated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 250 spectrometer (Thermo Electron, U.K.), using Al K α X-ray source (1486 eV). Infrared transmission spectra were measured on a Perkin Elmer 2000 Fourier-transform infrared spectrometer (FTIR) in the range of 400 – 4000 cm $^{-1}$. The proton nuclear magnetic resonance (^1H -NMR) spectra were recorded in DMSO-d $_6$ (deuterium labeled DMSO-d $_6$) at 20 °C in 5-mm NMR tubes with a Bruker 400 MHz spectrometer.

Cyclic Voltammetry (CV) was carried out to evaluate the electrochemical performance of NH $_2$ -G at room temperature using 0.5 M H $_2$ SO $_4$ as electrolyte in a three-electrode cell setup on Autolab PGSTAT302 electrochemical test system (Eco Chemie, The Netherlands). The working electrode was prepared by casting DI water impregnated graphene ink onto 5 mm diameter vitreous glassy carbon electrode. 20 mg of graphene sample was ultrasonically dispersed into 5 mL of DI water to prepare graphene ink. 20 μL of the graphene ink was coated on the electrode and dried at 60 °C. After dried, 5 μL of 2-propanol containing Nafion solution (5 wt%, dupont) was deposited onto the electrode.

2.2 Results and Discussion

Ethylene glycol and ammonia were used as the solvent and nitrogen precursor to prepare $\text{NH}_2\text{-G}$ at 180 °C with G-O as graphene precursor in a solvothermal method. This reaction is featured by ammonia radicals nucleophilic substitution of carboxyl and epoxides groups, as shown in Fig. 2.1.

The interaction of G-O with ammonia has been reported previously [136-138]. NH_3 can react or be easily adsorbed onto the oxygenous-groups-abundant G-O surface.[137] G-O has O-containing functional groups in the form of epoxide ($-\text{O}-$) groups or hydroxyl ($-\text{OH}$), together with a number of carbonyl functionalities, such as lactones, quinines and anhydrides. Nitrogen from ammonia can react with carbonyl groups produce aromatic Schiff base.[136] In this project, ammonia was selected as the nitrogen source, and ethylene glycol was used as solvent to treat G-O in solvothermal conditions and both the introduction of primary amine and reduction of G-O were achieved at the same time. G-O turned from dark brown to black after reduction, which is the colour of rG-O [61].

Figure 2. 1 Chemical reaction mechanism of conversion of graphene oxide (G-O) to amine modified graphene ($\text{NH}_2\text{-G}$) in the addition of ammonia water. Below show the SEM images of G-O (a) and $\text{NH}_2\text{-G}$ (b), inset are photographs of G-O (right) and $\text{NH}_2\text{-G}$ (left) dispersed in DI water, DMF and THF with a concentration of 0.3 mg/mL.

SEM images reveal that the NH₂-G consists of numerous graphene sheets that randomly aggregated, thus forming a disordered and porous solid (Fig. 2.1). It is worth to note that, the as-obtained NH₂-G could be well dispersed in N,N-dimethylformamide (DMF), water, and tetrahydrofuran (THF) with comparable solubility with that of G-O (inset in Fig. 2.1). NH₂-G is polydispersible in water and several organic solvents, which might be due to the hydrophilic behaviour of primary amines, and further make NH₂-G an easy for further modification.

High temperature treatment of carbon and ammonia would cause carbon network condensation or carbonization, with decreased BET surface area value and pore volume [139]. NH₂-G has a more porous structure than that of pristine G-O as seen from SEM (Fig. 2.2). The isotherms of NH₂-G and pristine G-O are both of type IV with H II (for G-O) or H I (for NH₂-G) hysteresis, indicating a mesoporous structure with ink-bottle pores or open cylindrical pores respectively. NH₂-G has BET surface area of 346 m²/g and the total pore volume is 2.88 cm³/g vs. 272 m²/g and 1.77 cm³/g for pristine G-O. Although the BET surface area of NH₂-G is smaller than that of hydrazine hydrate reduced graphene oxide (466 m²/g) [61], it is higher than as-prepared pristine G-O. NH₂-G has increased pore volume and surface area, indicating our solvothermal process does not induce graphene aggregation or condensation.

Figure 2. 2 Nitrogen adsorption-desorption isotherms at 77 K for pristine G-O and NH₂-G. The inset is the pore size distribution plot calculated by BJH method using desorption branch of the isotherms.

The XRD patterns of G-O and NH₂-G are shown in Fig. 2.3. The [001] peak of G-O shifts from 11.72° to 12.48° after modified by amine, indicating the slight decreased *d*-spacing. However, both patterns of NH₂-G and G-O show typical hydrated G-O feature [140]. This phenomenon indicates the introduction of amine does not significantly change the G-O crystalline structure. Our result is different from the XRD data of octylamine modified G-O [141], which has an enlarged *d*-spacing due to the insertion of long alkyl chains.

Figure 2. 3 XRD patterns of G-O and NH₂-G.

In order to analyze the atomic ratio and chemical state of each element in NH₂-G, XPS measurement was performed. The XPS survey scan of NH₂-G shows intensified N peak at ~ 399 eV and decreased oxygen peak at ~ 530 eV as compared with that of G-O (Fig. 2.4 a and b), which signifying the removal of O-containing functional groups or oxygen substitution by nitrogen. The atomic ratio of C : O for NH₂-G is ~10.6 : 1, which is comparable to those chemically reduced G-O (10.3 : 1 by hydrazine hydrate [142], and 13.4 : 1 by sodium boronhydride[143]), and much higher than that of pristine G-O (~1.7 : 1). The increased C to O atomic ratio indicating the reduction of G-O during the reaction. More importantly, changing the amount of ammonia water during the solvothermal synthesis can influence the molar ratio of carbon to nitrogen (Fig. 2.5, Table 2.1).

Figure 2. 4 XPS survey spectra for $\text{NH}_2\text{-G}$ and G-O ; (b) N1s spectrum of $\text{NH}_2\text{-G}$; (c) C1s spectrum of G-O ; and (d) C1s spectrum of $\text{NH}_2\text{-G}$.

N1s spectrum of $\text{NH}_2\text{-G}$ shows two deconvoluted peaks with binding energies of 398.36 and 399.76 eV (Fig. 2.4b), which can be ascribed to the presence of pyridinic (398.3 ± 0.2 eV) [129] and $-\text{NH}_2$ (399.5 ± 0.2 eV) [144, 145]. The C1s peak of G-O (see Fig. 2.4c) can be deconvoluted into four different components with binding energies of 284.5, 285.1, 286.7, and 288.3 eV respectively, corresponding to sp^2 hybridized C atoms, C-OH [61], C-O (epoxy/ether) groups, and the C=O (carbonyl/carboxyl) [61] respectively. In Fig. 2.4d, $\text{NH}_2\text{-G}$ C1s spectrum has an additional component at 285.90 eV which could be assigned to C-N groups [61]. The decrease of C1s intensity at 286.7-288.3 eV manifested the significant decrease of oxygen content in the forms of C-O, and the C=O groups.

Figure 2. 5 XPS survey scans of $\text{NH}_2\text{-G}$ prepared from different weight ratio of ammonia from 1.82 : 1 ~ 10.90 : 1 (ammonia : G-O) (up to down)

XPS survey scans show the increased N1s/O1s peak intensity ratio with the increase of the ammonia water adding ratio (Fig. 2.5). The molar ratio of carbon to nitrogen can be tuned from 52.2 to 9.68 by changing the ammonia ratio during the synthesis (Table 2.1). However, it is worth to note that, further raise of ammonia water to G-O weight ratio results in a reduction of the nitrogen content in $\text{NH}_2\text{-G}$, which indicates that high alkaline environment is not beneficial for amine graft. The alkaline environment has also been reported as unfavorable for adsorption of ammonia gas [136].

Table 2.1 Carbon to nitrogen atomic ratio in $\text{NH}_2\text{-G}$ as function of ammonia-water to G-O weight ratio during the solvothermal process

Weight ratio of ammonia : G-O	Atomic ratio (C : N)
1.82 : 1	52.24 : 1
7.28 : 1	15.05 : 1
9.10 : 1	11.21 : 1
10.90 : 1	9.68 : 1
13.71 : 1	10.64 : 1

The FT-IR spectrum of pristine G-O (Fig. 2.6) illustrates the presence of C-O ($\nu_{\text{C-O}}$ at 1097 cm^{-1}), C-OH ($\nu_{\text{C-OH}}$ at 1384 cm^{-1}), C=O in carbonyl and carboxylic acid moieties ($\nu_{\text{C=O}}$ at 1630 and 1726 cm^{-1}) and the H-bonded from -OH groups (broad peak around 3438 cm^{-1}) [73]. After modified with amino groups, the peaks at 1384 , 1630 and 1726 cm^{-1} of G-O almost disappear, while the peak at 3438 cm^{-1} decays considerably, representing the reduction and dehydration of O-H and C=O groups after amine modification. The appearance of new bands at 1580 cm^{-1} corresponds to N-H in-plane bond stretching. The band at $3300\sim 3600\text{ cm}^{-1}$ remains, but it has symmetric peak shape and much lower peak intensity, which may be assigned to the -NH_2 stretching.

The decreased intensity of -O- (1384 cm^{-1}) and C=O (1630 and 1726 cm^{-1}) stretching [136], and the emergence of C-N and N-H in-plane bond stretching (1020 and 1580 cm^{-1} respectively) [146] are suggestive of the presence of nitrogen and reduction of G-O.

Figure 2. 6 FT-IR spectrum of G-O before (down) and after amine modification (up).

Figure 2. ^1H -NMR spectrum of G-O (a) and $\text{NH}_2\text{-G}$ (b) in $\text{DMSO}-d_6$, and their proposed structural formula (inset).

Deuterium labelled $\text{DMSO}-d_6$ (CD_3SOCD_3) was used as NMR solvent here. Since the deuterium isotope of hydrogen has a different magnetic moment and spin, it is detectable in a spectrometer tuned to protons. Therefore, the ^1H -NMR analysis was used in order to get detailed information of $\text{NH}_2\text{-G}$. The chemical shift of carboxyl protons with NMR line at 9.99 ppm in G-O (Fig. 2.7a) is totally diminished in $\text{NH}_2\text{-G}$ (Fig. 2.7b). The signal of the protons from aromatic rings at 8.3 ppm is clearly observed, which can be attributed to naphthalene ring proton resonances (Fig. 2.7b).

The enhanced signal of naphthalene proton signal implicit our solvothermal system is helpful to restore the graphene π -system. The appearance of the $-\text{NH}_2$ protons at 5.75 ppm implies the presence of $-\text{NH}_2$ to the graphene sheet, similar to that of primary amine reported previously.[147] The hydroxyl proton resonance at 4.37 ppm is significantly attenuated in Fig. 2.7b, which is in good agreements with the IR examination of noteworthy shrinkage of the OH vibration at 3438 cm^{-1} (Fig. 2.6). The appearance of amine protons and decrease of hydroxyl resonance intensity support the reaction mechanism proposed in Fig. 2.1.

2.4 Performance of $-\text{NH}_2$ -G as Supercapacitor Electrode

The addition of N heteroatoms to carbon to create pseudocapacitance has long been studied [127, 128, 134, 148]. The presence state of N depends on the temperature and precursors of nitrogen enriched carbon. Recent reported investigation of N enriched carbon nanomaterials is mostly based on high temperature (higher than 400°C) introduction of N heteroatoms [127, 128, 134, 148]. Therefore, the reported nitrogen enriched carbon is N embodied in carbon in form of pyridinic N or pyrrolic. However, the influence of N in form of $-\text{NH}_2$ on the electrochemical capacitor performance of carbon has not been reported.

The electrochemical performance of NH_2 -G was investigated and compared with that of pristine G-O as shown in Fig. 2.8. The CV curves of G-O and NH_2 -G at different scan rates (from 5 to 100 mV/s) are shown in Fig. 2.8a and b. A perfect rectangular shape with high current density is observed on NH_2 -G (Fig. 2.8b), while G-O shows low current density and shallow shape of CV curves (Fig. 2.8a), and especially at high scan rates. The poor electrochemical performance of G-O can be ascribed to the low faradic reaction rate and poor electrical conductivity. The specific capacitance (SC) calculated from CV curves under scan rate of 100, 50, 20, 10 and 5

mV/s are 87.1, 115.7, 126.9, 131.7 and 145.0 F/g respectively. However, the SC of G-O is lower than 30 F/g.

The pseudocapacitive charge generated on NH₂-G electrode in acidic medium could be proposed based on the following Faradaic reactions expressed by eq. (2.1) and (2.2):

where C* stands for the carbon network.

Figure 2. 8 (a) and (b) Cyclic voltammograms (CV) of pristine G-O (a) and NH₂-G (b) in 1M H₂SO₄ at a scan rate from 5 to 100 mV/s; (c) galvanostatic charge/discharge curves of NH₂-G at the current load of 0.8 and 0.4 A/g respectively; and (d) specific capacitance (SC) of NH₂-G within first 700 cycles at the scan rate of 50 mV/s.

The SC values calculated from galvanostatic charge/discharge curves of NH₂-G in Fig. 2.8c are 187.6 and 217.8 F/g at current density of 0.8 and 0.4 A/g respectively. These values are much higher than those reported previously, chemically reduced G-O (135 F/g), activated carbon (63 F/g), such as commercial G-O (28 F/g), and CNT (50

F/g). The above results imply that introduction of -NH_2 to carbon network is efficient to prepare fast charge-discharge energy storage device.

The cycle behaviour of supercapacitors is crucial for their practical applications. Pristine carbon shows excellent cycling stability due to the pure electrochemical double layer charge storage mechanism. However, the performance of all carbon based supercapacitor device is still far from what is expected.[149, 150] Although carboxyl, hydroxyl, or even carbonyl functional groups are capable of generating pseudocapacitance charge in acid-oxidized carbon, a gradual decreasing of pseudocapacitance value is usually observed after long cycling due to its quasi-reversible reaction mechanism[150]. Different from the electrochemical performance of O-containing carbon prepared from acid or alkaline activation, the as-prepared $\text{NH}_2\text{-G}$ shows excellent cycle stability > 1000 cycles, with stable capacitance value of 117.0 F/g at a scan rate of 50 mV/s (see Fig. 2.8d). In sulfuric acid electrolyte, amine functional groups are much more stable than -OH although both amine and hydroxyl groups distribute homogeneously on graphene surface. Due to the poor leaving ability of ammonia than that of water in acid medium, it is more difficult to eliminate amines than hydroxyl groups from graphene carbon network. Therefore, unlike O-containing functional groups abundant carbon, the $\text{NH}_2\text{-G}$ shows superb stability in H_2SO_4 electrolyte.

2.5 Conclusions

This chapter showed for the first time, that G-O could be reduced and functionalized with -NH_2 through a one-step solvothermal process. The presence of primary amine in graphene is identified by $^1\text{H-NMR}$, XPS, and FT-IR. The atomic ratio of nitrogen to carbon can be tuned within 2-10% by changing the ammonia water to G-O ratio during the solvothermal process. The resulting $\text{NH}_2\text{-G}$ is an excellent

electrode material for supercapacitor application, and high specific capacitance up to 217.8 F g^{-1} was measured on $\text{NH}_2\text{-G}$ under a current density of 0.4 A/g . Unlike electrochemical behaviour of O-containing groups functionalized carbon prepared from harsh acid activation, the as-prepared $\text{NH}_2\text{-G}$ shows excellent cycling performance. Moreover, the one-step solvothermal process reported here could be extended for post-synthesis modification or activation of other carbon nanomaterials, which will show great promise in catalysis, biosensors, and energy storage fields.

Chapter 3

Polyaniline/graphene composite as supercapacitor electrodes

3.1 Significance of Prepare Polyaniline/Graphene Electrodes

Electrochemical supercapacitors have drawn much interest in recent years due to their high power density, long cycle life and small environmental impact.[150] They can be divided into two basic types according to their charge storage mechanism. The electric double-layer capacitance (EDLC) type generates capacitance from charge separation at the electrode/electrolyte interface,[1, 150] while the pseudocapacitance type generates capacitance from fast Faradic reactions in the electrode material.³ Porous carbonaceous materials are regarded as EDLC supercapacitors, where surface area, pore structure and conductivity of the electrode are critical and Faradic reactions are not involved. Porous carbon supercapacitors feature long cycle life and good mechanical properties, they require materials with high surface area and pores adapted to ion size.[150] Metal oxides (e.g. RuO₂,[151] MnO₂,[152] and IrO₂) and conducting polymers (e.g. polyaniline,[153] polypyrrole[154] and polythiophene) are typical pseudocapacitive materials which can achieve relatively high capacitance but are limited by poor cyclability due to structural degradation of the electrode through the redox process.[155, 156] Therefore, composites incorporating a porous carbon backbone coated with pseudocapacitive materials suggest a potential breakthrough for a new generation of supercapacitors.[150] Therefore, research on carbonaceous materials loaded with metal oxides or polymers is widely reported.[151, 153, 157, 158]

Polyaniline (PANi) is a highly favourable electrode material due to its low cost, straightforward synthesis method, good conductivity, fast redox rate and high pseudocapacitance. It has been reported that when paired with various electrode materials such as carbon,[159] metal[160] or metal oxides[161] in supercapacitors, PANi can greatly enhance the capacitance of the modified electrodes. Additionally, the stability, conductivity and redox behaviour of PANi may be also improved by the presence of the carbon. This improvement relies on the morphology and pore structure of the modified electrode material, which can be measured in the specific surface area, electronic properties, and ion diffusivity.

As a carbon nanomaterial, graphene exhibits many extraordinary and attractive physical, electrochemical and mechanical properties. In particular, these properties make graphene a stronger candidate electrode material for supercapacitor applications than ordinary porous carbon, activated carbon, and carbon nanotubes.[75] Graphene/PANi composites have shown higher capacitances than activated-carbon/PANi and carbon-nanotube/PANi composites. [14, 162, 163]

Graphene/PANi composites can be produced by in-situ chemical oxidative polymerization of aniline in the presence of graphene oxide (G-O) or reduced graphene oxide (RG-O). Pure graphene is not easily dispersed in aqueous solution which limits its application and to date no scalable method of making pure graphene flakes has been reported. To solve this problem, surface modified graphene with various functional groups are used to prepare graphene/PANi composites, among which G-O is the most easily synthesized and most widely employed. G-O contains a large amount of O-containing groups such as OH, CO, COC and COOH. These groups aid dispersion of G-O in solution and aniline monomer adsorption, which favours achieving a uniform coating of PANi on G-O. It was also reported that carboxyl

groups from G-O could link to the nitrogen atoms in the PANi backbone, providing doping for the interaction in addition to bonding, and thus taking the place of an additional dopant such as Cl⁻. [90] Nevertheless, the poor electrical conductivity of G-O will hinder efficient charge transfer in the graphene network and reduce cyclability. [164] This drawback can be overcome by chemical reduction or by thermal annealing to partly remove O-containing groups, thus partially restoring the graphene sp² network. It is obvious that the graphene surface functionalities are important to the performance of supercapacitors. However, little work has been done to explore the effect of graphene surface chemistry on PANi loading and the effect of such loading on capacitive performance.

In this part, four different surface functionalized graphenes: graphene oxide (G-O); reduced G-O (RG-O); nitrogen doped graphene (N-RG-O), and primary amine modified graphene (NH₂-RG-O) were synthesized for use in 'graphene'/PANi composites. In an attempt to achieve the highest synergistic effect between the chemically modified graphenes and PANi, the amount of conducting polymer loading was fixed at ~9 wt%. This value was chosen to prevent the blockage of micropores and the degradation of the graphene composite conductivity from excessive polymer loading. Among the four samples, NH₂-RG-O showed an 8-fold capacitance increase after PANi loading. The 500 F g⁻¹ capacitance of NH₂-RG-O/PANi was larger than that of G-O/PANi (4.7 F g⁻¹), N-RG-O/PANi (68.47 F g⁻¹) and RG-O/PANi (207.11 F g⁻¹). Moreover, the NH₂-RG-O/PANi composite exhibited an unusually good cyclability and an increase in capacitance by a factor of 1.19 after 680 cycles at 2 mV s⁻¹. The effect of -NH₂ functional groups on the electrochemical performance of 'graphene'/PANi supercapacitors was carefully studied and elucidated for this paper.

3.2 Experiment and Characterization

GO was prepared from natural flake graphite powder using a technique which has been reported elsewhere, as introduced in section 2.2.[57]

NH₂-RG-O was prepared with experimental procedures as-mentioned in section 2.2.[165] Since the reactant G-O platelets are subjected temperatures which are capable of reducing them, we label this product as 'NH₂-RG-O'.

N-RG-O was prepared by annealing G-O at 550 °C under NH₃ gas flow. Briefly, 500 mg of G-O was annealed with 5% NH₃ in Ar flow of 50 sccm in a tube furnace. It was then heated to 550 °C in 20 minutes and maintained for half an hour. The resultant samples were ground, washed repeatedly with distilled water, and dried at 60 °C for 24 h for further use.

RG-O was prepared by chemical reduction: 500 mg of G-O powder were dipped in aqueous NaBH₄ (50 mM) solution for 2 h. The resultant sample was washed repeatedly with large amount of DI water and dried at 60 °C in vacuum.

The PANi/graphene composites were synthesized *via* polymerization of aniline on the 4 different surface functionalized graphenes by using ammonium persulfate as an oxidant. The aniline monomer was doubly distilled before use. 200 mg of each type of functionalized graphene was individually dispersed in 20 mL of methanol. Then 2.38 mL of 0.1 M aniline in methanol was added drop by drop into the solution, which was contained in an ice bath under magnetic stirring. After another 10 min, 4.76 mL of 0.02 M ammonium persulfate and 0.2 M LiClO₄ in 1M H₂SO₄ was dripped in. The solution was magnetic stirred in an ice bath for 8 h to achieve full polymerization. The product was then washed with water, ethanol to remove the remaining oxidants. All of the composites were dried at 60 °C in vacuum.

The near-edge X-ray adsorption fine-structure (NEXAFS) spectra were obtained at the Surface, Interface, and Nanostructure Science (SINS) beamline of the Singapore Synchrotron Light Source. The XPS was collected with a Kratos Axis Ultra DLD (delay line detector) spectrometer. This XPS has a monochromatic Al K α X-ray source with a resolution of 0.1 eV. FT-IR were recorded on a Shimadzu IR prestige-21 FTIR spectrophotometer.

The electrochemical performance of the samples was measured by CV and galvanostatic spectroscopy at room temperature using 0.5 M H₂SO₄ as the electrolyte in an Autolab PGSTAT302 electrochemical workstation (Eco Chemie, The Netherlands). Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency from 10 kHz to 10 mHz in a 1M H₂SO₄ electrolyte. The applied voltage was 10 mV. The 5 mm diameter glassy carbon electrode was used as working electrode, DI water-impregnated graphene ink was casted onto the surface. The graphene composite ink was prepared by dispersing 20 mg of a graphene/PANi into 5 mL of DI water. 20 μ L of the graphene/PANi ink was collected for the electrode coating and further dried at 60 °C. After drying, the electrode was deposited with 5 μ L of Nafion solution containing 2-propanol (5 wt%, dupont).

3.3 Results and Discussion

NH₂-RG-O was prepared via a solvothermal process in which ammonia water reacted with G-O in the presence of ethylene glycol. Ammonium ions in ammonia water can attack the oxygenated groups of G-O and generate primary amine groups at NH₂-RG-O surface by nucleophilic replacement.[165] The ethylene glycol in the solvothermal system functions as a reducing agent and assists the removal of oxygenated groups in the G-O. Alternately, N-RG-O was produced from a reaction between G-O and NH₃ gas at high temperatures ~550 °C (vs. < 200°C for NH₂-RG-O).

During this synthesis process, some C-C and C-O bonds may rupture, forming pyridinic and graphitic C-N species in the N-RG-O. Hence, the nitrogen atoms in the N-RG-O sample exist mostly in the pyridinic and graphitic form, while in NH₂-RG-O primary amine functional groups coexist with pyridinic N. NaBH₄ efficiently reduces G-O and can decrease the presence of O-containing groups.[76]

Figure 3. 1 Chemical structure of NG, NH₂-G, RG and their derivation process from GO.

The surface character of the different chemically modified graphenes was identified by FT-IR, XAS, and XPS. G-O contains a wide range of O-containing functional groups both on the basal planes and at the edges of the G-O sheets.[166] The FT-IR spectrum (Fig. 3.2a) of G-O demonstrates the presence of C-O in carbonyl ($\nu_{\text{C-O}}$ at 1056 cm^{-1}), C-O in carboxylic acid ($\nu_{\text{C-O}}$ at 1162 cm^{-1}), C-O-C ($\nu_{\text{C-O}}$ at 1226 cm^{-1}), C-OH ($\nu_{\text{C-O}}$ at 1307 cm^{-1}), and C=O in carboxylic acid and carbonyl moieties ($\nu_{\text{C=O}}$ at 1631 and 1730 cm^{-1}), in addition to the strong C=C stretching deformation of honeycomb carbon network at 1497 cm^{-1} . After the G-O is reduced by NaBH₄, the peak intensities of C-O (1056 cm^{-1}) and C=O (1631 and 1730 cm^{-1}) decrease significantly while the C=C graphene network vibration remains strong around 1600 cm^{-1} . A broad band of strong absorption around 1200 cm^{-1} is due to the overlapping of B-C vibration (1225 cm^{-1}) and -OH vibration (1200 cm^{-1}), which indicates the introduction of boron from the NaBH₄ reduction reaction and an incomplete reduction

of G-O. For NH₂-RG-O samples (Fig. 3.2b), the two distinct vibration bands besides the characteristic C=C peaks are IR absorptions at 1565 and 2800-2980 cm⁻¹; the former is the sp² C=N bond while the latter is the C-H stretching vibration of the NH₂-G bond. The C=N bond at 1565 cm⁻¹ is not observed in the IR spectrum of N-RG-O (Fig. 3.2b) and indicates that NH₂-RG-O has higher nitrogen content than N-RG-O. From Fig.3.2 we can also conclude that RG-O, NH₂-RG-O and N-RG-O have very low oxygen content compared to G-O.

Figure 3.2 FT-IR spectrum of G-O, RG-O (a), and NH₂-RG-O, N-RG-O (b).

The carbon K near-edge x-ray absorption fine-structure spectra (NEXAFS) of the four different surface modified graphenes are shown in Fig. 3.3. The graphite spectrum is displayed as a reference. The main peak around 285 eV can be assigned to the C K edge π^* resonance and is observable in all 5 spectra. The strong peak at 293 eV is associated with the σ^* resonance, while higher energy absorption bands at 295-315 eV are due to the transitions from C1s to higher conduction π or σ states. The absorption peak between 286 and 290 eV may be attributed to an interlayer transition according to Pacile et al.[167] and/or the presence of COOH and alkyl functional groups as proposed by Jeong et al.[168] This peak is remarkably strong in the G-O spectrum, indicating a high concentration of COOH and CO species. The σ^* resonance feature at

293 eV is prominent in the G-O spectrum. This may be associated with the presence of large amount of COC and COH groups which are upright with respect to the carbon basal plane and therefore possess σ symmetry. It is noted that, compared to the other four samples, the main resonance of G-O at 284.8 eV possesses a low intensity and shift to lower photon energy, and both are indicative of more defects in the G-O sp^2 carbon network.[169] For RG-O, the intensity ratio between the peaks at 288.1 and 293 eV and the main resonance peak at 284.9 eV suggest the removal of O-containing functional groups and the repair of the graphene π network. The C K NEXAFS spectra of NH_2 -RG-O and N-RG-O are basically similar to that of RG-O in that the attachment of NH_2 groups or incorporation of substitution N to the carbon sp^2 network do not affect the C K edge absorption directly.

Figure 3. 3 NEXAFS spectra at the C K edge of G-O, RG-O, NH_2 -RG-O, and N-RG-O. The spectrum of graphite is also included for comparison.

Figure 3. 4 N K-edge NEXAFS spectra of $\text{NH}_2\text{-RG-O}$ and N-RG-O (a), and XPS of N 1s spectra of $\text{NH}_2\text{-RG-O}$ and N-RG-O (b).

Nitrogen K near-edge x-ray absorption fine spectra of $\text{NH}_2\text{-RG-O}$ and N-RG-O are displayed in Fig. 3.4a. Strong π^* resonance features at 397-403 eV and a strong broad σ^* resonance band between 403 and 425 eV are observed both in N-RG-O and $\text{NH}_2\text{-RG-O}$. Three well-resolved peaks, denoted N1 (398.5), N2 (399.8) and N3 (401.5), are observed and agree with peaks seen in similar studies in N doped carbon and CN composites.[170] The N1 (398.5 eV) peak is attributed to pyridinic N atoms, which replace carbon atoms in the graphene layer but only bond to two carbon atoms and donate one electron to the carbon network ($\text{C-N=C } \pi^*$). The N2 peak is assigned to primary amine-type N bonds (C-NH_2).[171-173] N3 can be assigned to the π^* transition from N1s to amide N ($-\text{OCNH}_2$ or secondary admide $-\text{OCNHCO}-$) according to the *ab-initio* calculation. N2 and N3 are strong in $\text{NH}_2\text{-RG-O}$ but absent or weak in the N-RG-O spectrum. The strong peak located around 407 eV is assigned to the transition from the N1s core level to C-N σ^* states.[170] These N K-edge NEXAFS assignments are confirmed in the XPS N1s data. As shown in Fig. 3.4b, the N 1s signal of N-RG-O is relatively weak at 398.5 eV and can be attributed to pyridinic

nitrogen. For NH₂-RG-O, in addition to the prominent pyridinic N peak at 398.3 eV, there exists a strong peak of –NH₂ at 399.5 eV and a minor component peak at 401.0 eV due to graphitic and/or amide N atoms.[165]

Based on the detailed analysis of XPS spectra, the surface elemental composition of these four graphene samples can be identified and quantified. As summarized in Table 3.1, the G-O sample has an oxygen content of 37% which is higher than RG-O (~15%), N-RG-O (~6%) and NH₂-RG-O (~8%). The N-RG-O and NH₂-RG-O samples have ~5% and 9% N, respectively (hydrogen is not taken into account for the calculation).

The electrochemical performance of the four graphene samples without PANi loading, i.e. G-O, N-RG-O, NH₂-RG-O and RG-O, were evaluated by cyclic voltammetry in 1 M H₂SO₄ electrolyte. The CV curves of N-RG-O and NH₂-RG-O as shown in Fig. 3.5 have a nearly rectangular shape, which would be characteristic of a perfect EDLC. On the other hand, both RG-O and G-O exhibit a pair of red-ox peaks which could be ascribed to the transition between quinone/hydroquinone groups [150]. The NH₂-RG-O curve shows a current density of 2.5 A g⁻¹ at a scanning rate of 100 mV/s, which is larger than G-O (0.078 A g⁻¹), N-RG-O (1.23 A g⁻¹) and RG-O (2.0 A g⁻¹). It is also noted that at high scan rates, the increment of cathodic current to potential is sluggish as shown in Fig. 3.5a, which demonstrates the poor conductivity of GO.

Figure 3. 5 Cyclic voltammograms of G-O (a), N-RG-O (b), NH₂-RG-O (c), and RG-O (d) recorded at different scan rate from 2 to 100 mV s⁻¹.

Fig. 3.6 displays CV curves at various scan rates for the four graphene/PANi samples after loading ~9 wt% PANi. All of the graphene/PANi samples show a great increase in the current density compared to their counterpart graphenes without PANi. The capacitance can be calculated from the CV curves according to the eq. 3.1.

$$C = \frac{(\int idV)}{vmV} \quad \text{eq. 3.1}$$

where *i* is the current density (A), *V* is potential (V), *v* stands for scan rate (mV s⁻¹) and *m* represents mass of the graphene/PANi composite in the electrode (g).

Figure 3. 6 Cyclic voltammograms of G-O/PANi (a), N-RG-O/PANi (b), NH₂-RG-O/PANi (c), and RG-O/PANi (d) recorded at different scan rate from 2 to 100 mV s⁻¹.

As shown in Fig. 3.7, NH₂-RG-O increases its capacitance 8-fold due to the PANi loading, reaching 420 F/g at a scan rate of 2 mV s⁻¹. This is larger than that of G-O/PANi (4.7 Fg⁻¹), N-RG-O/PANi (68.47 Fg⁻¹) and RG-O/PANi (207.11 Fg⁻¹) under identical measurement conditions. BET surface area of G-O/PANi, RG-O/PANi, NH₂-RG-O/PANi, N-RG-O/PANi, and the G-O, which are around 289, 265, 320, 358, and 310 m²g⁻¹ respectively. The PANi/N-RG-O has largest BET surface area, and also relatively higher conductivity. However, the four samples do not show significant difference of BET value. Therefore, their different electrochemical behaviours would come from the synergistic effect from both graphene and PANi. Note that the specific capacitance of NH₂-RG-O/PANi is more than twice that of RG-O/PANi. The capacitance value of NH₂-RG-O/PANi remains as high as 291 F g⁻¹ even under high

scan rates of 100 mV s^{-1} , which may be a benefit of the high conductivity of the graphene/PANi composites.

Similar to those of pristine $\text{NH}_2\text{-RG-O}$, the CV curves of $\text{NH}_2\text{-RG-O/PANi}$ are nearly rectangular in shape (Fig. 3.6c), which indicate that both behave as electrochemical double layer-type supercapacitors. A pair of new redox peaks (0.52/0.46 V with $\Delta V=0.057 \text{ V}$) appear in $\text{NH}_2\text{-RG-O/PANi}$, which represent the pseudocapacitance contribution of the PANi in the transformation from emeraldine to pernigraniline.[14, 174] It is important to note that the cathodic and anodic peak positions of $\text{NH}_2\text{-RG-O/PANi}$ do not shift with the change in potential sweep rates, indicating fast pseudocapacitive charge transfer from PANi to $\text{NH}_2\text{-RG-O}$. As the pseudocapacitive charge producer, PANi can generate capacitance values which are several times larger than those of rG-O.[89, 90, 175] However, the polymer in the polymer/graphene composite normally leads to low percolation thresholds. In other words, only the top layers of the composite can contribute to the capacitance. Graphene serving as the current collector provides active sites for electrical current to pass between layers. Recent reports showed that composite electrodes with thin film ($<10\text{nm}$) conducting polymers were effective for fully reversible and rapid Faradic reactions, thus the conducting polymers contribute as pseudocapacitive charge storage.[176, 177] On the contrary, Gomez et al. has recently reported that the redox peaks in the CV curves shift position with scan rate changes.[162] This may be due to high PANi loading (PANi to graphene ratios of 50-100%) and poor charge transfer between the PANi and graphene carrier. In our experiments, the weight ratio of PANi was kept at a moderate level of $\sim 9\%$ so that the prepared $\text{NH}_2\text{-RG-O/PANi}$ electrode could act as highly conducting micro-electrodes for electron transport from PANi to the chemically modified graphenes. RG-O/PANi (Fig. 3.6d) also shows characteristic red-ox peaks at 0.52 and

0.46 V, which represent a Faradic reaction in the conducting polymer. Nevertheless, the CV curve shows non-idealities, particularly at high scan rates, indicating reduced conductivity of the RG carrier in comparison to $\text{NH}_2\text{-RG-O/PANi}$. The CV curves (Fig. 3.6a and b) of G-O/PANi and N-RG-O/PANi are shallow with low current density ($0.2\text{-}4\text{ A g}^{-1}$ vs. $15\text{-}20\text{ A g}^{-1}$ for $\text{NH}_2\text{-RG-O/PANi}$ and RG-O/PANi) and deviate from a rectangular shape. Their measured capacitances are 8-10 times smaller than that of $\text{NH}_2\text{-RG-O/PANi}$.

Figure 3. 7 Specific capacitance of different surface functionalized graphene before (a) and after (b) loading of 10 wt% PANi at different scan rate (from 2 - 100 mVs^{-1}) in 1 M H_2SO_4 electrolyte.

Figure 3. 8 Galvanostatic charge/discharge curves of $\text{NH}_2\text{-RG-O/PANi}$ at a current density of 1 and 1.5 A g^{-1} in 1 M H_2SO_4 with potential range from -0.3 to 0.8 V.

Fig. 3.8 shows the galvanostatic charge-discharge profiles of NH₂-RG-O/PANi at current density of 1 and 1.5 A g⁻¹. The linear symmetric charging and discharging profiles indicate that the capacitive behaviour of NH₂-RG-O/PANi is fully reversible. This composite also demonstrates fast charge transfer and red/ox kinetics. The specific capacitance calculated using eq. 3.2:

$$C = \frac{i \times \Delta t}{m \times \Delta V} \quad \text{eq. 3.2}$$

where i is the discharge current, m mass of the active material (weight of PANi + graphenes), Δt discharge time, and ΔV the potential window, which is 388 and 372 F g⁻¹ at 1 and 1.5 A g⁻¹ respectively, they agree well with the values calculated from the CV curves using eq. 3.1.

A stability study of NH₂-RG-O/PANi and RG-O/PANi was performed by cyclic voltammetry. RG-O/PANi exhibits a decay in the capacitance with increasing cycle number (see Fig. 3.9a). An interesting phenomenon is observed with NH₂-RG-O/PANi where the specific capacitance increases significantly with increasing cycle number (Fig. 3.9 b). After 100 cycles of charge/discharge activation at a scan rate of 50 mV s⁻¹, the CV curves were recorded at scan rate 20 mV S⁻¹ from 120 to 220 cycles and then at scan rate of 2 mV s⁻¹ from 220 to 680 cycles. The different scan rates were adapted in order to shorten the activation time period. The capacitance value gradually increases from 420 F/g initially, to 500 F/g at 200 cycles and remains stable up to 680 cycles.

High conductivity with reversible redox properties is regarded as necessary to achieve supercapacitors with long cycle-life. Increases in the capacitance with cycling number were reported previously with a MWCNT-GO composite. In that system, the improved conductivity was reasoned to be due to the reduction of oxygen content in GO with increasing cycles. In our case, the capacitance increase is possibly due to the

doping and dedoping of sulfate ions on the PANi polymer assisted by the simultaneous fast Faradic reactions of primary amine with H^+ . The doping and dedoping of ions during the oxidation and reduction of PANi is responsible for the pseudocapacitive charge generation in these capacitors.

Figure 3.9 Cyclic-life data of RG-O/PANi electrode (a) and NH_2 -RG-O/PANi (b). The specific capacitance value is calculated from CV curves at a scan rate of $50 mV s^{-1}$ in $1 M H_2SO_4$ electrolyte. Inset figure shows the CV curves during the 1000 cycles.

In previous reports, researchers found that the presence of heteroatoms, especially widely-used N compounds, in the carbon network could improve capacitance and were the origin of stable pseudo-Faradaic reactions. In our recent studies, we find that the amine functional groups in NH_2 -RG-O react with protons to produce imine or protonated amine,[165] while the consumption of H^+ in electrolyte helps $H_2SO_4 \rightarrow HSO_4^-$ dissociation. The amine redox reactions can therefore assist charge doping and

de-doping in PANi. This synergistic effect can result in the doubled charge storage processes as shown in Fig. 3.10.

Figure 3.10 Faradic reactions of PANi and $\text{NH}_2\text{-RG-O}$ in acidic electrolyte.

Controlling the carbon surface chemistry is of significant importance when growing polymer on the carbon carrier. Fang et al. reported that the modification of carbon could improve its wettability and further enhance its electrochemical performance in supercapacitors.[178] While the chemical content and type of surface groups have a pronounced effect on the capacitance,[179] only basic or neutral groups such as phenol and ethers etc. were thought to be able to improve capacitance.[180] $\text{NH}_2\text{-RG-O}$ and RG-O contain unreduced hydroxyl groups, which are advantageous for supercapacitors. N-RG-O , which was reduced under an inert gas atmosphere, was doped with graphitic and pyridinic nitrogen atoms with poor wettability. GO holds a high concentration of oxygen functionalities, but the poor conductivity severely hinders it for electrochemical applications. Therefore, $\text{NH}_2\text{-RG-O}$ and RG-O , containing N heteroatoms, can improve the capacitance of the electrode, with unreduced hydroxyl groups on $\text{NH}_2\text{-RG-O}$ also possibly contributing to the capacitance.

Figure 3. 11 Electrochemical impedance plots of G-O/PANi, N-RG-O/PANi, NH₂-RG-O/PANi and RG-O/PANi. The spectra were taken in 1M H₂SO₄ in a frequency range from 10k Hz to 10 mHz. A Randles equivalent circuit representing the circuit elements for the Nyquist plot is shown in the inset. R_s is solution resistance, C or CPE represents double layer capacitance or constant phase element, R_{ct} is charge transfer resistance, and Z_{war} is diffusion-controlled Warburg impedance.

Electrochemical impedance spectroscopy (EIS) was used to measure the internal resistance, charge transfer kinetics, and ion diffusion process of the four graphene/PANi composites. The EIS was measured over a frequency range of 10 kHz to 10 mHz. As shown in the Fig. 3.11 inset, the intercept between the impedance spectrum and real impedance axis (Z') is almost the same (0.035 Ohm) for all four graphene/PANi electrodes. This indicates that the series resistance, which includes the electrolyte solution resistance and contact resistance at the interface of active material/current collector, is very low for all four graphene/PANi cells. The Nyquist plots in Fig. 3.11 exhibit an incomplete semicircle in the high frequency region and a vertical linear feature in the mid-to-low frequency region.

Among the four graphene/PANi composites, the vertical curve of NH₂-RG-O/PANi has the largest slope with respect to the Z' axis, i.e. closest to the imaginary impedance axis (Z''), which implies that NH₂-RG-O/PANi exhibits the highest conductivity or lowest internal resistance, including polarization impedance. In contrast, the low frequency Nyquist plot of G-O/PANi is almost 45 degrees with respect to Z' . That is, the real and imaginary components of the impedance vector are almost equal at all frequencies, which is a characteristic of Warburg impedance; where ion diffusion effects at the electrolyte/electrode interfaces dominate the electrochemical reaction mechanism on the G-O/PANi electrode. The structural defectives and abundance of oxygen-containing groups in G-O that hinder the ion diffusion through the G-O/PANi layers are the main reasons for the high Warburg impedance. The Nyquist plots in the high frequency region in Fig. 3.11a resemble an incomplete semi-circle. The semicircle impedance plots have been reported for many carbon, CNTs, and graphene-based supercapacitors.[181-183] They can be well-modelled using a complex equivalent circuit as shown in the inset to Fig. 3.11. R_s is the series solution resistance, which may include the electrolyte resistance and the active material/current collector contact resistance. Two capacitors C (or more realistically, two constant phase elements, CPE, which take into consideration the electrode surface inhomogeneity) represent double layer capacitance and Faradic capacitance, respectively. R_{ct} , in parallel to C , is the charge transfer resistance at the electrode/solution interface, while Z_{war} is the ion diffusion-controlled Warburg impedance.

These components form a mixed control Randles circuit, which is usually used to model capacitance in a process with a combination of kinetic and diffusion processes determining the rate. The second capacitance circuit consists of a capacitor impedance

C and charge transfer resistance R_{ct} . At high frequencies, the capacitor impedance becomes much smaller and the system resistance is dominated by the resistors and polarization impedances. With decreasing frequency, the capacitor's impedance increases and the cell become more capacitive. At low frequencies, an ideal polarizable capacitance would give a straight line with large angles with respect to Z' or almost parallel to Z'' . This is the case we observed for NH_2 -RG-O/PANi and RG-O/PANi in Fig. 3.11. It is noted that in Fig. 3.11, the semicircles partially (in the mid-frequency region) disappear. The absence of the semicircle in the complex impedance plane has been reported and is explained by high ionic conductivity at the electrode/electrolyte interface.[184] This explanation can also be applied to our graphene/PANi composites.

In the NH_2 -RG-O/PANi case, when the frequency decreases and the impedance vector moves further from ($Z' = 3 \text{ Ohm}$, $Z'' = 1 \text{ Ohm}$), the phase angle does not decrease as in an ideal semicircle. Instead, the phase angle increases continuously with further decreases in frequency. This means that the polarization impedance reduces its contribution (i.e., the kinetic and charge transfer are no longer rate-determining steps) while mass capacitance remains the dominant component of the system impedance. Hence the EIS data are consistent to the other electrochemical measurements shown and discussed above, and they indicate that NH_2 -RG-O/PANi is the best electrode material for supercapacitor applications, demonstrating low internal resistance, very good charge transfer and excellent ionic conductivity.

It is known that the three-electrode cell used for evaluating the electrochemical performance of an active material usually shows a high sensitivity to Faradic reactions. This may lead to large errors in estimating the energy storage capability of the electrode material for supercapacitor applications.

It should be mentioned that it is difficult to achieve a high specific capacitance value if the supercapacitor cells are fabricated using a single conducting-polymer-based active material for both the cathode and anode. Therefore, we used N-RG-O as the cathode material and $\text{NH}_2\text{-RG-O/PANi}$ as the anode electrode. The electrochemical performance of the $\text{NH}_2\text{-RG-O/PANi//N-RG-O}$ cell is measured in 1 M H_2SO_4 (Fig. 3.12). The capacitance of the full cell is 35, 43, 52, 69, and 79 F g^{-1} respectively, during scan rates of 500, 300, 150, 50 and 10 mV s^{-1} .

Figure 3. 12 (a) Cyclic voltammograms taken at various scan rates of 10 500 mV s^{-1} and (b) Galvanostatic charge/discharge curves taken between 0 and 1 V at various constant currents of 2-7 A g^{-1} for the asymmetric capacitor $\text{NH}_2\text{-RG-O/PANi//N-RG-O}$ in 1 M H_2SO_4 .

The specific capacitance per mass of one pellet electrode is calculated according to eq. 3.3:

$$C_{\text{spec}} = \frac{2C}{m} \quad \text{eq. 3.3}$$

where C is the experimental measured capacitance of the supercapacitor and m is the mass percentage of the $\text{NH}_2\text{-RG-O/PANi//N-RG-O}$ electrode. Therefore, the specific capacitance of the $\text{PANi-NH}_2\text{-RG-O}$ electrode under scan rates of 500, 300, 150, 50, and 10 mV s^{-1} are 175, 213, 261, 346, and 395 F g^{-1} , respectively, which were higher than those reported for PANi/CNT (320 F g^{-1}) in a two-electrode testing environment, 45 but in our case the loading weight ratio of PANi decreased to $\sim 10\%$. At a

charge/discharge rate of 2.0, 5.0, and 7.0 A g⁻¹, they are 69.4, 56, and 48 Fg⁻¹, while the SCs of the PANi-NH₂-RG-O electrode are 345, 280, and 240 Fg⁻¹ respectively.

These results agree well with the values calculated from the CVs. At a charge/discharge rate of 2.0 A g⁻¹, the energy density of our two-electrode cell can be as high as 9.6 Wh kg⁻¹, as calculated from eq. 1.2 (pg. 4). The cycling performance, which is analyzed by galvanostatic charge/discharge of the NH₂-RG-O/PANi//N-RG-O cell under 1.0 V with a current density of 2 Ag⁻¹, gave a 85% capacitance maintained after 1000 cycles.

3.4 Conclusions

Four different surface functionalized graphenes were used as carriers for preparing chemically-modified-graphene/PANi composites. The largest capacitance of 500 Fg⁻¹ (all values are with respect to the combined mass of PANi and chemically modified graphene that are derived from measurements on a 3-electrode cell) was measured for a 'NH₂-RG-O/PANi' composite, which was an 8-fold improvement over a 'NH₂-RG-O' without PANi loading composite and was much larger than that of 'G-O/PANi' (4.7 Fg⁻¹), 'N-RG-O/PANi' (68.47 Fg⁻¹) and 'RG-O/PANi' (207.11 Fg⁻¹). Most importantly, an increase in capacitance with a factor of 1.19 was observed for NH₂-RG-O/PANi as the cycle number increased to 680 cycles, while the capacitance decay with increasing cycle numbers was measured for the other three graphene/PANi composites. The amine functional groups in NH₂-RG-O react with protons to produce imine or protonated amine, while the consumption of H⁺ in the electrolyte helps H₂SO₄ → HSO₄⁻ dissociation. The amine redox reactions can therefore assist the doping and de-doping in PANi, and might be responsible for the increased capacitance in long cycling. Introducing -NH₂ into the carbon honeycomb network before loading

the PANi helps the PANi/graphene composite to achieve high capacitance values for supercapacitor applications.

Chapter 4

Graphene/Polypyrrole as Supercapacitor Electrodes

4.1 The PPy and PPy Composite

Polypyrrole (PPy) as supercapacitor electrode material has been the focus since the last decade.[99, 177, 185-188] Composites of PPy with carbon have been proposed as most effective option to improve the mechanical properties and electrochemical performance of electrodes.[177, 186, 188] Here, the conducting polymer on the surface of the carbon carrier provides the high pseudocapacitance while each carbon nanosupport acts as the micro-electrode for current collector. Carbon with high conductivity also facilitates the electron transfer from redox reactions in conducting polymers matrix. It has been reported that 5 nm coating of PPy on MWNTs can increase the capacitance of MWNTs from 50 Fg⁻¹ to 163 Fg⁻¹. [188] Thin PPy coated carbon electrode (< 10 nm) is useful in obtaining a fully reversible and fast Faradic reaction, hence, in thin PPy layer, the majority of the PPy could contribute to the pseudocapacitive charge storage.[176, 177]

In chapter 3, we elucidated the enhanced charge storage behavior of NH₂-RG-O/PANi. However it is worth to note that, due to the different acidity of monomers, electrolyte, as-prepared graphene/conducting polymer composites may have announced different contributions. O-containing functional groups may lead to the decrease of carbon conductivity. The conductivity of carbon increase with reducing the content of surface oxygen and sulphur groups are reported.[189, 190] However, the oxygenated groups may also cause the capacitance rise due to Faradic charge transfer and/or electrostatic interactions.[4, 191] Different from oxygen, the electron-

donor character of nitrogen could increase the carbon Fermi level, thus giving superior electronic properties.[127, 128, 134, 192] The functional groups on carbon can be electron donor [128, 134, 193] and/or electron acceptor groups,[194, 195] which not only generate pseudocapacitance from fast Faradic reactions,[128, 193] but also provide sites for pyrrole anchor as well. Carbon without surface functional groups is not suitable for polymer growth due to the lack of monomer attachment sites. Both N and O containing functionalities help the growth of polymer, however the diverse synergistic effect induced by their pseudocapacitance contribution have not been thoroughly studied until now.

Carbon surface chemistry plays a significant role in conducting polymer growth and contributes to capacitance improvement, in this paper, four kind of surface modified graphene: amine modified graphene ($\text{NH}_2\text{-G}$), reduced graphene oxide (RG), nitrogen doped graphene (NG), and graphene oxide (GO) are used as carbon carriers. These four types of carbon carriers were selected to load with 10 wt% PPy by chemical method to obtain graphene/PPy composite. Cyclic voltammetry, galvanostatic technique and impedance spectroscopy were utilized to evaluate the performance of various graphene/PPy composites. Surface functionalities of graphene are found to have close relationship to the capacitance increment magnitude of graphene composite and cycling stability.

4.2 Experiment and Characterization

GO was prepared from natural flake graphite powder as introduced in section 2.2.[57] Synthesis of $\text{NH}_2\text{-G}$, N-G and R-G was mentioned in section 3.2.

Synthesis of PPy/graphene composite: The chemical polymerization of pyrrole on different graphene was performed with FeCl_3 as an oxidant. 200 mg of different graphene was dispersed in 200 mL of methanol under ultrasonication, 3.31 mL of 0.1

M pyrrole in methanol is added dropwise. After 10 mins, 6.62 mL of 0.2 M FeCl_3 is added dropwise. The solution was magnetic stirred for 8 hours in icy bath and then washed with excessive water, ethanol and acetone before dried in vacuum under 60 °C.

The as-synthesized materials were characterized by SEM, XPS with the same equipments and parameters, as shown in chapter 3.

Cyclic Voltammetry (CV) electrochemical impedance spectroscopy (EIS) and galvanostatic were measured on Autolab PGSTAT302 electrochemical workstation (Eco Chemie, The Netherlands). EIS measurements were carried out in the frequency from 100 k Hz to 0.01 Hz with 10 mV of voltage applied. The graphene/PPy composite were assembled onto nickel foam current collectors. 80 wt% of PPy/graphene composite (20 mg), 10wt% poly (vinylidene fluoride) (PVDF) and 10wt% carbon black, were dispersed in ethanol and mixed with mortar to form slurries. The slurries were coated on nickel foam and further dried at 80 °C under vacuum. As formed electrodes were then pressed at a pressure of 2 Mpa cm^{-2} , and then dried again under vacuum at 80 °C.

4.3 Results and Discussion

NG, RG, and $\text{NH}_2\text{-G}$ were prepared from GO by different methods having a chemical structure shown in Fig. 4.1, also seen from chapter 3.

Figure 4. 1 Chemical structure of NG, NH₂-G, RG and their synthetic methods from GO.

XPS were utilized to identify the surface element and the bonding state of each elements in GO, RG, NG, and NH₂-G Fig. 4.2. The survey scans of GO shows the strongest oxygen intensity at ~ 530 eV as compared with those of RG, NG, and NH₂-G. The C1s peak of GO and RG can be deconvoluted with three components centered at 286.8, 285.8, and 284.5, eV, corresponding to C=O groups, C-OH / C-O groups, and sp² hybridized C, respectively. RG shows a significant decrease of oxygen concentration in the form of C-O and C=O groups (Fig. 4.2c). The carbon to oxygen atomic ratio as calculated is 10.7:1, 9.8:1, 1.9:1, and 13.5:1 for NH₂-G, RG, GO and NG, respectively. NH₂-G, RG and NG has relatively high C to O atomic ratio demonstrating the reduction of GO, therefore the oxidation induced structural deformations would be ameliorated and the conductivity would be recovered.[73]

The N narrow scan of NG has binding energies at 398.1, 399.7 and 400.2 eV, correspond to pyridinic, pyrrolic, and quaternary N respectively with atomic ratio of 0.43: 0.32: 0.25 (Fig. 4.2d). On the other hand, NH₂-G have two peaks at 399.5 and 398.2 eV which are assigned as N from primary amine (-NH₂) functional groups and

pyridinic N, respectively with a atomic ratio of 0.24: 0.76 (Fig. 4.2b). We found that -NH₂ modification of graphene is an efficient to enhance the graphene capacitance value due to the introduction of pseudocapacitive interactions and improved wettability. Although NH₂-G has higher N concentration (8.6 %) than that of NG (4.3 %), NG has abundant pyridinic and quaternary N which are confirmed to be helpful enhancing electron transfer and pseudocapacitance generation.[109, 128-130]

However, compared to N doping in graphene network in the form of mostly pyridinic and pyrrolic N, ionizable -NH₂ are supposed to be better facilitators for the growth of polymer. Therefore, NG and NH₂-G should have different effects on polymer growth and pseudocapacitance increment magnitude.

Figure 4. 2 GO, RG, NG and NH₂-G survey scan (a); N1s narrow scan of NH₂-G (b), NG (d); C1s narrow scan of GO and RG (c).

In order to discover the optimal loading weight ratio of PPy in the graphene to achieve highest specific capacitance value, NH₂-G is employed as a model carbon carrier. The weight ratio of PPy to NH₂-G is tuned from 1 to 80% during the synthesis of NH₂-G/PPy composite. The CVs of different NH₂-G supercapacitor electrodes with PPy weight ratio from 1 ~ 80% were carried out at a scan rate of 50 mV s⁻¹ (Fig. 4.3).

We found that 10% weight ratio loading of PPy gives the highest specific capacitance value as compared to that of 1%, 50% and 80% graphene/PPy composite. Therefore, PPy weight ratio of 10% is loaded on to various surface modified graphenes.

Figure 4.3 CVs of $\text{NH}_2\text{-G}$ with various PPy loading weight ratio from 1 to 80% PPy at a scan rate of 50 mVs^{-1} in 6 M KOH as electrolyte. Specific capacitance of $\text{NH}_2\text{-G-1%PPy}$ and 10% PPy calculated from CVs from 5 to 250 mV s^{-1} (b).

Figure 4.4 SEM images of GO-PPy (a), $\text{NH}_2\text{-G-PPy}$ (b), NG-PPy (c), and RG-PPy (d).

The morphology of PPy coated on different graphenes was observed by SEM as shown in Fig. 4.4. All the as-prepared graphene maintained layered structure. As the PPy loading weight ratio is controlled as low as 10 wt% in the composite, therefore, the aggregation of PPy in the composite, and blockage of graphene interlayers is not observed for all the samples. The PPy uniform coating on the surface of different graphenes is supposed to increase the electrochemical reaction sites due to the considerable high surface area given by graphene.

Figure 4. 5 Cyclic voltammetry curves of GO-PPy (a), RG-PPy (b), $\text{NH}_2\text{-G-PPy}$ (c), and NG-PPy (d) with scan rates from 5 to 50 mVs^{-1} in 6 M KOH in black line. The inset red-lined curves show corresponding GO, RG, $\text{NH}_2\text{-G}$, and NG respectively at scan rate of 50 mVs^{-1} .

CV was used to examine the electrochemical performance of supercapacitor electrodes. Fig. 4.5 shows the comparison of the CVs of GO (a), NG (b), $\text{NH}_2\text{-G}$ (c), RG (d), before and after loaded with 10% PPy. All four kinds of graphene show increase of current density (y -axis) after loaded with 10% PPy. GO-PPy has comparable capacitance with that of RG-PPy. CV curves of RG, NG, and $\text{NH}_2\text{-G}$

exhibit rectangular shape and show large under curve integration area, which is a distinctive characteristic for an ideal capacitor with good dynamic charge propagation. The specific capacitances of GO, NG, NH₂-G, RG calculated from the CV at 50 mV s⁻¹ are 6.56, 82.09, 94.73, and 42.90 F g⁻¹, respectively, with 20 mg of graphene composite on nickel foam. NG and NH₂-G show larger capacitance value compared with that of RG, although NG, NH₂-G and RG all have small oxygen content. The specific capacitance of GO-PPy, NG-PPy, NH₂-G-PPy, and RG-PPy measured are 98, 267.38, 116.50 and 93.97 Fg⁻¹, respectively. After loaded with 10 wt% PPy, all the graphene electrodes show improved performance, among which GO and NG show capacitance increment magnitude of about 14 and 3 times.

GO-PPy and RG-PPy has comparable capacitance value, although GO has poor conductivity. The functional groups abundant NG, GO and NH₂-G surface are advantageous for pyrrole monomer adsorption and further polymerization. GO containing O-functional groups which aid in homogeneous coating of polymer, and GO itself might be slightly reduced during the polymerization. Hence, GO-PPy achieved capacitance value of 165.25 F g⁻¹, larger than that of RG-PPy (150.00 F g⁻¹). Although N-containing functional groups on NG and NH₂-G will facilitate the PPy growth, the high conductivity of NG will be advantageous for the charge separation and transportation after loaded with PPy as compared with that of NH₂-G. Therefore, the NG which has both surface functional groups and relative high conductivity are beneficial for PPy growth and more favorable for their corresponding electrochemical application.

Figure 4. 6 Comparison of CVs of GO, NG, NH₂-G, and RGO at a scan rate of 50 mV s⁻¹; and b) charge-discharge curves of GO-PPy and RG-PPy at 0.26 A/g, c) charge-discharge curves of NG-PPy, NH₂-G-PPy at 0.1 A/g, and d) NG-PPy, NH₂-G-PPy at 0.26 A/g.

Fig. 4.6 shows the comparison of electrochemical performance of NG-PPy, NH₂-G-PPy, GO-PPy, and RG-PPy electrodes. The charge-discharge curves of GO-PPy under 0.26 Ag⁻¹ (Fig. 4.6b) have asymmetrical curve shape and low coulomb efficiencies indicating the poor conductivity due to the presence of O-containing functional groups. Although carboxyl, hydroxyl, or even carbonyl functional group are reported to be helpful to generate pseudocapacitance, carbon materials containing these functional groups only demonstrated quasi-reversible redox reactions which slowly decrease after long cycles.[196]

Most of the O-containing groups were removed in RG and the electronic properties of RG is recovered compared with that of GO. However, the reduction of oxygenous functional groups of RG will inevitably induce poor wetting ability, which may hinder pyrrole monomer adsorption, and further leading to the inhomogeneous PPy coating.

In such case, the pseudocapacitive charge produced from PPy and charge transfer efficiency in graphene network will be decreased accordingly. From this aspect, GO with abundant O-containing functional groups can lead to more uniform PPy coating with significantly improved pseudocapacitive charge production efficiency. Fig. 4.6c shows charge-discharge curves of NH₂-G-PPy and NG-PPy electrodes at a current density of 0.1 A g⁻¹. The galvanostatic curves show symmetric triangular shape representing the highly reversible Faradic reactions together with enhanced conductivity as compared with that shown in Fig. 4.6b. The IR drop of NG-PPy (-0.2 V) is much lower than that of GO-PPy or RG-PPy. The superior electrical properties due to N doping and high redox charge generation/transfer efficiency should be ascribed for the superior supercapacitive behavior of NG-PPy. The SEM image of NG-PPy (Fig. 4.4 C) shows that NG retains porous and layered structure after 550 °C thermal annealing and coated with PPy. The specific capacitance of NH₂-G-PPy and NG-PPy are 338.8 and 230.1 F g⁻¹ as calculated from galvanostatic curves under a current density of 0.26 A g⁻¹, which are in good agreements with the values obtained from CV curves.

Fig. 4.7 shows the rate performance of the graphene/PPy electrodes under scan rates from 2 to 50 mVs⁻¹. At a scan rate of 2 mVs⁻¹, NG-PPy electrode has highest capacitance value (393.67 Fg⁻¹), followed by NH₂-G-PPy (225.33 Fg⁻¹), GO-PPy (165.25 Fg⁻¹) and RG-PPy (150.00 Fg⁻¹). Even under a scan rate of 50 mV s⁻¹, the capacitance value of NG-PPy can maintain 267 Fg⁻¹, which further indicates the prospective of NG-PPy as fast energy storage devices.

Figure 4. 7 Specific capacitance of NH₂-G, N-G, RG, GO before (a) and after loaded with 10% PPy at different scan rates from 2 to 50 mV s⁻¹.

Figure 4. 8 Cycling stability of NG-PPy and GO-PPy, with specific capacitance calculated from successive charge-discharge cycles at current density 0.26 A g⁻¹.

Cycling instability is regarded to be one of the most important parameters for currently developed pseudocapacitors. As shown in Fig. 4.8, the capacitance of GO-PPy lost 59% (from 111.3 to 43.9 F g⁻¹) after 540 charging-discharging cycles. However, there is only 10% of capacitance loss for NG-PPy (296.9 to 267.8 F g⁻¹) under same conditions. The degradation of specific capacitance of GO-PPy electrode might be due to the large internal resistance of GO-PPy compared to that of NG-PPy electrode. NG-PPy has highest capacitance value and exceptional cycling performance which endow it a superior candidate as high capacity, cycling stable supercapacitors.

EIS data is used to investigate the electrochemical performance of different electrodes. The complex-plane impedance plots for NG-PPy and NH₂-G-PPy

electrodes with frequency ranging from 0.01 to 100 K Hz at an applied potential of 10 mV are shown in Fig. 4.9. The impedance plot of NG-PPy is nearly perpendicular to real axis, which indicates fast charge-transfer kinetics and the electric responses resembling a circuit with large capacitance and low resistance connected in parallel. However, the as-prepared GO-PPy, RG-PPy, and NH₂-G-PPy show 45 degree phase angle at low frequency, representing the low charge transfer efficiency or ion mobility in these electrode. NG-PPy and NH₂-G-PPy are the best two electrodes, and NH₂-G-PPy shows slightly lower internal resistance than that of NG-PPy. As reported earlier, there are multiple origins for the internal resistance, for example, inter-granular electronic resistance between carbon particles, contact resistance between current collector and electrode material,[197] charge transfer resistance at electrode-electrolyte interface.[160] Superior performance of NG-PPy may be ascribed to the improved electronic properties from introduction of N in NG. NG with high conductivity enhances the charge transfer efficiency from ion doping and dedoping of PPy, which might be responsible for the vertical lined response of Nyquist curve at low frequency. Therefore, NG-PPy has best electrochemical performance among the four electrodes.

Figure 4. 9 Impedance Nyquist plots of NH₂-G-PPy, NG-PPy, GO-PPy, RG-PPy electrodes between 100 kHz and 10 mHz at 10 mV signal level.

Figure. 4.10 CVs of asymmetric capacitor N-RG-O/PPy//N-RG-O cell taken at various scan rates 20-450 mV s^{-1} and (b) Galvanostatic charge/discharge curves taken between 0 and 1.25 V at various constant specific current 0.5 and 1 A g^{-1} in 6 M KOH. Above 8a and b shows the full cell configuration and image of as-prepared supercapacitor cell.

In the two electrode system, the NG-PPy also shows enhanced electrochemical activity superior to that of RG-PPy. The CV of the asymmetric capacitor device is shown in Fig. 4.10a. The hybrid device was cycles between 0 and 1.25 V. The specific capacitance of the full cell device is 44, 39, 31 and 25 Fg^{-1} respectively, at scan rates of 5, 10, 50 and 250 mVs^{-1} . The specific capacitance of NG-PPy electrode is around 179, 158, 124, and 101 Fg^{-1} . The energy density of the device could be as high as 7.2 Wh/kg. We also tried to assemble the RG-PPy//NG supercapacitor devices; however the capacitance of a full cell is less than 20 Fg^{-1} under the same measurement conditions, indicating NG is superior to RG for PPy loading for supercapacitor application.

4.4 Conclusion

The result of our study leads to the understanding of the combined effects of polypyrrole growth and capacitance increment magnitude on carbon/PPy based

supercapacitors. NG-PPy shows best capacitive performance (393.67 Fg^{-1}) compared with $\text{NH}_2\text{-G-PPy}$ (225.33 Fg^{-1}), RG-PPy (150 Fg^{-1}), and GO-PPy (165 Fg^{-1}). Incorporation of conducting polymer and porous carbon species with defined surface chemistry to form hybrid nanomaterials presents an opportunity for the design of novel materials with significantly improved performance as electrochemical supercapacitors. For graphene/PPy composite based supercapacitors, the introducing of nitrogen doping to graphene network is essential to improve graphene electrical properties and facilitate the uniform growth of PPy on graphene both sides. Therefore, largest synergistic effect can be achieved from pseudocapacitance generation in uniform PPy coating layers and improved charge transfer efficiency from nitrogen doping induced excellent conductivity. The N doping induced capacitance improvement effect is also applicable to other graphitic material/conducting polymer composite preparation for promising energy storage applications.

Chapter 5

Active Center Structure of Nitrogen-doped Graphene-based Catalysts for ORR

5.1 Introduction

Fuel cells are considered to be a promising green energy generation technology; however, the high cost of the catalyst, the inherent oxygen crossover from anode to cathode, and sluggish oxygen reduction reaction (ORR) kinetics at the cathode hinder its widespread commercialization.[198, 199] Traditionally, the catalyst cathode consists of Pt nanoparticles supported on carbon with high surface area. Recent investigations of alternative non-noble ORR catalysts include catalysts based on transition metal chalcogenides,[200] N-doped carbon nanomaterials,[201, 202] and N-containing polymer/metal chelates.[203] In the latter case, several reports have found that transition metal itself does not serve as an active site for ORR, but rather facilitates the integration of active N-containing functional groups into graphitic carbons at elevated temperature.[203, 204] Several research groups have reported enhanced ORR activities on N-doped carbon nanomaterials, where pyridinic N at the carbon edge plane help the reduction of oxygen.[205, 206]

Very recently, metal-free N-doped carbons have been reported to exhibit ORR catalytic activities superior to commercial Pt/C catalysts,[105, 106] representing a breakthrough for metal-free, N-containing catalysts and their use in applications such as metal-air batteries and fuel cells. For example, N-doped CNTs display higher catalytic activity than traditional Pt/C due to the existence of pyridinic and pyrrolic N species.[207, 208] N-graphene prepared using a chemical vapor deposition (CVD)

method has shown a high electrocatalytic activity toward ORR, with a limiting current density three times larger than 20 wt% Pt/C; this improvement in ORR activity was attributed to the pyridinic N-abundant structure.[105] Similar conclusions have been reported by other researchers.[108, 209] Pyridinic N, which possesses one lone pair of electrons together with electron donated to the conjugated π bond, facilitates reductive O_2 adsorption and therefore may be catalytic active.[210] We also have used a CVD method to produce N-doped graphene with pyridinic-N as dominant dopant; however, we found the as-prepared N-doped graphene does not show remarkable ORR catalytic ability as previously reported.[211] Therefore, pyridinic N content may not be the key parameter determining the ORR catalytic activity. Wang et al. reported that introducing of N to carbon network would improve its ORR activity, because the electronic density of states near the Fermi level of the N-doped carbon increased.[212] N, especially the graphitic N atoms in the carbon lattice facilitated electron transfer from the carbon electronic bands to the antibonding orbitals of O_2 . [212] Recently, Kim et al. proposed that N-doped edge structures, in particular graphitic N sites, gave the most pronounced ORR activity improvement.[213] In light of these conflicting results, it is therefore reasonable and important to identify the active sites of nonmetal-based ORR catalysts for better understanding of the reduction mechanism.

5.2 Experiment and Characterization

GO was prepared from natural flake graphite powder as introduced in section 2.2. N-doped RG-O was prepared by annealing of G-O powder at temperatures of 550 °C, 850 °C, and 1000 °C under NH_3 , and is henceforth labeled as N-RG-O 550°C, N-RG-O 850 °C, and N-RG-O 1000 °C, respectively. Briefly, 500 mg of G-O powder was put in a tube furnace under flow of 5% NH_3 in Ar (50 sccm) and annealed for one hour after

reaching the desired annealing temperature. The resulting sample was grounded up and washed repeatedly with large amount of distilled water and dried at 60 °C for 24 h.

Boron (B)- and N-doped RG-O (BN-RG-O) preparation: N-RG-O 550°C sample was ground by mortar with H_3BO_3 and annealed at 1000 °C for 1h under flowing Ar (50 sccm). The resulting sample was then post-treated, following the above mentioned steps.

Ppy/RG-O composite preparation: Pyrrole was distilled twice before use. 20 mg of G-O powder was ultrasonically dispersed in 20 mL of DI water and 1.5 mL of 0.1 M pyrrole in methanol was subsequently added dropwisely to the mixture. After 10 min, 0.662 mL of 1 M FeCl_3 was added dropwisely over the course of 10 min. The as-obtained solutions were then treated in the same procedures as introduced in the experiment section of chapter 4. The loading of polypyrrole in the composite was ~ 50wt%, and the total N content in the Ppy/G-O composite was ~ 10.4 wt %. After drying at 60 °C, the resulting product was annealed at 850 °C under Ar protection (50 sccm) for 1 h, and washed by ethanol then DI water for further use. The sample is labeled as Ppy/RG-O.

PANi/RG-O composite preparation: Aniline monomer was distilled twice before use. 20 mg of G-O was ultrasonically dispersed in 20 mL of DI water; 1.54 mL of 0.1 M aniline was then added drop by drop to the mixture on an ice bath with magnetic stirring. After 10 min, 0.676 mL of 0.1 M ammonium persulfate and 1 M LiClO_4 in 1 M H_2SO_4 was added dropwisely over the course of 10 min. The as-obtained solutions were then treated in the same procedures as introduced in the experiment section of chapter 3. The loading of polyaniline was ~70wt%, and the total N content in PANi/G-O composite is ~ 10.5 wt %. After drying at 60 °C, the product was annealed at 850 °C

under Ar protection (50 sccm) for 1 h, and then washed by ethanol then DI water for further use. The sample is labeled as PANi/RG-O.

The as-synthesized materials were characterized by SEM, XPS, BET with the same equipments setup and parameters as shown in chapter 3. All of the electrochemical tests were carried out in a standard three-electrode cell with a Pt plate as the counter electrode. The electrochemical cell was controlled with an Autolab PGSTAT302 electrochemical test system (Eco Chemie, The Netherlands). ORR tests were conducted in an O₂-saturated 0.1 M KOH electrolyte (Ag/AgCl reference electrode) on a rotating-disk electrode system, in which the rotational speed was varied from 100 to 3000 rpm and with scan rate at 10 mV s⁻¹. The electrolyte was bubbled with purified oxygen flow at around 140 sccm for about 30 min before each experiment. The oxygen flow was then kept constant at 140 sccm throughout the whole measurement. The fabrication of working electrode was followed the same procedure in chapter 3. The bare glassy carbon electrode was tested without catalyst casting for comparison. The commercial Pt-loaded carbon catalyst (Pt/C 20% on Vulcan XC-72R, E-TEK division, PeMEAS Fuel Cell Technologies) was also used for comparison.

5.3 Results and Discussion

Figure 5. 1 Schematic diagram for preparation of N doped graphene with different N states. N-RG-O 550, 850, 1000 °C are prepared by annealing of G-O powder at temperatures of 550 °C, 850 °C, and 1000 °C under NH₃. N precursor. PANi/RG-O and Ppy/RG-O are prepared by annealing of PANi/G-O and Ppy/G-O composites at 850 °C.

In order to alter the identities of the N moieties, G-O, together with aniline, pyrrole, and ammonia gas are used as precursors for preparation of N-doped graphene as shown in Fig. 5.1. BN-RG-O is prepared from N-RG-O 550 °C sample, with B covalent bonded with pyridinic N. SEM images of N-RG-O 850 °C and N-RG-O 1000 °C samples are shown in Fig. 5.2. The SEM images show that the morphologies of the N-RG-O 850 °C and N-RG-O 1000 °C samples are similar, but both of them show platelets in crumpled conformations with more edges appearing to be exposed compared with pristine G-O. These edge planes, like stacked pallets, provide appropriate locations for N to incorporate into the graphite matrix.[214] The total

surface area of N-RG-O 850 °C was measured to be 350 m²g⁻¹ by the BET method, larger than that of the freeze-dried G-O specimen which was measured to be 280 m²g⁻¹. Thermal annealing of G-O sheets has been reported to cause significant atomic rearrangement leading to a highly disordered graphene-like structure.[215] SEM images clearly show the wrinkles on graphene layers. Chemical reactivity on or near the wrinkles may be enhanced due to the appearance of mid-gap states which lead to additional strong increase of chemisorption energy.[216] Therefore, the wrinkles and disordered structure along with the increased surface area could facilitate the adsorption of O₂, which would be advantageous for ORR applications.

Figure 5. 2 SEM images of G-O (a), N-RG-O 850 °C (b) and N-RG-O 1000 °C (c).

The XPS broad scan shows the presence of C, N, and O in the N-RG-O and Ppy/RG-O samples, and also confirms that boron was successfully introduced into the BN-RG-O samples. The oxygen content in BN-RG-O after annealing at 1000 °C is higher than that of Ppy/RG-O, N-RG-O 850°C or N-RG-O 1000°C. The high annealing temperature is known to increase the probability for oxygen integration as ether rings and carbonyl groups; therefore, high temperature annealing does not always decrease oxygen content.[215] The relative elemental compositions of the different catalysts were analyzed from XPS spectra. The total surface N content in N-RG-O is around 5.2 ~ 5.6%, lower than that of Ppy/RG-O which is around 6.6%. BN-RG-O has the highest oxygen content among these catalysts (Table 5.1).

Figure 5. 3 XPS survey scan of Ppy/RG-O, PANi/RG-O, BN-RG-O, and N-RG-O samples annealed at various temperatures (a) and boron 1s spectra (b).

Table 5.1 Surface species concentration for various N-containing catalysts summarized by XPS results

	Species concentration (atomic %)		
	C	O	N
BN-RG-O	78.10	13.60	2.91
Ppy/RG-O	86.30	6.10	6.60
PANi/RG-O	84.31	8.33	7.36
N-RG-O 550 °C	84.90	9.70	5.40
N-RG-O 850 °C	89.70	4.70	5.60
N-RG-O 1000 °C	90.10	4.70	5.20

*Hydrogen is not taken into account for the calculation

The deconvoluted high-resolution N1s spectra of N-RG-O, Ppy/RG-O and BN-RG-O are shown in Fig. 5.4. Generally, there are several N-containing functional groups in N-doped carbon which can be identified by the bonding state of the N atom in the composite. These groups include pyridinic N (~ 398.7 eV), pyrrolic N (~ 400.3 eV), quaternary N (~ 401.2 eV), and N-oxides of pyridinic N (~ 402.8 eV).[217, 218] Pyridinic N refers to N atoms at the edges of graphene planes, where each N atom is bonded to two carbon atoms and donates one p-electron to the aromatic π system.[108, 205, 211] Pyrrolic N atoms are incorporated into five-membered heterocyclic rings,

which are bonded to two carbon atoms and contribute two p-electrons to the π system. Quaternary N atoms are incorporated into the graphene layer and substitute carbon atoms within graphene plane. N-oxides of pyridinic N, pyridinic-N⁺-O⁻, are N atoms bonded to two carbon atoms and one oxygen atom. The pyridinic and pyrrolic N are always located at the graphitic edge, whereas quaternary N can be both “edge-N” and “bulk-like-N”.[218]

Figure 5. 4 N 1s spectra of N-RG-O 550°C (a), BN-RG-O (b), N-RG-O 850°C (c), Ppy/RG-O (d), N-RG-O 1000°C (e) and PANi/RG-O (f).

Analysis of the N1s peaks around 398, 400, and 401 eV provides the relative atomic ratios of each type of N species. In order to reveal the chemical states of N in detail, the N1s spectra were decomposed into different peaks according to different

aforementioned chemical states of N. The binding energy and relative composition ratio of N in the different catalysts are summarized in Table 5.2. It is worthwhile to note that the pyridinic N content appears to decrease as the annealing temperature is increased to 1000°C. This is because the pyridinic groups are not thermally stable and they convert to pyrrolic- and graphitic N groups at higher annealing temperatures. The N atomic ratio in Ppy/RG-O before annealing is around 10 %; however, the N atomic ratio remains 6.6% after annealing, which is still higher than in the N-RG-O based catalyst. 84% of the N in Ppy/RG-O is present in the form of pyrrolic-N. No deconvoluted peak at 401 eV can be resolved for Ppy/RG-O annealed at 850 °C, indicating that the pyrrolic-N in Ppy is stable and does not transform to graphitic -N even under high temperature annealing. For the BN-RG-O sample annealed at 1000 °C, 68.43% N atoms are in form of pyridinic N, as most of pyridinic N is covalently bonded with B as determined from analysis of the B1s spectra (Fig. S1). This may prohibit the transformation of pyridinic N to graphitic N as with graphene, although the BN-RG-O samples are annealed under 1000°C. It has been reported that B and N co-doped carbon has improved catalytic activity compared with N-doped carbon.[219-221] The O₂ molecules bind easily to N-B-N complexes at zigzag edges due to the strong inter-atomic attraction between neighbouring B and N atoms. Therefore, N-B-N-dominated zigzag edges could yield improved ORR activity.[219] However, it is important to point out that, in this study, B does not replace C but instead covalently bonds with one pyridinic N.

Table 5.2 Detailed breakdown of N1s spectra from Ppy/RG-O and BN-RG-O and N-RG-O samples under different annealing temperatures from XPS analysis, indicating peak position and relative atomic ratios of N species.

N species	N-RG-O 550°C		N-RG-O 850 °C		N-RG-O 1000 °C	
	Peak position/ eV	% N	Peak position/ eV	% N	Peak position/ eV	% N
Pyridinic	398.1	3.48	397.9	4.03	398.1	0.96
Pyrrolic	400.3	1.29	399.4	0.38	399.5	2.76
Quaternary	401.5	0.63	400.9	0.98	401.1	1.12
Pyridine oxide	-----	-----	402.6	0.21	403.6	0.36
N species	BN-RG-O		Ppy/RG-O		PANi/RG-O	
	Peak position/ eV	% N	Peak position/ eV	% N	Peak position/ eV	% N
Pyridinic	398.1	1.99	397.4~ 399.4	2.94	398.4, 399.2	3.58
Pyrrolic	399.2	0.49	400.2	3.66	400.4	3.29
Quaternary	401.1	0.34	-----	-----	401.4	0.49
Pyridine oxide	403.3	0.09	-----	-----	-----	-----

*Hydrogen is not taken into account for the calculation

Although there are reports that the introduction of N doping can effectively improve the ORR catalytic activity of carbon,[105, 106] the identity and role of the electrocatalytically active centres are still controversial as its contribution to catalytic activity is not well defined. Pyridinic-N modifies the band structure of carbon by raising the density of π states near the Fermi level and lowering the work function. However, pyridinic-N is not an effective promoter for ORR activity of carbon, as evidenced by the sluggish ORR activity as reported in our previous study on N-doped CVD grown graphene.[211] Meanwhile, the relative electronegativity of graphitic N atoms reduce the electron density on the adjacent C nuclei, which help electrons transfer from the adjacent C to N atoms, and N backdonates electrons to adjacent C p_z orbitals.[222] The donation and backdonation processes not only facilitate O_2 dissociation on the adjacent C atoms, but also helps forming a strong chemical bond between O and C.[222] For example, surprisingly high ORR activity has been achieved with only 2.8% N content on N-RG-O, from which the authors claimed that quaternary-type N species played the most important role in ORR activity.[106]

Figure 5. 5 (a) Linear sweep voltammograms for N-RG-O 1000°C, bare GC electrode, PANi/RG-O Ppy/RG-O, BN-RG-O, bare Pt electrode and 20% Pt/C electrodes in O₂ saturated 0.1 M KOH (scan rate: 10 mV s⁻¹, rotation rate 2500 rpm).

We acquired rotating disk electrode voltammograms to investigate the electrocatalytic properties of N-RG-O, PANi/RG-O, and Ppy/RG-O in comparison with bare glassy carbon and commercial 20% Pt/C catalysts. Fig. 5.5 shows the linear voltammetric (Lv) scans of different catalysts in an O₂-saturated 0.1 M KOH electrolyte with a rotation rate of 2500 rpm. In terms of limiting current density, the highest value was obtained on N-RG-O 1000 °C, followed by bare Pt, PANi/RG-O, Ppy/RG-O, BN-RG-O, and bare glassy carbon, but still lower than that of 20% Pt/C. The Lv curves of different catalysts under various electrode rotating rates ranging from 100 to 3000 rpm, along with their corresponding ORR performance in the diffusion and kinetically limited regions, were evaluated using Koutecky-Levich (K-L) plots as shown in Fig. 5.6 and 5.7. The K-L plot presents a linear relationship between the reciprocal of measured current density (j), kinetic current density (j_k), and reciprocal of the square root of rotation speed (ω) as following:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l^{\text{diff}}} \quad \text{eq. 5.1}$$

where j_k is the kinetic current density and $j_l^{\text{diff}} = B\omega^{1/2}$ is the limiting diffusion current density, B is the Levich constant, and ω is the rotation rate of electrode.

Figure 5.6 Linear sweep voltammograms and Koutecky-Levich plots for N-RG-O550 °C (a and b) 850°C (c and d) , and 1000 °C (e and f) with rotation rate from 100 to 3000 rpm in 0.1 M KOH.

Figure 5.7 Linear sweep voltammograms and K-L plots for BN-RG-O550 °C (a and b) PANi-RG-O (c and d), and PPy-RG-O (e and f) with rotation rate from 100 to 3000 rpm in 0.1 M KOH.

As seen from Fig. 5.6 and 5.7, all of the K-L plots of rotating disk electrode curves from different catalysts show a linear relationship between $1/j$ and $\omega^{-1/2}$ at a potential of -0.95 V. Furthermore, the Levich slopes show minor variations at applied potentials for all the samples, which is an indication of first order ORR kinetics with respect to the concentration of dissolved O_2 . [223, 224] By extrapolation of the K-L line to the

origin of the plot, or as ω approaches ∞ , the y -intercept yields the kinetic current density, while the x -intercept indicates catalytic activity towards ORR.[217]

The number of electrons transferred for each oxygen molecule can be calculated from Levich constant via the following equation:

$$B = 0.62 n F D^{2/3} \nu^{-1/6} C_o \quad \text{eq. 5.2}$$

where F (Faradic constant) = 96486 C mol^{-1} , D is the diffusion coefficient of O_2 in the electrolyte ($1.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) in 0.1 M KOH , ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), C_o is the concentration of oxygen ($1.21 \times 10^{-6} \text{ mol L}^{-1}$), n is the number of exchanged electrons per oxygen molecule.

According to eq. 5.1 and 5.2, the number of electrons transferred (n) and j_K can be obtained from the slope and the intercept of the K-L plots. The number of electrons transferred in the ORR process for the N-RG-O 550°C , N-RG-O 850°C , and N-RG-O 1000°C samples are 3.14, 3.01, and 2.85, respectively, while the electron transfer numbers in 20% Pt/C, BN-RG-O, PANi/RG-O and Ppy/RG-O are 3.98, 3.45, 2.96 and 2.93 respectively. For N-RG-O prepared from annealing under NH_3 , the limiting current densities are much larger than those prepared from annealing of graphene/N-containing polymer composites. Increasing the N-RG-O annealing temperature will raise the limiting current density, but it shifts the ORR to a $2e^-$ mechanism. The primary difference between the N-RG-O 550°C , N-RG-O 850°C , and N-RG-O 1000°C samples are the different types of N species present. N-RG-O 1000°C contains more graphitic N than N-RG-O 550°C and N-RG-O 850°C , while N-RG-O 850°C has a higher pyridinic N component than N-RG-O 550°C and N-RG-O 1000°C . The N-RG-O 1000°C sample exhibited largest limiting current density (Fig. 5.6), as well as the largest graphitic N component with an atomic ratio of 1.08% (Table 5.2). Ppy/RG-O and PANi/RG-O have comparable ORR activities, relative limiting current density

and onset potential. However, from voltages of -0.15 to -0.9 V, the kinetic current density of PANi/RG-O is larger than that of Ppy/RG-O. The N-doping state of Ppy/RG-O is dominated by pyrrolic N with atomic percentage of 3.66 %, while pyridinic N is the primary N bonding state in PANi/RG-O with atomic percentage of 3.58% (Table 5.2). One reasonable interpretation is that pyridinic N is more catalytically active than pyrrolic N during the ORR process. The ORR activity of BN-RG-O is lower than that of PANi/RG-O and Ppy/RG-O as seen from the smaller kinetic current density over the voltage range of -0.2 to -0.9 V. B-N co-doped carbon in a N-B-N complex at zigzag edges should give improved ORR activity.[219] However, in this study, B does not replace C but rather covalently bonds with pyridinic-N atoms, which prohibits the transformation of pyridinic N to graphitic N due to the covalent bonding of B to N. In this case, even though the BN-RG-O sample is annealed at 1000 °C, the graphitic N content is still low with an atomic percentage of 0.34%. Comparing the RDE curves of BN-RG-O with N-RG-O 1000 °C, it is reasonable to conclude that the graphitic N-abundant N-RG-O is more catalytic active with higher limiting current density than pyridinic N-dominated BN-RG-O.

Graphitic N atoms have been reported to serve as ORR catalytic sites both experimentally and theoretically due to the reduced adsorption energy.[213, 218, 225] Kim et al. found that graphene edge structures would become more catalytically active after introduction of graphitic N; furthermore, such structures would not only enhance the first electron transfer rate, but also preference for the 4e⁻ reduction pathway.[213] The graphitic N at graphene edge may catalyze ORR through a ring-opening of the cyclic C–N bond, which results in the formation of pyridinic N.[211, 217] However, as a marker of edge plane exposure, pyridinic N and pyrrolic N are always located at edge sites, which is chemically active itself.[218, 226] Thus, it is uncertain as to

whether or not the pyridinic or pyrrolic N provide actual active sites for promoting ORR, or whether the reaction is simply more favorable due to the abundance of highly active edges and/or defect sites.[218, 227] Comparing a series of as-prepared catalysts shows that the graphitic N-dominated catalysts have higher catalytic activity with larger limiting current density than that of pyrrolic or pyridinic N-dominated N-containing catalyst.

Figure 5. 8 (a) Koutecky-Levich plots for BN-RG-O, PANi/RG-O, PPy/RG-O, N-RG-O 550°C, N-RG-O 850°C, N-RG-O 1000°C and commercial 20% Pt/C in 0.1 M KOH at -0.95 V vs. Ag/AgCl. (b) The number of electrons transferred per O₂ molecule at different potentials based on Koutecky-Levich equation for N-RG-O and PANi/RG-O.

The enhancement of ORR performance should be ascribed to the increased electron density and electron donating properties resulting from the valence electrons donated by the N dopant. Pyridinic N could reduce the adsorption energy of O₂,[210] whereas graphitic N is capable of electroreduction of O₂ to H₂O₂ via adsorbed OOH intermediates through a 2e⁻ way.[228] The electron transfer number as calculated from K-L curves also shows N-RG-O 1000 °C is 2.85 per O₂ molecular. It is also worthwhile to note that, although N-RG-O 1000 °C has a larger portion of graphitic N atoms compared with N-RG-O 850 °C or N-RG-O 550 °C, the onset potential of N-RG-O 1000 °C is much smaller than that of N-RG-O 850 °C and N-RG-O 550 °C, while the slope of N-RG-O 1000 °C K-L curves indicates the reduced derivation in

number of electrons transferred per O₂ molecule. This further confirms that N-RG-O 850 °C and N-RG-O 550 °C samples, with an abundance of pyridinic-N species, tends to drive ORR through a 4e⁻ mechanism, while N-RG-O 1000 °C gives the highest limiting current density. Although PANi/RG-O and Ppy/RG-O has highest N atomic ratio, they show even worse catalytic activity than that of as-prepared N-RG-O based catalyst. This phenomenon indicates the total atomic content of N in the metal-free, graphene-based catalyst did not play a role in the ORR process.

5.5 Conclusion

N-doped graphene is a promising material for the use as an ORR catalyst, but a deeper understanding of the relationship between the type and concentration of N species and catalyst activity is missing. In this study, we prepared N-doped RG-O by annealing of G-O under ammonia and found that this material tends to show superior ORR catalytic performance to catalysts produced by annealing of G-O with N containing polymer composites, maybe due to the considerable content of both pyridinic N and graphitic N. Annealing of PANi/RG-O and Ppy/RG-O give products containing predominately pyridinic N and pyrrolic N species, respectively. Most importantly, the electrocatalytic activity of N-containing metal-free catalysts is highly dependent on the graphitic N content while pyridinic N species improve the onset potential for ORR. However, the total atomic content of N in the metal-free, graphene-based catalyst did not play a role in the ORR process. Graphitic N can greatly increase the limiting current density; while pyridinic N species might convert the ORR reaction mechanism from 2e⁻ dominated process to 4e⁻ dominated process.

Chapter 6

Active Center and Catalytic Mechanism of Graphene-Supported Non-precious Metal Electrocatalysts

6.1 Introduction

A growing research effort is focused on non-precious metal oxygen reduction reaction (ORR) catalysts for fuel cells to replace Pt catalysts, with the aim of optimizing fuel cell performance and reducing fabrication cost. To date, research on non-precious metal ORR catalysts has focused on pyrolyzed transition metal/N-containing ‘Me-N-C’ complexes (Me=Fe, Co or their alloys).[229] Many efforts have been devoted to the investigation of the electrocatalytic active center for ORR of non-precious metal catalysts.[201] But the composition of Me-N-C catalytic sites remains a point of controversy, and the mechanism of ORR at these sites is uncertain.[230]

The presence of N has been deemed a critical factor in the formation of catalytically active sites,[203, 231, 232] while the transition metal is said to simply catalyze the stable incorporation of N.[231] Therefore, one possible approach to increase the active site density in Me-N-C catalysts is through the use of N-doped carbon.[232, 233] However, some researchers believe that N-stabilized metal cores are the source of ORR activity, which they claim is related to the metal redox potential $\text{Me(II)} / \text{Me(III)}$.[226, 232, 234, 235] their work suggests that the increase of metal loading could lead to improved catalytic activity.[236] Thus, elucidation of the mechanism of the non-precious metal based ORR would be an important advance for the field. Furthermore, understanding of the relationship between Me, N, and O_2 would help the design of ORR catalysts for fuel cells.

Several recent studies have focused on the N-doped graphene-catalyzed ORR in alkaline electrolytes, and high ORR activities have been reported.[105, 237] However, development of such catalysts for acidic environments has hitherto remained a challenge. In this work, we describe a simple but effective chemical method to prepare a transition metal nitride (MeN) / N-modified graphene (N-G) composite from graphene oxide (G-O). These MeN-N-G composites show considerably higher ORR catalytic activity in acidic electrolytes than MeN-N-C, where C represents active carbon or graphite. In this study, we also investigated the ORR mechanism and the nature of the active centre of the FeCoN-N-G catalyst by ultraviolet photoemission spectroscopy (UPS).

6.2 Experiment and Characterization

Preparation of Fe-N-G catalysts: 400 mg of iron acetate was fully dissolved in 125 mL of ethanol before adding 2 mL of ethylenediamine (ED). The solution was stirred for half an hour to form a Fe-ED complex. G-O (0.25 g) was separately dispersed in 125 mL of ethanol and then added to the Fe-ED complex solution. The combined solution was then refluxed for an hour under ambient condition. The remaining dried precipitate was ground down and pyrolyzed at several temperatures between 550 and 1050 °C for an hour under flowing Ar (40 sccm). The sample was then ground further and treated with 2 M H₂SO₄ at 50 °C for 8 h before being filtered, washed with 1 L of deionized water and oven-dried overnight at 80 °C.

Preparation of FeCo-N-G catalysts: Iron acetate and cobalt (II) nitrate, at various Fe:Co molar ratios, were fully dissolved in 125 mL of ethanol before adding 2 mL of ED. This solution was stirred for half an hour, forming a FeCo-ED complex. GO (0.25 g) was then dispersed in 125 mL of ethanol and added to the FeCo-ED complex solution. The combined solution was then refluxed for an hour under ambient pressure.

The remaining dried precipitate was ground and pyrolyzed at a temperature between 550 and 1050 °C for an hour under flowing Ar (40 sccm). The sample was then grounded further and treated with 2 M H₂SO₄ at 50°C for 8 h before being filtered, washed with 1 L of deionized water and oven-dried overnight at 80 °C.

The as-synthesized materials were characterized by SEM, XPS, BET with the same equipments setup and parameters as shown in chapter 3. Raman spectroscopy was performed on a WITEC CRM200 Raman system with an excitation source of 532 nm laser (2.33 eV) with a laser power below 1 mW. UPS studies of the Fe-N-G and FeCo-N-G were performed on an ESCALAB 250 (Thermo VG Scientific) instrument, using monochromatic Al K α ($h\nu$ =1486.6 eV) as the X-ray source and He I (21.2 eV)/He II (40.8 eV) as the UV light sources. The elemental composition of the catalysts was analyzed on an inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Vista-MPX CCD Simultaneous ICP-OES). The individual catalysts for the analysis were digested using aqua regia and 10 μ L was collected and kept in 2 mL of 2% HNO₃.

The deposition of catalyst to glassy carbon electrode for the measurement of linear voltammetry curves are the same as mentioned in the experimental section of chapter 5. To assemble a full cell, FeCo-N-G (7 mg catalyst cm⁻²) and Pt (0.5 mg Pt cm⁻²) were used as the cathode and anode catalyst, respectively, while Nafion 112 was used as the membrane. The polarization curves were obtained under H₂ (200 sccm) and O₂ (200 sccm) flow for the anode and cathode respectively, with a cell temperature of 80 °C and back pressure of 0.2 MPa.

6.3 Results and Discussion

In this work, G-O and ethylenediamine were used as the carbon precursor and the N source, respectively. The catalysts were obtained by impregnation of G-O/ethanol

suspensions with an ethanol solution of metal ion precursor and ethylenediamine. 2 M H_2SO_4 is used to soak the MeN-G catalyst to remove elemental metal and metal oxides. Compared with as-prepared G-O, the FeCo-N-G catalyst has FeCoN particles homogeneously distributed, with an average particle size of roughly 20 nm (Fig 6.1 a and b). The XRD patterns of the FeCo-N-G catalyst prepared at different annealing temperatures, with that of dried-down G-O platelets as a reference is shown in Figure 1c. The FeCoN-N-G samples show new bands at 26.4 ± 0.4 and $\sim 44.8 \pm 0.4^\circ$, corresponding to the (002) faces of reduced G-O and the (220) faces of Fe_{16}N_2 , [238] respectively. New bands at 26 and 45° , corresponding to the (002) faces of reduced G-O and metal nitrides species, respectively. Iron could form various stable nitrides, such as Fe_2N , Fe_3N , Fe_4N , and Fe_{16}N_2 , which are crystalline, metallic solids. According to phase diagrams of Fe-N and Fe-C, [239] N can dissolve rapidly into iron at $\sim 590^\circ\text{C}$ while dissolution into carbon occurs at higher temperatures ($\sim 740^\circ\text{C}$). [240] Therefore, pyrolysis at 750°C allows stable N-deficient metal nitrides such as Fe_{16}N_2 to form. Co nitrides (such as CoN , Co_2N , Co_3N , Co_4N and Co_3N_2) also have major diffraction peaks in the 2θ region between 40 and 45 degrees. [241] Hence, the formation of FeN and/or CoN in the catalyst is desirable. HRTEM images of the sample show metal-containing particles encapsulated in graphitic nanoshells, with lattice spacing between the (002) basal planes around 0.37 nm, larger than that of pure graphite (~ 0.335 nm [242]) and rG-O (~ 0.35 nm [243]). The expanded layer distance of the carbon shells may be a result of the incorporation of N, [244] which may increase the number of active sites, and enhance the corrosion resistance of the Me-N-C catalysts. The interplanar distance within the nanoparticles in Figure 1e was measured to be ~ 0.20 nm, which corresponds to a N-deficient metal nitride such as Fe_8N whose interplanar distance in the (110) direction is 0.2 nm.

Figure 6.1 SEM images of (a) G-O and (b) FeCoN-N-G 750 °C. XRD pattern of FeCoN-N-G prepared by annealing of FeCoN-N-G under different temperatures ranging from 550 to 1050 °C, compared with dried-down G-O (c). High-resolution transmission electron microscope images reveal the graphitic shells of the catalysts (d-f).

Raman spectra of FeCo-N-G samples prepared at different temperatures are compared in Fig. 6.2. The strong peaks at 1380 and 1550 cm^{-1} can be assigned to D and G bands of RG-O, corresponding to the defect-related intervalley double-resonance mode and the in-plane vibrational mode (E_{2g} phonon at the Brillouin zone center), respectively.[21, 22] A larger I_G/I_D ratio indicates higher graphitization, or lower defect density. The I_G/I_D ratio clearly shows an increase with annealing temperature in Fig. 6.2, suggesting that the graphitic network is restored at higher temperatures. At 1050 °C, the 2D (or G') band at 2650 cm^{-1} is clearly noticeable, indicating recovery of the characteristic graphene structure by high temperature treatment.

Figure 6.2 Raman spectra of FeCo-N-G prepared in different annealing temperatures from 500 to 1050 °C.

UPS He I spectra of FeCo-N-G samples with different pyrolysis temperatures (550, 750 and 1050 °C) are shown in Fig. 6.3a. Transition metal nitrides all show re-hybridization of metal 3d and N 2p orbitals in the valence band, with the N 2p peak located around 5 eV below the Fermi level.[245] The FeCo-N-G 750 °C sample shows the highest intensity at around 5 eV below the Fermi level, which is indicative of MeN formation and the high concentration of N in the FeCo-N-G 750 °C sample. The spectral difference of curves 2 and 1 in Fig. 6.3a signifies the intensity increment in the region of 3.5 to 7 eV and the decay between 6 and 9 eV. These changes can be seen in He II spectra even more clearly. For the N-modified reduced G-O, the bands located at 3 and 5 eV below Fermi level are attributed to C 2p π and localized N lone pair electrons [211] respectively, while the band located at 9.5 eV is attributed to C 2p and N 2p electrons sharing in σ bonding.[246] Compared with FeCo-N-G-550 °C, the intensity of the C-N 2p π at 9.5 eV is significantly weakened while the nitride N 2p at 5 eV becomes extremely strong in FeCo-N-G 750 °C. UPS results strongly suggest that the primary contribution to the valence band of FeCo-N-G 750 °C is from nitride

and/or pyridinic N species, while the contribution of metal (Fe and Co) 3d electrons to the valence band (near the Fermi level) is not clearly observable.

At high pyrolysis temperatures (1050 °C), the metal nitrides were not stable, resulting in the weak UPS signals. Therefore, the pyridinic N and nitride ratio in the catalysts increased with increasing pyrolysis temperature from 550 to 750 °C, while the total N weight ratio decreased with a further increase of temperature from 750 to 1050 °C. The XPS spectrum together with the curve fitting, shown in Fig. 6.3 c and d, reveals the presence of N with well fitted peaks at 398.3, 399.0, 400.4 and 401.4 eV, corresponding to iron nitrides (398.1 eV), [245, 247] pyridinic N,[248] pyrrole-like N, and quaternary N. The ratio of N in the form of nitrides to total N content is around 21.6%, corresponding to 1.0 at% or 10 wt% metal nitride species in the FeCo-N-G 750°C, which agrees well with the results obtained from ICP-AES analysis.

Figure 6. 3 Relative variation of (a) He I and(b) He II UPS spectra of FeCoN-N-G 550 °C (1), FeCoN-N-G 750 °C (2), FeCoN-N-G 1050 °C (3) and difference spectrum of (2-1) in (a). High-resolution XPS spectra of (c) C 1s and (d) N 1s of FeCoN-N-G 750 °C.

For the ORR measurements, the as-prepared catalyst was transferred onto a glassy carbon electrode. The rotary disc electrode (RDE) voltammograms of ORR curves of

the FeCo-N-G-750°C sample were obtained at different rotating rates. The peak in the current (used to gauge relative activity) came about as oxygen both within the sample and in the vicinity of the sample surface was reduced to H₂O, with the current then becoming limited by the diffusion of oxygen through the solution to the catalyst surface. As the rotation rate of the electrode increases, the mass transfer of oxygen to the sample increases, thus increasing the mass transfer-limited current. The RDE curves in Fig. 6.4 were further analyzed using the Koutechy-Levich (K-L) equation. The number of electrons transferred per O₂ molecule on FeCo-N-G 750°C is calculated to be 3.8, indicating O₂ goes through a 4e⁻ reduction pathway which forms H₂O as the main product. All of the polarization curves of the FeCo-N-G samples exhibited the characteristic S-shape of RDE measurements, with no defined diffusion plateau. The curves are well-separated, suggesting that the ORR activity of FeCo-N-G is strongly dependent on the heat treatment temperature. The performance trend of FeCo-N-G with pyrolysis temperature is: 750 °C > 950 °C > 1050. FeCo-N-G 750 °C shows substantially higher activity toward ORR compared to the other samples, indicating the optimum temperature for formation of the FeCo-N-G based catalyst is thus about 750 °C. This sample had a high onset potential (E_{ORR} = 0.9 V versus less than 0.6 V for samples annealed at other temperatures) and a considerably higher half-wave potential (0.5 V for the 750 °C sample, compared with 0.3 V for the 950 °C samples and 0.25 V for the 550 °C sample). The effect of the Fe to Co weight ratio is not as dramatic as the effect of the pyrolysis temperature.

In the FeCo-N-G-750 °C system, the primary contribution to the valence electrons comes from pyridinic N atoms which are bonded to metal nitrides (based on UPS data). Thus the active center for O₂ adsorption should involve nitride species which donate electron density to the partially occupied O₂ π^* orbital, thus weakening the O-

O bond. The metal atom bonded to the nitride species has transferred its 3d electrons to the nitride species and thereby enhanced oxygen activation. Simultaneously, the metal accepts π bonding electrons from O_2 , weakening the O-O bond. It is well-known that the rate-determining steps in $4e^-$ ORR involve both the dissociative adsorption of O_2 [249] and the subsequent formation of OH^- . [250] Pt is the best catalyst for ORR because the Pt 5d band is centered at 2.5 eV and spans the energy region between 0 and 6 eV. Thus, O_2 can be effectively activated by Pt via π electron donation and π^* back-donation, while Pt-O bonding is weak and allows facile interconversion to OH^- . In the FeCo-N-G-750 °C system with abundant nitride species, the valence band is centered at 5 eV and spans the 3 to 9 eV region; hence, the adsorption and activation of O_2 can be achieved. The metal (Fe and/or Co) can provide electrons (*via* nitride formation) and accept oxygen ions to avoid the blockage of nitride species, i.e., the active site, allowing the $4e^-$ ORR to proceed efficiently. N, especially pyridinic N, is crucial for the promotion of the electrocatalytic reaction in ORR, [251] while the metal that donates electrons to the N enhances catalytic activity. The synergistic effects between the metal and N cause ORR to proceed through $4e^-$ transfer. The optimal annealing temperature of 750 °C is crucial for production of pyridinic N-bonded metal, as less N atoms are coupled to the metal at lower temperatures; [236] the thermally unstable metal-N complexes decompose at higher temperatures to form N_2 and metal. [230] The FeN and FeCo-N loading ratio, which is regarded as an important parameter in tuning the ORR activity, [236] [230] was studied to evaluate its impact on the electrocatalytic performance. FeCo-N-G catalyst was found to be more catalytically active than the FeN-G.

Figure 6.4 RDE curves (a) and K-L plots (inset) for oxygen reduction of FeCo-N-G 750 °C at various rotation rates. (b) RDE curves for oxygen reduction on a FeCo-N-G prepared by annealing of FeCo-N-G between 550 to 1050 °C (rotation rate: 1000 rpm). (c) RDE curves for oxygen reduction performance of FeCo-N-based catalysts on different carbon carrier, after annealed at 750 °C (rotation rates: 2500 rpm), as compared with that of bare Pt electrode. (d) Polarization and power density curves of membrane electrode assembly cell (MEA) with FeCo-N-G as the cathode catalyst, and 20% Pt/C as anode.

A membrane electrode assembly cell (MEA) was fabricated with FeCo-N-G-750 °C as cathode catalyst, and 20 wt% Pt/C as the anode catalyst, respectively. This cell gives the maximum power density of 130 mW cm⁻² at a cell voltage of 0.25 V and a current density of 0.53 A cm⁻² (Fig. 6.4d). Although the catalytic activity of the FeCo-N-G-750 °C system is lower than the maximum power density previously reported for a 10 wt% Pt commercial catalyst (0.31 Wcm⁻²),[252] it is two times that reported for Fe-N-based catalysts (0.07 Wcm⁻²).[201] The performance of FeCo-N-G-based MEA cells might be further improved by controlling the loading efficiency, reaction temperature, catalyst composition, and electrode preparation method.

It is often claimed that carbons with a high surface area[108, 253] and high electrical conductivity[108, 231] are important for increasing the catalytic site density for improving ORR catalyst performance. The BET surface area of some activated carbons is much higher than that of G-O, and graphite has good conductivity properties due to electron delocalization within the carbon layers. Even after loading with FeCo-N, the BET specific surface area of activated carbon was $171.1 \text{ m}^2 \text{ g}^{-1}$, higher than that of FeCo-N-G ($54.3 \text{ m}^2 \text{ g}^{-1}$) and FeCo-N-graphite ($16.8 \text{ m}^2 \text{ g}^{-1}$). Compared with FeCo-N-graphite and FeCo-N-activated carbon, the half-wave and onset potentials of FeCo-N-G were shifted to the positive side indicating better electrocatalytic activity. Therefore, FeCo-N-G has superior ORR activity among the three kinds of catalysts, indicating the surface area and conductivity of the carbon support are not the most critical factors in ORR catalyst performance. Compared with graphite or active carbon,[232] the basal plane of G-O can be easily doped with N atoms during annealing as a result of its disordered structure. G-O also has abundant surface functional groups distributed on both sides of the sheet that serve as anchoring sites for metal complexes and yield homogeneous distribution and control of catalyst sites. After pyrolysis at suitably high temperatures ($\sim 750^\circ\text{C}$), the N atoms are incorporated into the carbon network as pyridinic or pyrrolic N, while the pyridinic N coordinated with the metal nitride particles acts as the catalytically active site for ORR.

Figure. 6.5 Schematic of the active centre and electron transfer process for electrochemical reduction of oxygen on Me-N-G.

Regarding the present system, a suggested model of the active center for electrochemical reduction of O₂ on Me-N-G is illustrated in Fig. 6.5, consisting of pyridinic N and metal atoms. The activation and reduction process of O₂ is the filling of half-filled or emptying antibonding orbitals of O₂ with the electrons donated from the catalyst. This results in a weakening or breaking of the O-O bond and formation of H₂O₂ (2e⁻ path) or H₂O (4e⁻ path), respectively. The electrocatalytic activity of N-containing graphite-based materials for ORR is dependent on the presence of pyridinic N, which sits on the shell of carbon and donates electrons to the anti-bonding orbitals of O₂, as illustrated in ① in Fig. 6.5. The back-donation of electrons from O₂ to the transition metal d vacancies weakens the O-O bond further, and facilitates cleavage of the O-O bond as shown in ②. Furthermore, the metal center transfers its electrons to the pyridinic N atoms through 3d-2p hybridization (as indicated in ③, promoting the adsorption of O₂. Therefore, the presence of transition metal atoms is also essential.

6.5 Conclusion

In summary, a FeCoN catalyst was synthesized and loaded onto a material comprised of reduced graphene oxide platelets in a one-step pyrolysis process, as a composite material for ORR in a fuel cell. The ORR mechanism and the nature of the active center could be rationalized based on the UPS data. We propose that pyridinic N serves as the active center and donates its electrons to the anti-bonding orbitals of O₂. The metal core not only accepts back-donation of electrons from O₂, facilitating the cleavage of the O-O bond, but it also transfers its electrons to the pyridinic N. Our data suggest that non-precious metal catalysts can be effective for ORR.

Chapter 7

Transition Metal Nitride/oxide Based Anode Materials for Li-ion Battery

7.1 Transition Metal Nitride/rG-O Based Anode

7.1.1 Introduction

Among various energy conversion / storage system proposed over the two last centuries, electrochemical storage, or more specifically battery exhibiting improved energy densities and lifetimes, is very promising. At the same time, research aiming to meet commercial implementation requirements is still in imperious need. Graphite is the widely used anode material in lithium-ion batteries with superb cycle performance. However, the theoretical specific capacity of graphite is only 372mAh g^{-1} (LiC_6). [26] Metal and semimetals can electrochemically form alloys with lithium with large capacity achieved from alloying reactions ($\text{Sn} + 4.4\text{Li} \rightarrow \text{Li}_{4.4}\text{Sn}$). However, the large volume change associated to the dealloying process introduces large strain in metal, which subsequently causes the structural deformation, and capacity loss. Metal oxides, such as Co_3O_4 , [254, 255] SnO_2 [256, 257] and Fe_xO_y , [258, 259] which have been intensively investigated as anode for Li-ion batteries, can reversibly react with Li through conversion reaction (eg., $\text{Fe}_2\text{O}_3 + 6\text{Li} \rightarrow 2\text{Fe} + 3\text{Li}_2\text{O}$) which give capacity value two or three times larger than that of graphite. However, the practical utilization of these materials needs to apply carbon coating, carbon additives or reduce the size of metal oxides to nano scale in order to reduce the capacity loss from structural deformation during cycling. This structural and component control of metal oxides composite would somewhat alleviate the capacity loss during cycling, but are still far from satisfying. Metal nitrides have low and flat potentials close to Li metal, with large reversible capacities and high reversibility. There has been great interest in

exploration of twofold metal nitrides as superior materials, such as Sn_3N_4 , CrN , VN , [260] Mn_3N_2 , [261] NiN , [262] etc. Metal nitrides also exhibit excellent properties of high melting point and chemically inert behaviour. It is therefore advantageous for anode or cathode materials to be protected from moist or erosive environments. [263] Lithinated transition metal nitrides, such as LiMnN_2 , [264] $\text{Li}_{3-x}\text{M}_x\text{N}$ ($\text{M}=\text{Co}, \text{Ni}$), [265] $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ [266] has been found to be the most promising negative electrodes, [265] with reversible capacity between 400 and 760 mAhg^{-1} . There have been several reports concerning the preparation and application of transition metal nitrides in the past few years, in which magnetron sputtering is one commonly used method. [267-269] Nitrogen gas is used as the metal nitridation source. However, due to the inert nature of N_2 , the reaction is costly and not suitable for large-scale preparation.

Graphene, a monolayer of carbon has attracted numerous interests from fundamental research to practical applications due to its fascinating electrical properties, high surface area, chemical tolerance and a broad electrochemical window. [63, 270] It is found that the theoretical specific Li inversion capacity for graphene is 744 mAhg^{-1} , corresponding to the formation of LiC_3 . [38] However, graphene based all-carbon materials are reported to suffer from a large capacity fade, low initial columbic efficiency, low first charge efficiency, despite a large initial discharge capacity when investigated as an anode for lithium ion batteries. Recently, it is reported that N-doping is effective to improve the cycling stability and specific capacity of graphene. In this chapter, I will introduce my work on investigating transition metal nitride and metal oxide/nitrogen doped graphene as Li-ion battery anode, and their electrochemical performance.

7.1.2 Experiment and Characterization

Preparation of Fe₂O₃-rG-O: 500 mg of GO powder is put into a quartz tube and thermal exfoliated in 500°C under Ar protection for 1h. 200 mg of rG-O is dispersed in 50 mL of DI water with 1 mL of Na₂SO₄ and 1 mL of 0.5 M FeCl₃. The resultant suspension is ultrasonicated for 10 min before reflux at 160 °C for 2h. After cooling and washed by filtration with 1 L of DI water, the black solid is dried and annealed at 350°C for 3h. FeN-rG-O and FeCoN-rG-O were prepared following the procedure as-introduced in section 6.2.

The as-synthesized materials were characterized by SEM, XRD, XPS, BET with the same equipments setup and parameters, as shown in chapter 2 and 3.

Electrochemical measurements: For electrochemical measurements, the cells were constructed by using as-prepared metal nitrides as a working electrode and lithium metal at a counter electrode. The working electrodes were prepared by mixing 80 wt % active material, 10 wt % acetylene black (Super-P), and 10 wt % polyvinylidene fluoride (PVDF, 5 wt %) binder dissolved in N-methyl-2-pyrrolidinone. The slurries was then coated on Cu foils, and dried at 110 °C in vacuum remove the solvent before pressing. Then the electrodes were cut into disks with diameter of 12 mm and further dried at 100 °C for 24 h in vacuum. Electrochemical measurements were carried out in CR2032 (3 V) coin-type cell with lithium metal as the reference electrode. Celgard 2400 membrane was used as separator and the electrodes was assembled in dimethyl carbonate (DMC) (EC/ DMC, 1:1 v/v, with addition of 1M LiPF₆). CV measurements were carried out on a Solartron 1287 electrochemical workstation at a scanning rate of 1 mVs⁻¹. Galvanostatic charge discharge cycles were tested by LAND CT2001A electrochemical workstation at various current densities between 0.01 and 3 V vs Li⁺/Li at room temperature. The capacity of electrode materials is calculated with

respect to the total weight of electrode (including the weight of binder and carbon black).

7.1.3 Results and Discussion

The growth of transition metal nitrides requires the presence of active N atoms and metal ions. Ethylenediamine (ED) is a well-known chelating ligand for coordination compound, which forms derivatives with carboxylic acid, carbon disulfide, and ketones. Therefore, It is easy for ED to coordinate with transition metal ions to form a Me(ED)_n^{m+} complex. G-O is known for its abundance of O-containing functional groups, which is capable of adsorbing ED chelates through electrostatic interaction. After refluxing Fe-ED complex and G-O under 110°C , some of the O-containing functional groups in G-O might be replaced by ED complex and lead to the formation of a covalent C-N bond between ED and graphene network. As shown in Fig. 7.1, the ED chelates might sits on the surface and in the same space with graphene or intercalate between the graphene layers. After annealing under Ar, the transition metal is formed while G-O is further reduced and modified with N by ED.

Figure 7. 1 Schematic illustration for the preparation of transition metal nitrides.

The composition of the FeN-rG-O is confirmed by XRD pattern shown in Fig. 7.2c. For the FeN-G annealed under 550°C (FeN-rG-O 550°C), has several sharp peaks correspond to the (104), (110), (024) and (116) faces of Fe_2O_3 (JCPDS: 01-1053), with peak positions well fitted. XRD pattern of FeN-rG-O 550°C indicate the

presence of iron oxides which were not removed by acid bleaching. There may be some iron oxides enwrapped by graphene layers, which could not be eliminated unless harsh acid is applied. Both FeN-rG-O 550 and 850 °C show broad peaks at 27°, suggesting increased interlamellar spacing of rG-O compared with that of G-O as reported elsewhere.[74]

Iron has four nitrides: Fe₂N, Fe₃N, Fe₄N, and Fe₁₆N₂, and they are crystalline metallic solids. According to phase diagrams of Fe-N and Fe-C,[239] nitrogen can dissolve rapidly into iron at temperatures ~590 °C while dissolution into carbon occurs at higher temperatures (~740 °C).[240] Therefore, pyrolysis of ED chelates under 850°C is favourable to obtain metal nitrides. X-ray diffraction patterns (XRD) shows FeN-rG-O has diffraction peak at 43.49 associated with (111) face of Fe₃N (JCPDS: 049-1662). SEM (Fig. 7.2b) images show FeN is uniformly distributed onto graphene layers with size of roughly 10-20 nm. There is negligible change of morphology for FeN-rG-O that annealed under different temperatures from 550 to 1000 °C. The Me-ED chelates which have –NH₂ at the outer end, adsorb or link to G-O sheets through covalent or non-covalent bonds, therefore, after refluxed and annealed, the uniform distribution on graphene can be achieved. The TEM images show the distribution of FeN in graphene is homogeneous, and some of FeN has obvious carbon shell. The FeN-rG-O has lattice spacing of 0.21 nm, corresponding to the (111) lattice planes of FeN, which is consistent with the XRD results shown in Fig. 7.2. The graphitic shells with lattice spacing from 0.29-0.41 nm, is quite irregular, probably due to the expansion of graphene layers after incorporated with N atoms, or the shell itself is the amorphous carbon from carbonization of G-O or/and ED molecules.

Figure 7. 2 SEM images of G-O (a) and FeN/N-rG-O 850 °C (b). XRD patterns (c) corresponding to samples prepared by annealing of FeN/N-rG-O composite at 850 and 550 °C respectively. TEM (d, e) and HRTEM (f) of FeN/N-rG-O 850 °C.

XPS broad spectra (Fig. 7.3) of FeN-rG-O show the presence of N and O together with Fe. The low signal intensity of Fe indicates the low ratio of Fe in FeN-rG-O. The N bonding states are identified by C1s and N1s spectra. The C1s peak of FeN-rG-O can be fitted with three different components with binding energy of 284.5, 285.1 and 286.0 eV, corresponding to sp^2 hybridized C atoms, C-N bond and C-O bond, respectively. N1s spectrum of FeN-rG-O shows four deconvoluted peaks. The peak at 398.4 eV is similar to reported values for iron nitrides (398.1 eV).[245, 247] The peak entered at 399.6 eV corresponding to “pyridinic” nitrogen, which contributes to π -conjugated system with a pair of π electrons in graphene layers. The peak at 401.7 eV indicates presence of “quaternary nitrogen”, which is sp^2 hybridized N bonded with three sp^2 hybridized C neighbours. The peak at 400.9 eV can be ascribed to “pyrrole-like” nitrogen where N incorporated in five-membered heterocyclic ring. The N in the

composite is predominantly present in the form of pyridinic nitrogen. The weight ratio of metal on FeN-rG-O composite is around 7.6 % to 10 % as determined by ICP-OES.

Figure 7. 3 C1s (a) and N1s (b) core-level X-ray photoelectron spectra and survey scan of FeN-rG-O (inset of a).

The lithium insertion/extraction properties in FeN-G are shown in Fig. 7.4. CVs of FeN-rG-O at a scan rate of 1 mVs^{-1} are shown in Fig. 7.4a. The first cycle had cathodic peak at 0.3 V and disappeared in the second cycle, which could be due to the decomposition of electrolyte and formation of SEI layer. After the first cycle, peaks around 0.8 V was observed, corresponding to Li reversible reaction with FeN similar to previously reported metal nitrides.[263, 271]

Figure 7. 4 Electrochemical characterizations of a half-cell composed of FeN/N-rG-O and Li. The specific capacities are calculated based on the mass of FeN/N-rG-O composite including binder and carbon black. (a) the first 3 cycles of CV curve under a current density of 1 mV s⁻¹; (b) charge and discharge curves of FeN/N-rG-O composite for the first three cycles at a current density of 100 mA g⁻¹; (c) capacity retention of FeN/N-rG-O at current density of 50 mA g⁻¹ for 50 cycles; and (d) the electrochemical capacity comparison of rG-O, N-rG-O and FeN/N-rG-O at current density of 100 mA g⁻¹.

Fig. 7.4 b shows the initial 3 discharge and charge curves of FeN-rG-O at current density 50 mA g⁻¹ in the voltage window of 0.005- 3.0 V vs. Li⁺/Li. During the first discharge, which is reaction with Li, the voltage drops from open circuit voltage (OCV ~ 2.7 V) continuously to ~ 0.75 V. At this point, the capacity is around 100 mAhg⁻¹. After this, there are two broad plateaus around 0.35 V. After the first discharge and charge cycle, the discharge plateau of the cell is around 1.1 V and below 0.5 V, with capacity of 110 and 280 mAhg⁻¹. The FeN-rG-O delivers 750 and 510 mAhg⁻¹ capacities for the first discharge and charge, respectively. Therefore, the irreversible capacity loss for FeN-rG-O cell is 240 mAhg⁻¹, and the first cycle efficiency is 68%.

The third cycle shows minor difference compared with the second circle on curve shape, peak intensity and integral area, indicating the electrochemical reversibility of MeN-G is gradually built after the first cycle. With an increase in the cycle number, the reversible capacity decreases slowly. However, the capacity increases from 665 mAhg⁻¹ in the 2nd cycle to 698 mAhg⁻¹ at the end of 80th cycle at current of 50 mA g⁻¹. The increase of capacity with cycle is interesting, but this phenomenon has already been reported for some metal nitrides electrodes.[272] For CoN and FeCoN, NiN, the general trend of cycling behaviour is similar, which is the compensation of first few cycle capacity losses in the following tens or hundreds of cycles.

For rG-O material, the reversible capacity after 100 cycles was only about 278 mAh g⁻¹. However, the capacity values of rG-O are 1577 and 618 mAh g⁻¹ in first discharge and charge. The irreversible capacity loss for rG-O is 959 mAh g⁻¹. rG-O has large amount of defects at edge sites and internal / basal plane (vacancies etc.), with nanodomains embedded planer space. These defects predominated Li storage mechanism results in a larger capacity than theoretical value of graphene (744 mAh g⁻¹).[38] However, these defects would also lead to large irreversible first discharge capacity loss due to the formation of SEI layer. Not only defects for example, acid treatment introduced defects and amorphous structure,[273] elemental doping is also advantageous for Li storage. The heteroatoms doping, especially N is effective for Li ion battery capacity and cycling performance improvement. N doping increases the capacity of pristine graphene by two times,[110] and N doped CNTs delivered a reversible capacity of 494 mAh g⁻¹. [274] Recently, numerous reports indicate graphene/metal and graphene/metal oxides composite exhibiting improved cyclability compared to both bare graphene and corresponding metal or metal oxides. It is also worth to note that, most of the reported non-degradation of capacity composites,

hydrazine or N-containing reducing agent is utilized. For example, urea or hydrazine were used as reducing agents to prepare Co₃O₄/graphene,[275] Fe₂O₃/graphene,[276] and NiO/graphene.[277] Hydrazine is a commonly used reducing agent to obtain rG-O with high relative high conductivity, and presence of N in the form of aromatic N₂ in five-membered ring in rG-O could also be identified.[278] [61] Therefore, the presence of N in graphene/metal oxides composite might help to achieve the stable cycling, except the synergistic effect from metal/metal oxides and graphene as-claimed.[275, 279-281]

However, the introducing of N to graphene also has shortcomings, for example, large irreversible capacity loss in the first time discharge.[275] CNT prepared from 100% acetonitrile with N content of 2.89 at.% has a first discharge capacity of 827 mAhg⁻¹, with irreversible capacity of 586 mAhg⁻¹, while the CNT grown from 20% acetonitrile with lower N content (1 at.%) shows largest reversible capacity.[282] Similar phenomenon is found in N doped graphene, which shows first cycle efficiency of 32%, which is 40% of first time discharge capacity.[110] The N might react with Li irreversibly via the following reaction:

The transition metal oxides, such as Co₃O₄, Fe₂O₃, or NiO could react with Li as expressed in eq.7.2. Upon oxidation, metal (Me) react with Li₂O and reform metal oxide at voltages ranging from 1.5 to 2.5 V vs. Li/Li⁺

While, the reaction of binary nitrides behave as Li “sink”. Reports indicate that the reaction of Me_xN_y with Li⁺ consists of a conversion reaction of Me_xN_y into lithium metal alloys (LiMe) in a β-Li₃N matrix. Upon oxidation, LiMe is transformed to Me, while β-Li₃N contribute to the transformation into LiMeN. LiMeN which is N

abundant, like $\text{Li}_{3-x}\text{M}_x\text{N}$ in eq. 7.4, where M is a transition metal as Co, Ni, are isostructural to the hexagonal layered Li_3N . LiMeN would further react with Li and further transform to Me and Li_3N , as eq. 7.4. The Li ion is reported to exhibit good cycling stability and large capacity in LiMeN such as $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$. [266] From equation 7.3- 7.5 as explored by previous researchers, the reaction mechanism of Me_xN_y with Li will produce LiMeN , which is regarded as the most promising anode materials in recent years. [26, 265]

Lithium nitride (Li_3N) is stable binary alkali metal nitride and has a unique layered structure in which Li_2N layers are separated by layers of Li atoms. The 3d metals of Ni, Co, and Fe could also greatly enhance the electrochemical activity of lithium ion anode toward the formation/decomposition of Li_3N by reaction of metal nitride with lithium (eq. 7.5). Fu et al., also found that the Fe_3N produced Fe and Co during reaction with Li ions, which acts as driving force for the decomposition and formation of Li_3N during the subsequent electrochemical reaction. [263]

Therefore, for CoN or FeN as anode during reaction in eq. 7.3 and 7.4, one part of metallic Co and Fe is nitrated and reduced in the lithium electrochemical reaction; another part of Co and Fe seems to act as an active spectator to help drive the formation and decomposition of Li_3N as shown in eq. 7.5.

Therefore, MeN is responsible for the reversible conversion reaction of MeN/carbon composites with Li metal. As the specific capacity of nanophase is strongly dependent on lithium transport distance, [283] the reduction of MeN crystal size while introduce of electron conductive coating layer would be greatly helpful. In

as-developed method, the N containing ED is also effective in introducing N doping to rG-O, as determined by XPS results. The reaction of N in N-rG-O with Li will produce Li_3N during the first time discharge. The Li_3N is possible to react with transition metal to produce LiMe_xN_y , which is proven to be capable of reacting with Li reversibly eq. 7.3. For example, $\text{Li}_2(\text{Li}_{0.7}\text{Fe}_{0.3})\text{N}$ prepared from Fe and Li_3N annealing at 800 °C deliver a reversible capacity of 550 mAhg⁻¹. [265] From this point, the Li_3N produced from Li metal and N-modified graphene, is possible to be decomposed by Fe, as indicated by eq. 7.3 and 7.4. Therefore, after the 2nd cycle, there is steady capacity increase, in all as-prepared FeN-rG-O FeCoN-rG-O, CoN-rG-O and NiN-rG-O samples. The N doping of graphene, on the other hand, has improved the conductivity, which contributes to the fast charge separate and transportation, further leading to large capacity and excellent cyclability.

7.2 Transition Metal Oxide/Graphene Anode

7.2.1 Introduction

Although metal nitride/rG–O composites have relatively low discharge plateau and good cycle performance, the uncontrollable loading weight ratio during chemical preparation method makes it difficult to examine the effect of metal amount on the performance of graphene based anode materials. Metal oxides, eg., Fe_2O_3 , [284] Co_3O_4 , [121] NiO , [285] MnO_2 , [286] TiO_2 , [287] and SnO_2 [120] are also promising due to their high theoretical capacity and easy preparation approach. Metal oxides always suffer from rapid capacity fading because of the large volume expansion occurred during cycling, which hindered their practical application as LIB anode. In recent studies, researchers find the performance of metal oxide/carbon composites is advantageous over metal oxide, where carbon function as cushion layer to reduce the volume expansion and structural degradation caused during Li-ion insertion. Various

carbon nanomaterials, like CNT,[288] mesoporous carbon [289] are vastly used as carrier to load metal oxides.

The unique properties of graphene, such as high surface area,[61, 81] excellent conductivity,[49, 290] wide electrochemical potential window,[291] have attracted intensive research interest on its synthesis, characterization as well as exploration of energy storage applications.[49, 291, 292] Preparations of various transition metal oxides (SnO_2 , [293] TiO_2 , [294] Fe_2O_3 , [295] Co_3O_4 , [121] Mn_3O_4 , [296] NiO [297]) combined with graphene composites, and their applications as anode material for LIBs are vastly reported in recent years. Among these graphene/transition metal oxide composites, Co_3O_4 /graphene shows excellent performance.[121, 298-302] However, it is worth to note that the above mentioned composites, including pure chemically derived graphene [303-305], suffer from lower initial charge-discharge capacity efficiency compared with graphite.

LIBs cell are generally composed of Li-containing transition metal oxides cathode (LiFePO_4 , LiMnO_2 , LiCoO_2), [30] and carbon or transition metal oxides/nitrides/sulfides anode.[26] During the charge/discharge process, the Li-ion will transfer between the cathode and anode, either by alloying, reversible redox reaction or intercalation process. As in these real LIBs prototypes, the Li-containing transition metal oxides which has limited Li atoms is the only source of Li ions, and the irreversible reaction of Li ions with anode, or exhaustion of Li during cycling will directly decrease cell capacity and energy density.[306] Normally, in the first cycle, Li ions reacts irreversibly with organic electrolyte on the anode surface and cause irreversible capacity loss by forming solid electrolyte interface (SEI) layer.[307] The first cycle efficiency, the cyclability, and the rate performance are critical evaluation parameters of anode materials for practical applications. Chemically derived graphene

has abundant dangling bonds, defects, oxygen content, which have higher reactivity toward the electrolytes and easily results in decomposition of electrolyte in the initial cycle.

Although graphene is reported to have a theoretical capacity of 744 mAhg^{-1} , which is significantly more than that of graphite (372 mAhg^{-1}), the large irreversible capacity in the first cycle is a notable drawback. Wang et al. reported that the capacity of graphene was 945 mAhg^{-1} in the first cycle and maintained 460 mAhg^{-1} after 100 cycles, probably because Li ion can be incorporated on both sides of graphene.[308] Many efforts have been made to improve the performance of graphene by introducing heteroatom dopants [4] or combining with various metal/metal oxides[309]. Graphene doped with N is reported to deliver a reversible capacity of 872 mAhg^{-1} , but the capacity in the first cycle is around 2127 mAhg^{-1} with 1255 mAhg^{-1} of irreversible capacity loss.[4] The first discharge and charge capacities of few layered graphene sheets were 2035 and 1264 mAhg^{-1} . [304] Chemically derived graphene prepared from oxidation of graphite has large amounts of residual O-containing functional groups, which react with electrolyte or Li ions during charge/discharge. The oxygen released from decomposition of O-containing functional groups may partly oxidizes the electrolyte, and cause cell instability and capacity degradation.[4]

Here we report an electrode prepared from microwave exfoliated graphite oxide (MEGO). In order to reduce the effect of O-containing groups, N doping were introduced to MEGO (abbreviated as NMEG in this chapter). The Co_3O_4 nanoparticles were grown on NMEG with different weight ratio, and the effect of the Co_3O_4 weight ratio on the first cycle efficiency and rate performance were investigated. The first cycle efficiency of $\text{Co}_3\text{O}_4/\text{NMEG}$ composite with Co_3O_4 weight ratio of 10 %, 40%, 70% and 100% are 50.4 ± 2.4 , 73.7 ± 1.6 , $77.3 \pm 1.3\%$, and 64.0 ± 1.5 respectively. After

100 cycles, the capacity of $\text{Co}_3\text{O}_4/\text{NMEG}$ composite with Co_3O_4 weight ratio of 10%, 40%, 70% and 100% are 823, 762, 910 and 295 mAh g^{-1} at a current density of 63 mA g^{-1} . The first cycle efficiency of 70% $\text{Co}_3\text{O}_4/\text{tR-G-O}$ (thermal reduced graphene) electrode is 51.3 ± 2.5 . 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ deliver a largest reversible capacity of 910 mAh g^{-1} with an electrode active material loading of 1.2~1.8 mg for 2032 type coin cell. These results indicating the N modification is effective to ameliorate the poor first cycle efficiency of those chemically derived graphene composites, indicating the potential of NMEG based composites as high performance LIBs anode materials for practical application.

7.2.2 Experiment and Characterization

The syntheses of microwave exfoliated GO followed the method described previously.[10, 71] Briefly, GO synthesized from modified Hummers' method were irradiated in a domestic microwave oven operated at 1100 W for 1 min.[10] The GO powder was expanded in microwave rapid heating to form a fluffy MEGO powder. The MEGO powder was further annealed at 850 °C for 1h in a mixed gas of NH_3 and Ar (1:2 v/v) with a total gas flow rate of 180 mL min^{-1} , and dried after washing by large amount of DI water to prepare NMEG. In a typical preparation process of $\text{Co}_3\text{O}_4/\text{NMEG}$, 200 mg of NMEG was dissolved in 50 mL of DI water, followed by addition of 75, 450, 1400 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 100, 850, 1800 mg of urea to obtain $\text{Co}_3\text{O}_4/\text{NMEG}$ with Co_3O_4 weight ratio of 10%, 40% and 70% respectively. The resulting solution was refluxed at 90 °C with magnetic stirring for 3 hours to form $\text{Co}(\text{OH})_2/\text{NMEG}$. $\text{Co}(\text{OH})_2/\text{NMEG}$ was collected by filtration, and dried in an oven at 60 °C overnight. Finally, the $\text{Co}_3\text{O}_4/\text{NMEG}$ was produced by annealing $\text{Co}(\text{OH})_2/\text{NMEG}$ at 300 °C in air for 4 hours.

Co₃O₄/tRG-O sample was synthesized in a similar procedure, except that NMEG was replaced by tRG-O, which was pre-made by annealing. GO was annealed at 850 °C (ramping rate: 10 °C /min) in Ar protection for 4 h to prepare tRG-O. Pure Co₃O₄ nanoparticles were also prepared in the similar procedure, without addition of NMEG or tRG-O.

The as-synthesized materials were characterized by SEM, TEM, XRD, XPS, with the same equipments setup and parameters as shown in chapter 2 and 3. The graphene content in the composite was determined by thermogravimetric analysis (TGA) on a Mettler Toledo TGA/SDTA 851 by ramping from 25 to 850 °C in air. The crystal structure of the graphene was examined by a Bruker D/MAX 2500 X-ray diffractometer (XRD) with Cu K radiation ($\lambda = 1.54056 \text{ \AA}$). The half cell assembly of electrodes and measurement of cells can be seen in section 7.1.2. The cells were galvanostatically charged and discharged at various current from 63 to 625 mA g⁻¹, within the range of 0.01 to 3.0 V.

7.2.3 Results and Discussion

The overall synthetic procedure of Co₃O₄/NMEG involves four steps as shown in Fig. 7.5. GO was firstly prepared by oxidation of graphite. The MEGO is obtained from microwave expansion of GO, which was further doped with N by annealing of MEGO at 850 °C for 1h in a mixed gas of NH₃ and Ar (1:2 v/v). The NMEG was then refluxed at 90°C in CoCl₂ aqueous solution with urea as reducing agent to prepare Co(OH)₂/NMEG. The Co(OH)₂/NMEG is further annealed at 300 °C in air to obtain Co₃O₄/NMEG. The weight ratio of Co₃O₄ in Co₃O₄/NMEG is controlled according to the amount of precursor, and identified by TGA. TGA data shows the weight ratio of Co₃O₄ in Co₃O₄/NMEG are 11, 42, and 69% when 75, 450, and 1400 mg of CoCl₂

6H₂O was applied. And they were labelled as 10%, 40%, and 70% Co₃O₄/NMEG for better understanding in the following content.

Figure 7. 5 Schematic illustration of the preparation of Co₃O₄/NMEG composite.

The morphology of Co₃O₄/NMEG and Co₃O₄ was observed by SEM as shown in Fig. 7.6. Co₃O₄ nanoparticles with a size of ~100 nm was found to be distributed on the surface of NMEG sheets in 40% Co₃O₄/NMEG, and the amount of Co₃O₄ nanoparticles increased in 70% Co₃O₄/NMEG composite. The Co₃O₄ prepared without addition of NMEG showed a flower like structure, which is composed of numerous Co₃O₄ needles with length over several micrometers. The 10% Co₃O₄/NMEG, however, only shows the curly and corrugated NMEG sheets when observed under SEM. However, the HRTEM observation of 10% Co₃O₄/NMEG showed nanoparticles with size below 5nm was uniformly distributed on NMEG sheets (data not shown).

Figure 7. 6 FESEM images of 10% Co_3O_4 /NMEG (a), 40% Co_3O_4 /NMEG (b), 70% Co_3O_4 /NMEG (c), and Co_3O_4 (d).

The XRD patterns of NMEG, Co_3O_4 /NMEG, and Co_3O_4 are shown in Fig. 7.7. The diffraction peak around 37.5° could be indexed to the (311) plane of the Co_3O_4 . The peaks around 19° , 31° , 37° , 45° , 59° , and 65° are the diffraction peaks from crystalline Co_3O_4 indicative of the presence of Co_3O_4 (JCPDS: 76-1802). NMEG displays broad graphitic (002) peak at around $24.5 \pm 0.3^\circ$, and the weak (100) peak at $42.3 \pm 0.3^\circ$ imply the breaking of interplanar carbon bonds of graphite with increased layer distance.[301] The diffraction peaks of Co_3O_4 increase with the increase of Co_3O_4 weight ratio in Co_3O_4 /NMEG composite.

Figure 7. 7 XRD pattern of as-synthesized NMEG, Co_3O_4 and Co_3O_4 /NMEG composite.

As seen from the HRTEM images focusing the edge of NMEG sheet in 40% Co_3O_4 /NMEG composite (Fig. 7.8), the Co_3O_4 is densely grown on NMEG with crystal size of $\sim 5\text{nm}$. The d-spacing of clearly observed Co_3O_4 nanoparticles was derived to be 0.24 nm corresponding to the spacing between (311) planes of nanocrystalline Co_3O_4 . It is worth to note that, the Co_3O_4 could also be seen uniformly distributed in the basal plane of NMEG sheets. The charge density and chemical reactivity of graphene edge are regarded to be stronger than graphene basal plane by calculation.[310] Therefore, the rG-O has rare functionalities will facilitate the grown of Co_3O_4 in the edges. We found the enrichment of Co_3O_4 nanoparticles both at the edges and the basal planes in all Co_3O_4 /NMEG samples. The presence of N functional groups in NEMG as anchoring sites for Co_3O_4 nucleation might be the main reason leading to the homogeneous distribution of Co_3O_4 even under 70% loading weight ratio.

Figure 7. 8 HRTEM image shows the edge structure of 40% Co_3O_4 /NMEG (a) and (b) and the uniform distribution of Co_3O_4 nanoparticles in the 2D NMEG sheets (c) and (d).

XPS is used to explore the probable interactions between Co_3O_4 and NMEG sheet (Fig. 7.9). There is no obvious difference in the C1s and N1s peak positions from the broad scan of 10% Co_3O_4 /NMEG and NMEG. The high resolution C1s spectra of NMEG and 10% Co_3O_4 /NMEG can be fitted to four peaks around 284.6 ± 0.1 , 285.6 ± 0.1 , 286.4 ± 0.1 , and 287.3 ± 0.1 corresponding to the C-C, C-OH/C-N, C=O, and O=C-N- bonds. The relative intensity of fitted peaks of the two samples are similar. The N1s spectra of Co_3O_4 /NMEG and NMEG can be divided to four peaks positioned at 398.1 ± 0.1 , 399.7 ± 0.1 , 400.9 ± 0.1 , and 402.4 ± 0.1 eV, which could be attributed to pyridinic,[305, 311] C=N double bond,[312] pyrrolic N or C≡N bond, and graphitic N. The atomic ratio of N in form of pyridinic N, C=N, pyrrolic N, and graphitic N in NMEG and 10% Co_3O_4 /NMEG are determined to be 56:15:21:8, and 47:31:14:8 respectively from the curve fitting. The relative peak intensity around 398.1 ± 0.1 and 400.9 ± 0.1 eV decreased notably in Co_3O_4 /NMEG compared with NMEG, which

might due to the covering of Co_3O_4 on pyridinic and pyrrolic bond abundant area. The total N atomic ratio is also decreased from 4.9% in NMEG to 3.5% in $\text{Co}_3\text{O}_4/\text{NMEG}$. Considering the atomic ratio of Co_3O_4 (<1% in molar ratio), the decreasing of N atomic ratio is probably due to the covering of N sites by Co_3O_4 crystals. It is reasonable to propose that the pyridinic and pyrrolic N is more advantageous for Co_3O_4 growth, compared the N in other presence states.

Figure 7.9 $\text{N}1\text{s}$ spectra of NMEG (a), $\text{Co}_3\text{O}_4/\text{NMEG}$ (b), and $\text{C}1\text{s}$ spectra of NMEG (c), $\text{Co}_3\text{O}_4/\text{NMEG}$ (d).

Fig. 7.10 show galvanostatic charge/discharge curves of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{NMEG}$ in the 1st, 2nd, 3rd and 95th cycles at a current density of 63 mA g^{-1} . In the first discharge step both the Co_3O_4 and $\text{Co}_3\text{O}_4/\text{NMEG}$ present a long voltage plateau at 1.05~1.07V, followed by a slop curve down to 0.01V, indicative of typical discharge behaviour of Co_3O_4 electrode.[254, 313] However, the 10% $\text{Co}_3\text{O}_4/\text{NMEG}$ show capacity gradually increase without obvious voltage plateau from 1.5 to 0.01 V during discharge, which is different from the other samples tested. After 95 cycles, the charge/discharge curves of

Co_3O_4 , 40% and 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ changed significantly. Although there is notable voltage plateau at ~ 1.05 V during discharging, the voltage plateau at 2.2 V during charging disappeared for 40% and 70% $\text{Co}_3\text{O}_4/\text{NMEG}$. Capacity value increase was observed on both 40% and 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ electrodes after 100 cycles. The $\text{Co}_3\text{O}_4/\text{NMEG}$ electrode performed much better than bare graphene electrode or pure Co_3O_4 electrode, by exhibiting a highly reversible Li-ion capacity and excellent cyclability. The enhancement of electrochemical properties of $\text{Co}_3\text{O}_4/\text{NMEG}$, compared to bare Co_3O_4 can be attributed to the contributions from both good conductivity, high surface area of graphene and high capacity value of Co_3O_4 . The uniform dispersion of Co_3O_4 with nanosized distribution is especially important for the electrode performance.

Figure 7. 10 Typical charge-discharge curves of $\text{Co}_3\text{O}_4/\text{NMEG}$ and Co_3O_4 cycled at the 1st, 2nd, 3rd and the 95th cycles between 0.01 V and 3.00V.

We then investigated the rate performance of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{NMEG}$, and $\text{Co}_3\text{O}_4/\text{tR-G-O}$ (see Fig. 7.11). Note that the reversible capacities of $\text{Co}_3\text{O}_4/\text{NMEG}$

electrodes are greatly improved in comparison with Co_3O_4 . The 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ delivered a first cycle efficiency of 77.3%, which is higher than that of 10% $\text{Co}_3\text{O}_4/\text{NMEG}$ (50.4%), 40% $\text{Co}_3\text{O}_4/\text{NMEG}$ (73.7%), and Co_3O_4 (64.0%). The 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ exhibit reversible capacity of 799 mAhg^{-1} , and increased to 910 mAhg^{-1} , give a capacity retention of 113.8% after 100 cycles. The capacity of 10% and 40% $\text{Co}_3\text{O}_4/\text{NMEG}$ reached 1014 mAhg^{-1} and 704 mAhg^{-1} at the 2nd cycle. However, the capacity of 10% $\text{Co}_3\text{O}_4/\text{NMEG}$ electrode decreased from 1014 to 823 mAhg^{-1} , while 40% $\text{Co}_3\text{O}_4/\text{NMEG}$ exhibit a capacity increase of 8% after 100 cycles.

Figure 7.11 Rate performance of $\text{Co}_3\text{O}_4/\text{NMEG}$ and Co_3O_4 (a), 70% $\text{Co}_3\text{O}_4/\text{tRG-O}$ (b) at various current densities from 63 mA g^{-1} to 625 mA g^{-1} .

In order to compare the initial irreversible capacity of $\text{Co}_3\text{O}_4/\text{NMEG}$ with Co_3O_4 that grown on conventional rG-O, thermal reduced graphene (tRG-O) is used as carbon carrier to prepare $\text{Co}_3\text{O}_4/\text{tRG-O}$ in the same method. Although the tRG-O used here is reduced by thermal annealed with Ar protection, there is also oxygen-containing functional groups remained. Different from reduced graphene, NH_3/Ar gas annealing removes some of O-containing groups and replace the oxygen position with

dangling bond or N doping. We would like to ascribe the reduced first cycle capacity loss to the reducing of oxygen content in carbon side. The oxygen functional groups which will not only cause irreversible capacity at initial charge/discharge, but may also oxidize the electrolyte, leading to the capacity loss at first cycle and electrode instability. The 70% $\text{Co}_3\text{O}_4/\text{tRG-O}$ although delivered a high reversible capacity of $750 \pm 20 \text{ mAhg}^{-1}$, the irreversible capacity loss during the first cycle was $700 \pm 20 \text{ mAhg}^{-1}$ (Fig. 7.12).

Figure 7. 12 Co_3O_4 weight ratio effect on the 1st cycle efficiency of $\text{Co}_3\text{O}_4/\text{NMEG}$ electrode (a), and on the capacity retention of $\text{Co}_3\text{O}_4/\text{NMEG}$ electrode after 95 cycles (b).

The most important advantage of $\text{Co}_3\text{O}_4/\text{NMEG}$ as compared with Co_3O_4 is their improved rate performance. At a current rate of 0.625 Ag^{-1} , the capacity values of $\text{Co}_3\text{O}_4/\text{NMEG}$ are maintained at 388 ± 5 , 491 ± 10 , $640 \pm 32 \text{ mAhg}^{-1}$ with Co_3O_4 weight ratio increasing from 10 to 70%, and significantly larger than that of Co_3O_4 ($52 \pm 3 \text{ mAhg}^{-1}$). Comparing the initial cycle efficiency, and the capacity retention of $\text{Co}_3\text{O}_4/\text{NMEG}$ with different Co_3O_4 weight ratio, the 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ clearly show largest first cycle efficiency of 77.3% and larger capacity retention ratio of 113.8 % after 100 cycles. Kim et al reported the $\text{Co}_3\text{O}_4/\text{graphene}$ could deliver a high reversible capacity of 800 mAhg^{-1} , and the first cycle efficiency was $\sim 66\%$. [298] Yang et al's work presented the graphene encapsulated Co_3O_4 delivered a reversible capacity of $\sim$

1000 mAhg⁻¹ with a first cycle efficiency of ~64%.[314] Compared the Li storage behaviour of as-prepared Co₃O₄/NMEG, Co₃O₄/tRG-O and recent report of Co₃O₄/graphene composite, initial cycle efficiency of Co₃O₄/NMEG notably increased. Therefore, introducing of N functionalization before the growth of metal oxides is not only useful to achieve a uniform distribution of metal oxides nanoparticles, but also reduce the initial capacity loss.

7.2.4 Conclusion

In summary, we present the utilization of Co₃O₄/NMEG for LIBs anode. The effects of Co₃O₄ weight ratios on the Co₃O₄/NMEG composite performance as anode in terms of 1st cycle efficiency, rate behaviour, cyclability, are investigated. NMEG with N functionalities is helpful for Co₃O₄ growth, and a uniform dispersion of Co₃O₄ is achieved at the edge and basal plane of NMEG sheets. After incorporated with Co₃O₄, the N functional groups in presence of pyrrolic and pyridinic N are reduced, which indicates these sites are active for Co-precursor anchoring. Co₃O₄/Graphene composites have better performance with higher capacity value and better rate performance than pure Co₃O₄. However, modifying the chemically derived graphene with N-containing groups to prepare graphene/metal oxide composite is advantageous for the practical application of LIBs anode with higher first cycle efficiency, but well maintained rate performance. Furthermore, it is possible that N-doping on carbon carrier induced irreversible capacity reduction is also applicable for various other carbon/metal oxide composites.

Chapter 8

Conclusions and Future Work

8.1 Conclusions

In this thesis, synthesis of graphene composites and their applications in energy storage are presented.

(1) The electrochemical performances of supercapacitor electrodes prepared by chemically modified graphene were investigated. The -NH_2 group was introduced to rG-O network by one-step solvothermal method, and the capacitance of $\text{NH}_2\text{-rG-O}$ was several times larger than that of rG-O. We further explored the effect of graphene surface chemistry on the conducting polymer (CP) growth and capacitance increment magnitude. We find that the electrolyte has obvious different effects on different CP/carbon composite due to the different acidity and pseudocapacitance generation mechanism. The N modified graphene / PPy and $\text{NH}_2\text{-rG-O/PANi}$ have significantly improved performance as supercapacitor electrodes when tested in alkaline and acidic electrolyte respectively. Incorporation of CP with porous carbon species with defined surface chemistry to form hybrid nanomaterials represents an opportunity for the design of novel materials with significantly improved performance as electrochemical supercapacitors.

(2) For graphene based non-precious metal catalyst for oxygen reduction reaction (ORR): the active structure and catalytic mechanism

a) N-graphene was produced by annealing of graphene oxide (G-O) under ammonia or by annealing of a N-containing polymer/reduced graphene oxide (RG-O) composite (PANi/rG-O or PPy/rG-O). The effects of the N precursors and annealing temperature on the performance of the catalyst were investigated. The bonding state of

the N atom was found to have a significant effect on the selectivity and catalytic activity for ORR. Annealing of G-O with ammonia preferentially formed graphitic N and pyridinic N centers, while annealing of PANi/RG-O and PPy/RG-O tended to generate pyridinic and pyrrolic N moieties, respectively. Most importantly, the electrocatalytic activity of the catalyst was found to be dependent on the graphitic N content which determined the limiting current density, while the pyridinic N content improved the onset potential for ORR. However, the total N content in the graphene-based non-precious metal catalyst did not play an important role in the ORR process.

b) Another very interesting non-precious metal catalyst for ORR is the pyrolyzed transition metal/N containing Me-N-C complex. Much effort has been devoted to the investigation of the electrocatalytic active center for ORR of non-precious metal catalysts. However the composition and/or structure of Me-N-C catalytic sites remains a point of controversy and the mechanism of ORR at these sites is uncertain. We successfully loaded FeN, CoN, and FeCoN catalyst onto rG-O platelet in one-step pyrolysis process and their performance as ORR catalysts were investigated. The ORR mechanism and the nature of the active center were rationalized based on UPS data. We propose that pyridinic N serves as the active center and donates its π electrons to the anti-bonding orbitals of O_2 . The metal core not only accepts back-donation of electrons from O_2 , facilitating the cleavage of the O-O bond, but also transfers its electrons to the pyridinic N. The data suggest that non-precious metal catalysts can be effective for ORR.

(3) For transition metal nitride/oxide and their Li-ion storage behaviour

Transition metal nitrides have low and flat potentials close to Li metal, with high reversible capacities. Conventional method use magnetron sputtering with nitrogen gas as a nitridation source. We found that the transition metal nitrides could also be loaded

onto rG-O surface by a simple chemistry method. Electrochemical measurements demonstrate that MeN present a higher relative specific capacity and excellent cycling stability. However, the disadvantage of MeN-rG-O based anode is the uncontrollable content of MeN. We therefore prepared $\text{Co}_3\text{O}_4/\text{NMEG}$ (N modified microwave exfoliated graphite oxide) with different weight ratio of Co_3O_4 , and investigated the electrochemical performance of $\text{Co}_3\text{O}_4/\text{NMEG}$ composite as anode for Li-ion batteries. Nitrogen functional groups, especially pyridinic and pyrrolic N are advantageous for Co_3O_4 growth. The N modification is effective to ameliorate the low first cycle efficiency of $\text{Co}_3\text{O}_4/\text{NMEG}$. The 70% $\text{Co}_3\text{O}_4/\text{NMEG}$ composite has an initial irreversible capacity of 230 mAhg^{-1} (first cycle efficiency of 77%), and 910 mAhg^{-1} of capacity is retained after 100 cycles.

8.2 Future Work

(1) The electron donor character of nitrogen endows excellent the electronic properties of carbon, and also provides active sites for polymer growth. The capacitance of NG-PPy electrode has a specific capacity of 179 Fg^{-1} . However, the capacitance values of electrode materials were tested in swagelok type two-electrode cells, which may be different from the results obtained in the pouch type cells. The pouch cell type supercapacitor is more comparable with industrial supercapacitors. More parameters, like current collector selection, binder to electro-active materials adaption, and assembly process need to be further justified to optimize supercapacitor with high performance.

(2) I tried to explore the active center of non-precious metal/graphene catalyst by UPS, XPS, and electrochemical method. The metal nitride coordinated with pyridinic N is the active center for ORR. However, the membrane-electrode-assembly cell with

FeCoN-N-G as cathode, and 20% Pt/C as anode still showed inferior performance compared with commercial 20% Pt/C as both cathode and anode. The reason is due to the Pt 5d band has energy region between 0-6 eV, and O₂ can be effectively activated by Pt, while the FeCoN has a energy band spanning from 3-9 eV, do not have vast enough overlapping with O₂ π^* orbitals. Therefore, it might be interesting for researchers to load hint content of Pt to FeCoN, and prepare low-Pt/nonprecious metal based catalyst to further improve the performance of FeCoN catalyst.

(3) The transition metal oxide and/or nitride combined with graphene show high capacity values over 500 mAhg⁻¹ in half cells. Although excellent cycle also has been achieved, these anode materials suffer from high discharge plateau and/or no obvious discharge plateau and low first cycle efficiency compared with commercial graphite anode. Therefore, the energy storage behaviour of Me_xO_y/graphene // LiFePO₄ full cell will be different from that of Me_xO_y/graphene // Li half cell. Therefore, the selection of suitable graphite precursor to prepare G-O, and controlling the battery assembly parameters adapt for graphene electrode are challenging, and need more effort.

References

- [1] Inagaki M, Konno H, Tanaike O. Carbon materials for electrochemical capacitors. *J Power Sources*. 2010 Dec;195(24):7880-903.
- [2] Simon P, Gogotsi Y. Materials for electrochemical capacitors. *Nature Materials*. 2008 Nov;7(11):845-54.
- [3] Vaari J, Lahtinen J, Hautajarvi P. The adsorption and decomposition of acetylene on clean and K-covered Co(0001). *Catalysis Letters*. 1997;44(1-2):43-9.
- [4] Pandolfo AG, Hollenkamp AF. Carbon properties and their role in supercapacitors. *J Power Sources*. 2006 Jun 19;157(1):11-27.
- [5] Frackowiak E, Khomenko V, Jurewicz K, Lota K, Beguin F. Supercapacitors based on conducting polymers/nanotubes composites. *J Power Sources*. 2006 Feb;153(2):413-8.
- [6] Wang GP, Zhang L, Zhang JJ. A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev*. 2012;41(2):797-828.
- [7] Rodriguez-Reinoso F, Pastor AC, Marsh H, Huidobro A. Preparation of activated carbon cloths from viscous rayon Part III. Effect of carbonization on CO₂ activation. *Carbon*. 2000;38(3):397-406.
- [8] Babel K, Jurewicz K. KOH activated carbon fabrics as supercapacitor material. *J Phys Chem Solids*. 2004 Feb-Mar;65(2-3):275-80.
- [9] Lillo-Rodenas MA, Marco-Lozar JP, Cazorla-Amoros D, Linares-Solano A. Activated carbons prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide. *J Anal Appl Pyrol*. 2007 Aug;80(1):166-74.
- [10] Zhu YW, Murali S, Stoller MD, Ganesh KJ, Cai WW, Ferreira PJ, et al. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science*. 2011 Jun 24;332(6037):1537-41.
- [11] Liang CD, Hong KL, Guiochon GA, Mays JW, Dai S. Synthesis of a large-scale highly ordered porous carbon film by self-assembly of block copolymers. *Angewandte Chemie-International Edition*. 2004;43(43):5785-9.
- [12] Ryoo R, Joo SH, Jun S. Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation. *J Phys Chem B*. 1999 Sep 16;103(37):7743-6.
- [13] Papagno M, Pacile D, Topwal D, Moras P, Sheverdyeva PM, Natterer FD, et al. Two Distinct Phases of Bilayer Graphene Films on Ru(0001). *Acs Nano*. 2012 Oct;6(10):9299-304.
- [14] Ryu KS, Kim KM, Park NG, Park YJ, Chang SH. Symmetric redox supercapacitor with conducting polyaniline electrodes. *J Power Sources*. 2002 Jan 1;103(2):305-9.
- [15] Berger C, Song ZM, Li XB, Wu XS, Brown N, Naud C, et al. Electronic confinement and coherence in patterned epitaxial graphene. *Science*. 2006 May;312(5777):1191-6.
- [16] Pandey D, Reifengerger R, Piner R. Scanning probe microscopy study of exfoliated oxidized graphene sheets. *Surface Science*. 2008 May 1;602(9):1607-13.
- [17] Gamo Y, Nagashima A, Wakabayashi M, Terai M, Oshima C. Atomic structure of monolayer graphite formed on Ni(111). *Surface Science*. 1997 Mar;374(1-3):61-4.
- [18] http://en.wikipedia.org/wiki/Activated_carbon.
- [19] Chunsheng Du NP. carbon nanotube-based supercapacitors. *Nanotechnology Law & Business*. 2007 March;4(1).
- [20] Pimenta MA, Dresselhaus G, Dresselhaus MS, Cancado LG, Jorio A, Saito R. Studying disorder in graphite-based systems by Raman spectroscopy. *Physical Chemistry Chemical Physics*. 2007;9(11):1276-91.
- [21] Ferrari AC. Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Commun*. 2007 Jul;143(1-2):47-57.
- [22] Ni ZH, Wang YY, Yu T, Shen ZX. Raman Spectroscopy and Imaging of Graphene. *Nano Res*. 2008 Oct;1(4):273-91.

- [23] Gamby J, Taberna PL, Simon P, Fauvarque JF, Chesneau M. Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors. *J Power Sources*. 2001 Oct 1;101(1):109-16.
- [24] Kottagoda IRM, Kadoma Y, Ikuta H, Uchimoto Y, Wakihara M. Enhancement of rate capability in graphite anode by surface modification with zirconia. *Electrochem Solid St*. 2002 Dec;5(12):A275-A8.
- [25] Babenco MG, Tao L, Akinwande D. Graphene Raman imaging and spectroscopy processing: characterization of graphene growth. *Proc Spie*. 2012;8466.
- [26] Tarascon JM, Armand M. Issues and challenges facing rechargeable lithium batteries. *Nature*. 2001 Nov;414(6861):359-67.
- [27] Bruce PG, Scrosati B, Tarascon JM. Nanomaterials for rechargeable lithium batteries. *Angewandte Chemie-International Edition*. 2008;47(16):2930-46.
- [28] Poizot P, Laruelle S, Grugeon S, Dupont L, Tarascon JM. Nano-sized transition-metaloxides as negative-electrode materials for lithium-ion batteries. *Nature*. 2000 Sep;407(6803):496-9.
- [29] Si P, Ding SJ, Lou XW, Kim DH. An electrochemically formed three-dimensional structure of polypyrrole/graphene nanoplatelets for high-performance supercapacitors. *Rsc Adv*. 2011;1(7):1271-8.
- [30] Kang B, Ceder G. Battery materials for ultrafast charging and discharging. *Nature*. 2009 Mar 12;458(7235):190-3.
- [31] Fan LZ, Maier J. High-performance polypyrrole electrode materials for redox supercapacitors. *Electrochem Commun*. 2006 Jun;8(6):937-40.
- [32] Landi BJ, Ganter MJ, Cress CD, DiLeo RA, Raffaele RP. Carbon nanotubes for lithium ion batteries. *Energy & Environmental Science*. 2009;2(6):638-54.
- [33] Yang J, Zhou XY, Li J, Zou YL, Tang JJ. Study of nano-porous hard carbons as anode materials for lithium ion batteries. *Materials Chemistry and Physics*. 2012 Aug;135(2-3):445-50.
- [34] Arie AA, Vovk OM, Song JO, Cho BW, Lee JK. Carbon film covering originated from fullerene C-60 on the surface of lithium metal anode for lithium secondary batteries. *Journal of Electroceramics*. 2009 Oct;23(2-4):248-53.
- [35] Pan DY, Wang S, Zhao B, Wu MH, Zhang HJ, Wang Y, et al. Li Storage Properties of Disordered Graphene Nanosheets. *Chem Mater*. 2009 Jul 28;21(14):3136-42.
- [36] Cheng F, Liang J, Tao Z, Chen J. Functional materials for rechargeable batteries. *Adv Mater*. 2011 Apr 19;23(15):1695-715.
- [37] Yue Y, Han P, He X, Zhang K, Liu Z, Zhang C, et al. In situ synthesis of a graphene/titanium nitride hybrid material with highly improved performance for lithium storage. *Journal of Materials Chemistry*. 2012;22(11):4938.
- [38] Wang GX, Wang B, Wang XL, Park J, Dou SX, Ahn H, et al. Sn/graphene nanocomposite with 3D architecture for enhanced reversible lithium storage in lithium ion batteries. *Journal of Materials Chemistry*. 2009;19(44):8378-84.
- [39] Du X, Skachko I, Barker A, Andrei EY. Approaching ballistic transport in suspended graphene. *Nature Nanotechnology*. 2008 Aug;3(8):491-5.
- [40] Lee C, Wei XD, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*. 2008 Jul 18;321(5887):385-8.
- [41] Novoselov KS, Geim AK, Morozov SV, Jiang D, Katsnelson MI, Grigorieva IV, et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*. 2005 Nov;438(7065):197-200.
- [42] Zhang YB, Tan YW, Stormer HL, Kim P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature*. 2005 Nov;438(7065):201-4.

- [43] Ni ZH, Yu T, Lu YH, Wang YY, Feng YP, Shen ZX. Uniaxial Strain on Graphene: Raman Spectroscopy Study and Band-Gap Opening (vol 2, pg 2301, 2008). *Acs Nano*. 2009 Feb;3(2):483-.
- [44] Abergel DSL, Apalkov V, Berashevich J, Ziegler K, Chakraborty T. Properties of graphene: a theoretical perspective. *Adv Phys*. 2010;59(4):261-482.
- [45] Castro Neto AH, Guinea F, Peres NMR, Novoselov KS, Geim AK. The electronic properties of graphene. *Reviews of Modern Physics*. 2009 Jan-Mar;81(1):109-62.
- [46] Geim AK, Novoselov KS. The rise of graphene. *Nature Materials*. 2007 Mar;6(3):183-91.
- [47] Hou JB, Shao YY, Ellis MW, Moore RB, Yi BL. Graphene-based electrochemical energy conversion and storage: fuel cells, supercapacitors and lithium ion batteries. *Physical Chemistry Chemical Physics*. 2011;13(34):15384-402.
- [48] Huang Y, Liang JJ, Chen YS. An Overview of the Applications of Graphene-Based Materials in Supercapacitors. *Small*. 2012 Jun;8(12):1805-34.
- [49] Sun YQ, Wu QQ, Shi GQ. Graphene based new energy materials. *Energy & Environmental Science*. 2011 Apr;4(4):1113-32.
- [50] Bae S, Kim H, Lee Y, Xu XF, Park JS, Zheng Y, et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotechnology*. 2010 Aug;5(8):574-8.
- [51] Kim KS, Zhao Y, Jang H, Lee SY, Kim JM, Ahn JH, et al. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*. 2009 Feb;457(7230):706-10.
- [52] Xu YX, Bai H, Lu GW, Li C, Shi GQ. Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets. *J Am Chem Soc*. 2008 May;130(18):5856-+.
- [53] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Electric field effect in atomically thin carbon films. *Science*. 2004 Oct;306(5696):666-9.
- [54] William S. Hummers JR, Richard E. Offeman. Preparation of graphitic oxide. *Journal of american chemical society*. 1958;80(6).
- [55] Hughes EEG, Thomas JM. TOPOGRAPHY OF OXIDIZED GRAPHITE CRYSTALS. *Nature*. 1962;193(4818):838-&.
- [56] Horton WS, Ballard DB. SCANNING ELECTRON-MICROSCOPY STUDIES OF OXIDIZED PYROLYTIC-GRAPHITE. *Carbon*. 1972;10(3):339-&.
- [57] Hummers WS, Offeman RE. Preparation of Graphitic Oxide. *J Am Chem Soc*. 1958;80(6):1339-.
- [58] Compton OC, Jain B, Dikin DA, Abouimrane A, Amine K, Nguyen ST. Chemically Active Reduced Graphene Oxide with Tunable C/O Ratios. *Acs Nano*. 2011 Jun;5(6):4380-91.
- [59] Schniepp HC, Li JL, McAllister MJ, Sai H, Herrera-Alonso M, Adamson DH, et al. Functionalized single graphene sheets derived from splitting graphite oxide. *J Phys Chem B*. 2006 May 4;110(17):8535-9.
- [60] Lerf A, He HY, Forster M, Klinowski J. Structure of graphite oxide revisited. *J Phys Chem B*. 1998 Jun 4;102(23):4477-82.
- [61] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, et al. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*. 2007 Jun;45(7):1558-65.
- [62] He HY, Klinowski J, Forster M, Lerf A. A new structural model for graphite oxide. *Chem Phys Lett*. 1998 Apr 24;287(1-2):53-6.
- [63] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. *Chem Soc Rev*. 2010;39(1):228-40.
- [64] Stankovich S, Piner RD, Chen XQ, Wu NQ, Nguyen ST, Ruoff RS. Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). *Journal of Materials Chemistry*. 2006;16(2):155-8.

- [65] Wang SR, Tambraparni M, Qiu JJ, Tipton J, Dean D. Thermal Expansion of Graphene Composites. *Macromolecules*. 2009 Jul;42(14):5251-5.
- [66] Chen WF, Yan LF, Bangal PR. Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves. *Carbon*. 2010 Apr;48(4):1146-52.
- [67] Gao XF, Jang J, Nagase S. Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design. *Journal of Physical Chemistry C*. 2010 Jan;114(2):832-42.
- [68] Zhou Y, Bao QL, Tang LAL, Zhong YL, Loh KP. Hydrothermal Dehydration for the "Green" Reduction of Exfoliated Graphene Oxide to Graphene and Demonstration of Tunable Optical Limiting Properties. *Chem Mater*. 2009 Jul;21(13):2950-6.
- [69] Long DH, Li W, Ling LC, Miyawaki J, Mochida I, Yoon SH. Preparation of Nitrogen-Doped Graphene Sheets by a Combined Chemical and Hydrothermal Reduction of Graphene Oxide. *Langmuir*. 2010 Oct;26(20):16096-102.
- [70] McAllister MJ, Li JL, Adamson DH, Schniepp HC, Abdala AA, Liu J, et al. Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem Mater*. 2007 Sep 4;19(18):4396-404.
- [71] Zhu YW, Murali S, Stoller MD, Velamakanni A, Piner RD, Ruoff RS. Microwave assisted exfoliation and reduction of graphite oxide for ultracapacitors. *Carbon*. 2010 Jun;48(7):2118-22.
- [72] Wissler M. Graphite and carbon powders for electrochemical applications. *J Power Sources*. 2006 Jun 1;156(2):142-50.
- [73] Si Y, Samulski ET. Synthesis of water soluble graphene. *Nano Letters*. 2008 Jun;8(6):1679-82.
- [74] Wang GX, Yang J, Park J, Gou XL, Wang B, Liu H, et al. Facile synthesis and characterization of graphene nanosheets. *Journal of Physical Chemistry C*. 2008 Jun;112(22):8192-5.
- [75] Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, et al. Graphene-based composite materials. *Nature*. 2006 Jul;442(7100):282-6.
- [76] Shin HJ, Kim KK, Benayad A, Yoon SM, Park HK, Jung IS, et al. Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance. *Advanced Functional Materials*. 2009 Jun;19(12):1987-92.
- [77] Wu ZS, Ren WC, Gao LB, Liu BL, Jiang CB, Cheng HM. Synthesis of high-quality graphene with a pre-determined number of layers. *Carbon*. 2009 Feb;47(2):493-9.
- [78] Fan XB, Peng WC, Li Y, Li XY, Wang SL, Zhang GL, et al. Deoxygenation of Exfoliated Graphite Oxide under Alkaline Conditions: A Green Route to Graphene Preparation. *Adv Mater*. 2008 Dec 2;20(23):4490-3.
- [79] Lai LF, Chen LW, Zhan D, Sun L, Liu JP, Lim SH, et al. One-step synthesis of NH₂-graphene from in situ graphene-oxide reduction and its improved electrochemical properties. *Carbon*. 2011 Aug;49(10):3250-7.
- [80] Zhou M, Wang YL, Zhai YM, Zhai JF, Ren W, Wang FA, et al. Controlled Synthesis of Large-Area and Patterned Electrochemically Reduced Graphene Oxide Films. *Chem-Eur J*. 2009;15(25):6116-20.
- [81] Stoller MD, Park SJ, Zhu YW, An JH, Ruoff RS. Graphene-Based Ultracapacitors. *Nano Letters*. 2008 Oct;8(10):3498-502.
- [82] Wang Y, Shi ZQ, Huang Y, Ma YF, Wang CY, Chen MM, et al. Supercapacitor Devices Based on Graphene Materials. *Journal of Physical Chemistry C*. 2009 Jul;113(30):13103-7.
- [83] Vivekchand SRC, Rout CS, Subrahmanyam KS, Govindaraj A, Rao CNR. Graphene-based electrochemical supercapacitors. *J Chem Sci*. 2008 Jan;120(1):9-13.
- [84] Zhu YW, Stoller MD, Cai WW, Velamakanni A, Piner RD, Chen D, et al. Exfoliation of Graphite Oxide in Propylene Carbonate and Thermal Reduction of the Resulting Graphene Oxide Platelets. *Acs Nano*. 2010 Feb;4(2):1227-33.

- [85] Yan J, Wei T, Fan ZJ, Qian WZ, Zhang ML, Shen XD, et al. Preparation of graphene nanosheet/carbon nanotube/polyaniline composite as electrode material for supercapacitors. *J Power Sources*. 2010 May 1;195(9):3041-5.
- [86] Du XA, Guo P, Song HH, Chen XH. Graphene nanosheets as electrode material for electric double-layer capacitors. *Electrochim Acta*. 2010 Jun 30;55(16):4812-9.
- [87] Lu T, Zhang YP, Li HB, Pan LK, Li YL, Sun Z. Electrochemical behaviors of graphene-ZnO and graphene-SnO₂ composite films for supercapacitors. *Electrochim Acta*. 2010 May 1;55(13):4170-3.
- [88] Chen S, Zhu JW, Wang X. One-Step Synthesis of Graphene-Cobalt Hydroxide Nanocomposites and Their Electrochemical Properties. *Journal of Physical Chemistry C*. 2010 Jul 15;114(27):11829-34.
- [89] Yan J, Wei T, Shao B, Fan ZJ, Qian WZ, Zhang ML, et al. Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance. *Carbon*. 2010 Feb;48(2):487-93.
- [90] Wang HL, Hao QL, Yang XJ, Lu LD, Wang X. Graphene oxide doped polyaniline for supercapacitors. *Electrochem Commun*. 2009 Jun;11(6):1158-61.
- [91] Reddy RN, Reddy RG. Sol-gel MnO₂ as an electrode material for electrochemical capacitors. *J Power Sources*. 2003 Oct;124(1):330-7.
- [92] Kierzek K, Frackowiak E, Lota G, Gryglewicz G, Machnikowski J. Electrochemical capacitors based on highly porous carbons prepared by KOH activation (vol 49, pg 515, 2004). *Electrochim Acta*. 2004 Mar 15;49(7):1169-70.
- [93] Lee BJ, Sivakkumar SR, Ko JM, Kim JH, Jo SM, Kim DY. Carbon nanofibre/hydrous RuO₂ nanocomposite electrodes for supercapacitors. *J Power Sources*. 2007 Jun 1;168(2):546-52.
- [94] Xiong SL, Yuan CZ, Zhang MF, Xi BJ, Qian YT. Controllable Synthesis of Mesoporous Co₃O₄ Nanostructures with Tunable Morphology for Application in Supercapacitors. *Chem-Eur J*. 2009;15(21):5320-6.
- [95] Yuan CZ, Zhang XG, Su LH, Gao B, Shen LF. Facile synthesis and self-assembly of hierarchical porous NiO nano/micro spherical superstructures for high performance supercapacitors. *Journal of Materials Chemistry*. 2009;19(32):5772-7.
- [96] Liang K, An K, Lee Y. Nickel oxide/carbon nanotubes nanocomposite for electrochemical capacitance. *J Mater Sci Technol*. 2005 May;21(3):292-6.
- [97] Fusalba F, Gouerec P, Villers D, Belanger D. Electrochemical characterization of polyaniline in nonaqueous electrolyte and its evaluation as electrode material for electrochemical supercapacitors. *J Electrochem Soc*. 2001 Jan;148(1):A1-A6.
- [98] An KH, Jeon KK, Heo JK, Lim SC, Bae DJ, Lee YH. High-capacitance supercapacitor using a nanocomposite electrode of single-walled carbon nanotube and polypyrrole. *J Electrochem Soc*. 2002 Aug;149(8):A1058-A62.
- [99] Xiao QF, Zhou X. The study of multiwalled carbon nanotube deposited with conducting polymer for supercapacitor. *Electrochim Acta*. 2003 Jan 15;48(5):575-80.
- [100] Laforgue A, Simon P, Sarrazin C, Fauvarque JF. Polythiophene-based supercapacitors. *J Power Sources*. 1999 Jul-Aug;80(1-2):142-8.
- [101] Lee JY, Liang K, An KH, Lee YH. Nickel oxide/carbon nanotubes nanocomposite for electrochemical capacitance. *Synthetic Met*. 2005 Apr 30;150(2):153-7.
- [102] Liu S, Liu XH, Li ZP, Yang SR, Wang JQ. Fabrication of free-standing graphene/polyaniline nanofibers composite paper via electrostatic adsorption for electrochemical supercapacitors. *New J Chem*. 2011;35(2):369-74.
- [103] Martins TB, Miwa RH, da Silva AJR, Fazzio A. Electronic and transport properties of boron-doped graphene nanoribbons. *Physical Review Letters*. 2007 May;98(19).
- [104] Boukhvalov DW, Katsnelson MI. Tuning the gap in bilayer graphene using chemical functionalization: Density functional calculations. *Physical Review B*. 2008 Aug;78(8).

- [105] Qu LT, Liu Y, Baek JB, Dai LM. Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells. *Acs Nano*. 2010 Mar;4(3):1321-6.
- [106] Geng DS, Chen Y, Chen YG, Li YL, Li RY, Sun XL, et al. High oxygen-reduction activity and durability of nitrogen-doped graphene. *Energy & Environmental Science*. 2011 Mar;4(3):760-4.
- [107] Li N, Wang ZY, Zhao KK, Shi ZJ, Gu ZN, Xu SK. Large scale synthesis of N-doped multi-layered graphene sheets by simple arc-discharge method. *Carbon*. 2010 Jan;48(1):255-9.
- [108] Lee KR, Lee KU, Lee JW, Ahn BT, Woo SI. Electrochemical oxygen reduction on nitrogen doped graphene sheets in acid media. *Electrochemistry Communications*. 2010 Aug;12(8):1052-5.
- [109] Li XL, Wang HL, Robinson JT, Sanchez H, Diankov G, Dai HJ. Simultaneous Nitrogen Doping and Reduction of Graphene Oxide. *J Am Chem Soc*. 2009 Nov 4;131(43):15939-44.
- [110] Reddy ALM, Srivastava A, Gowda SR, Gullapalli H, Dubey M, Ajayan PM. Synthesis Of Nitrogen-Doped Graphene Films For Lithium Battery Application. *Acs Nano*. 2010 Nov;4(11):6337-42.
- [111] Zhang LP, Xia ZH. Mechanisms of Oxygen Reduction Reaction on Nitrogen-Doped Graphene for Fuel Cells. *Journal of Physical Chemistry C*. 2011 Jun;115(22):11170-6.
- [112] Ji L, Lin Z, Alcoutlabi M, Zhang X. Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries. *Energy & Environmental Science*. 2011;4(8):2682.
- [113] Bak SM, Nam KW, Lee CW, Kim KH, Jung HC, Yang XQ, et al. Spinel LiMn_2O_4 /reduced graphene oxide hybrid for high rate lithium ion batteries. *Journal of Materials Chemistry*. 2011;21(43):17309-15.
- [114] Yoo E, Kim J, Hosono E, Zhou H, Kudo T, Honma I. Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Letters*. 2008 Aug;8(8):2277-82.
- [115] Pollak E, Geng BS, Jeon KJ, Lucas IT, Richardson TJ, Wang F, et al. The Interaction of Li^+ with Single-Layer and Few-Layer Graphene. *Nano Letters*. 2010 Sep;10(9):3386-8.
- [116] Uthaisar C, Barone V. Edge Effects on the Characteristics of Li Diffusion in Graphene. *Nano Letters*. 2010 Aug;10(8):2838-42.
- [117] Gerouki A, Goldner MA, Goldner RB, Haas TE, Liu TY, Slaven S. Density of states calculations of small diameter single graphene sheets. *J Electrochem Soc*. 1996 Nov;143(11):L262-L3.
- [118] Sato K, Noguchi M, Demachi A, Oki N, Endo M. A Mechanism of Lithium Storage in Disordered Carbons. *Science*. 1994 Apr 22;264(5158):556-8.
- [119] Chou SL, Wang JZ, Choucair M, Liu HK, Stride JA, Dou SX. Enhanced reversible lithium storage in a nanosize silicon/graphene composite. *Electrochem Commun*. 2010 Feb;12(2):303-6.
- [120] Yao J, Shen XP, Wang B, Liu HK, Wang GX. In situ chemical synthesis of SnO_2 -graphene nanocomposite as anode materials for lithium-ion batteries. *Electrochem Commun*. 2009 Oct;11(10):1849-52.
- [121] Wu ZS, Ren WC, Wen L, Gao LB, Zhao JP, Chen ZP, et al. Graphene Anchored with Co_3O_4 Nanoparticles as Anode of Lithium Ion Batteries with Enhanced Reversible Capacity and Cyclic Performance. *Acs Nano*. 2010 Jun;4(6):3187-94.
- [122] Yu AP, Park HW, Davies A, Higgins DC, Chen ZW, Xiao XC. Free-Standing Layer-By-Layer Hybrid Thin Film of Graphene- MnO_2 Nanotube as Anode for Lithium Ion Batteries. *J Phys Chem Lett*. 2011 Aug 4;2(15):1855-60.
- [123] Mai YJ, Shi SJ, Zhang D, Lu Y, Gu CD, Tu JP. NiO -graphene hybrid as an anode material for lithium ion batteries. *J Power Sources*. 2012 Apr 15;204:155-61.

- [124] Yue YH, Han PX, He X, Zhang KJ, Liu ZH, Zhang CJ, et al. In situ synthesis of a graphene/titanium nitride hybrid material with highly improved performance for lithium storage. *Journal of Materials Chemistry*. 2012;22(11):4938-43.
- [125] Wang XY, Zhou XF, Yao K, Zhang JG, Liu ZP. A SnO₂/graphene composite as a high stability electrode for lithium ion batteries. *Carbon*. 2011 Jan;49(1):133-9.
- [126] Zhou GM, Wang DW, Li F, Zhang LL, Li N, Wu ZS, et al. Graphene-Wrapped Fe₃O₄ Anode Material with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries. *Chem Mater*. 2010 Sep 28;22(18):5306-13.
- [127] Kim YJ, Abe Y, Yanagilura T, Park KC, Shimizu M, Iwazaki T, et al. Easy preparation of nitrogen-enriched carbon materials from peptides of silk fibroins and their use to produce a high volumetric energy density in supercapacitors. *Carbon*. 2007 Sep;45(10):2116-25.
- [128] Jurewicz K, Babel K, Ziolkowski A, Wachowska H. Ammoxidation of active carbons for improvement of supercapacitor characteristics. *Electrochim Acta*. 2003 May 15;48(11):1491-8.
- [129] Hulicova-Jurcakova D, Kodama M, Shiraishi S, Hatori H, Zhu ZH, Lu GQ. Nitrogen-Enriched Nonporous Carbon Electrodes with Extraordinary Supercapacitance. *Advanced Functional Materials*. 2009 Jun;19(11):1800-9.
- [130] Yang XQ, Wu DC, Chen XM, Fu RW. Nitrogen-Enriched Nanocarbons with a 3-D Continuous Mesopore Structure from Polyacrylonitrile for Supercapacitor Application. *J Phys Chem C*. 2010 May 13;114(18):8581-6.
- [131] Jurewicz K, Babel K, Pietrzak R, Delpeux S, Wachowska H. Capacitance properties of multi-walled carbon nanotubes modified by activation and ammoxidation. *Carbon*. 2006 Oct;44(12):2368-75.
- [132] Pietrzak R, Jurewicz K, Nowicki P, Babel K, Wachowska H. Nitrogen-enriched bituminous coal-based active carbons as materials for supercapacitors. *Fuel*. 2010 Nov;89(11):3457-67.
- [133] Guo HL, Gao QM. Boron and nitrogen co-doped porous carbon and its enhanced properties as supercapacitor. *Journal of Power Sources*. 2009 Jan 15;186(2):551-6.
- [134] Lota G, Grzyb B, Machnikowska H, Machnikowski J, Frackowiak E. Effect of nitrogen in carbon electrode on the supercapacitor performance. *Chem Phys Lett*. 2005 Mar 7;404(1-3):53-8.
- [135] Stevens JL, Huang AY, Peng HQ, Chiang LW, Khabashesku VN, Margrave JL. Sidewall amino-functionalization of single-walled carbon nanotubes through fluorination and subsequent reactions with terminal diamines. *Nano Lett*. 2003 Mar;3(3):331-6.
- [136] Seredych M, Bandosz TJ. Mechanism of ammonia retention on graphite oxides: Role of surface chemistry and structure. *J Phys Chem C*. 2007 Nov;111(43):15596-604.
- [137] Petit C, Bandosz TJ. Enhanced Adsorption of Ammonia on Metal-Organic Framework/Graphite Oxide Composites: Analysis of Surface Interactions. *Advanced Functional Materials*. 2010 Jan;20(1):111-8.
- [138] Slabaugh WH, Seiler BC. INTERACTIONS OF AMMONIA WITH GRAPHITE OXIDE. *Journal of Physical Chemistry*. 1962;66(3):396-8.
- [139] Hanzawa Y, Hatori H, Yoshizawa N, Yamada Y. Structural changes in carbon aerogels with high temperature treatment. *Carbon*. 2002;40(4):575-81.
- [140] Nakajima T, Mabuchi A, Hagiwara R. A NEW STRUCTURE MODEL OF GRAPHITE OXIDE. *Carbon*. 1988;26(3):357-61.
- [141] Stankovich S, Dikin DA, Compton OC, Dommett GHB, Ruoff RS, Nguyen ST. Systematic Post-assembly Modification of Graphene Oxide Paper with Primary Alkylamines. *Chem Mater*. 2010 Jul;22(14):4153-7.
- [142] Hernandez Y, Nicolosi V, Lotya M, Blighe FM, Sun ZY, De S, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotechnology*. 2008 Sep;3(9):563-8.

- [143] Gao W, Alemany LB, Ci LJ, Ajayan PM. New insights into the structure and reduction of graphite oxide. *Nat Chem*. 2009 Aug;1(5):403-8.
- [144] Lai LF, Huang GM, Wang XF, Weng J. Solvothermal syntheses of hollow carbon microspheres modified with -NH₂ and -OH groups in one-step process. *Carbon*. 2010 Sep;48(11):3145-56.
- [145] Gromov A, Dittmer S, Svensson J, Nerushev OA, Perez-Garcia SA, Licea-Jimenez L, et al. Covalent amino-functionalisation of single-wall carbon nanotubes. *Journal of Materials Chemistry*. 2005;15(32):3334-9.
- [146] Waschewsky GCG, Kitchen DC, Browning PW, Butler LJ. COMPETING BOND FISSION AND MOLECULAR ELIMINATION CHANNELS IN THE PHOTODISSOCIATION OF CH₃NH₂ AT 222 NM. *Journal of Physical Chemistry*. 1995 Mar;99(9):2635-45.
- [147] Xu RX, Nettesheim D, Otvos JD, Petering DH. NMR DETERMINATION OF THE STRUCTURES OF PEROXYCOBALT(III) BLEOMYCIN AND COBALT(III) BLEOMYCIN, PRODUCTS OF THE AEROBIC OXIDATION OF COBALT(II) BLEOMYCIN BY DIOXYGEN. *Biochemistry*. 1994 Feb;33(4):907-16.
- [148] Rufford TE, Hulicova-Jurcakova D, Zhu ZH, Lu GQ. Nanoporous carbon electrode from waste coffee beans for high performance supercapacitors. *Electrochem Commun*. 2008 Oct;10(10):1594-7.
- [149] Frackowiak E, Beguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*. 2001;39(6):937-50.
- [150] Frackowiak E. Carbon materials for supercapacitor application. *Physical Chemistry Chemical Physics*. 2007;9(15):1774-85.
- [151] Wu ZS, Wang DW, Ren W, Zhao J, Zhou G, Li F, et al. Anchoring Hydrous RuO₂ on Graphene Sheets for High-Performance Electrochemical Capacitors. *Advanced Functional Materials*. 2010 Oct;20(20):3595-602.
- [152] Hu CC, Tsou TW. Ideal capacitive behavior of hydrous manganese oxide prepared by anodic deposition. *Electrochemistry Communications*. 2002 Feb;4(2):105-9.
- [153] Wang DW, Li F, Zhao JP, Ren WC, Chen ZG, Tan J, et al. Fabrication of Graphene/Polyaniline Composite Paper via In Situ Anodic Electropolymerization for High-Performance Flexible Electrode. *Acs Nano*. 2009 Jul;3(7):1745-52.
- [154] Zhang LL, Zhao SY, Tian XN, Zhao XS. Layered Graphene Oxide Nanostructures with Sandwiched Conducting Polymers as Supercapacitor Electrodes. *Langmuir*. 2010 Nov 16;26(22):17624-8.
- [155] Snook GA, Kao P, Best AS. Conducting-polymer-based supercapacitor devices and electrodes. *Journal of Power Sources*. 2011 Jan;196(1):1-12.
- [156] Tu LL, Jia CY. Conducting Polymers as Electrode Materials for Supercapacitors. *Progress in Chemistry*. 2010 Aug;22(8):1610-8.
- [157] Xu JJ, Wang K, Zu SZ, Han BH, Wei ZX. Hierarchical Nanocomposites of Polyaniline Nanowire Arrays on Graphene Oxide Sheets with Synergistic Effect for Energy Storage. *Acs Nano*. 2010 Sep;4(9):5019-26.
- [158] Wang HL, Hao QL, Yang XJ, Lu LD, Wang X. A nanostructured graphene/polyaniline hybrid material for supercapacitors. *Nanoscale*. 2010;2(10):2164-70.
- [159] Meng CZ, Liu CH, Fan SS. Flexible carbon nanotube/polyaniline paper-like films and their enhanced electrochemical properties. *Electrochemistry Communications*. 2009 Jan;11(1):186-9.
- [160] Girija TC, Sangaranarayanan MV. Analysis of polyaniline-based nickel electrodes for electrochemical supercapacitors. *Journal of Power Sources*. 2006 Jun;156(2):705-11.
- [161] Hu ZA, Xie YL, Wang YX, Mo LP, Yang YY, Zhang ZY. Polyaniline/SnO₂ nanocomposite for supercapacitor applications. *Materials Chemistry and Physics*. 2009 Apr;114(2-3):990-5.

- [162] Gomez H, Ram MK, Alvi F, Villalba P, Stefanakos E, Kumar A. Graphene-conducting polymer nanocomposite as novel electrode for supercapacitors. *Journal of Power Sources*. 2011 Apr;196(8):4102-8.
- [163] Yang NL, Zhai J, Wan MX, Wang D, Jiang L. Layered nanostructures of polyaniline with graphene oxide as the dopant and template. *Synthetic Metals*. 2010 Aug;160(15-16):1617-22.
- [164] Shafeeyan MS, Daud W, Houshmand A, Shamiri A. A review on surface modification of activated carbon for carbon dioxide adsorption. *J Anal Appl Pyrolysis*. 2010 Nov;89(2):143-51.
- [165] Lai LF, Chen LW, Zhan D, Sun L, Liu JP, Lim SH, et al. One-step synthesis of NH(2)-graphene from in situ graphene-oxide reduction and its improved electrochemical properties. *Carbon*. 2011 Aug;49(10):3250-7.
- [166] Loh KP, Bao QL, Eda G, Chhowalla M. Graphene oxide as a chemically tunable platform for optical applications. *Nature Chemistry*. 2010 Dec;2(12):1015-24.
- [167] Pacile D, Papagno M, Rodriguez AF, Grioni M, Papagno L. Near-edge x-ray absorption fine-structure investigation of graphene. *Physical Review Letters*. 2008 Aug;101(6).
- [168] Jeong HK, Colakerol L, Jin MH, Glans PA, Smith KE, Lee YH. Unoccupied electronic states in graphite oxides. *Chemical Physics Letters*. 2008 Jul;460(4-6):499-502.
- [169] Hua WJ, Gao B, Li SH, Agren H, Luo Y. X-ray absorption spectra of graphene from first-principles simulations. *Physical Review B*. 2010 Oct;82(15).
- [170] Abbas G, Papakonstantinou P, Iyer GRS, Kirkman IW, Chen LC. Substitutional nitrogen incorporation through rf glow discharge treatment and subsequent oxygen uptake on vertically aligned carbon nanotubes. *Physical Review B*. 2007 May;75(19).
- [171] Roy SS, McCann R, Papakonstantinou P, Maguire P, McLaughlin JA. The structure of amorphous carbon nitride films using a combined study of NEXAFS, XPS and Raman spectroscopies. *Thin Solid Films*. 2005 Jun;482(1-2):145-50.
- [172] Zhang LS, Liang XQ, Song WG, Wu ZY. Identification of the nitrogen species on N-doped graphene layers and Pt/NG composite catalyst for direct methanol fuel cell. *Phys Chem Chem Phys*. 2010;12(38):12055-9.
- [173] Jansen RJJ, Vanbekkum H. XPS OF NITROGEN-CONTAINING FUNCTIONAL-GROUPS ON ACTIVATED CARBON. *Carbon*. 1995;33(8):1021-7.
- [174] Wu Q, Xu YX, Yao ZY, Liu AR, Shi GQ. Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films. *Acs Nano*. 2010 Apr;4(4):1963-70.
- [175] Zhang K, Zhang LL, Zhao XS, Wu JS. Graphene/Polyaniline Nanoriber Composites as Supercapacitor Electrodes. *Chem Mater*. 2010 Feb 23;22(4):1392-401.
- [176] Kim JH, Sharma AK, Lee YS. Synthesis of polypyrrole and carbon nano-fiber composite for the electrode of electrochemical capacitors. *Mater Lett*. 2006 Jun;60(13-14):1697-701.
- [177] Frackowiak E, Beguin F. Electrochemical storage of energy in carbon nanotubes and nanostructured carbons. *Carbon*. 2002;40(10):1775-87.
- [178] Fang B, Wei YZ, Suzuki K, Kumagai A. Surface modification of carbonaceous materials for EDLCs application. *Electrochimica Acta*. 2005 Jun;50(18):3616-21.
- [179] Lozano-Castello D, Cazorla-Amoros D, Linares-Solano A, Shiraishi S, Kurihara H, Oya A. Influence of pore structure and surface chemistry on electric double layer capacitance in non-aqueous electrolyte. *Carbon*. 2003;41(9):1765-75.
- [180] Bleda-Martinez MJ, Macia-Agullo JA, Lozano-Castello D, Morallon E, Cazorla-Amoros D, Linares-Solano A. Role of surface chemistry on electric double layer capacitance of carbon materials. *Carbon*. 2005 Nov;43(13):2677-84.
- [181] Shen JM, Liu AD, T Y, Foo GS, Yeo CB, Chan-Park MB, et al. How carboxylic groups improve the performance of single-walled carbon nanotube electrochemical capacitors? . *Energy & Environmental Science*. 2011.
- [182] Masarapu C, Zeng HF, Hung KH, Wei BQ. Effect of Temperature on the Capacitance of Carbon Nanotube Supercapacitors. *Acs Nano*. 2009 Aug;3(8):2199-206.

- [183] Abidian MR, Martin DC. Experimental and theoretical characterization of implantable neural microelectrodes modified with conducting polymer nanotubes. *Biomaterials*. 2008 Mar;29(9):1273-83.
- [184] Li X, Rong JP, Wei BQ. Electrochemical Behavior of Single-Walled Carbon Nanotube Supercapacitors under Compressive Stress. *Acs Nano*. 2010 Oct;4(10):6039-49.
- [185] Cuentas-Gallegos AK, Lira-Cantu M, Casan-Pastor N, Gomez-Romero P. Nanocomposite hybrid molecular materials for application in solid-state electrochemical supercapacitors. *Adv Funct Mater*. 2005 Jul;15(7):1125-33.
- [186] Du CS, Pan N. Supercapacitors using carbon nanotubes films by electrophoretic deposition. *J Power Sources*. 2006 Oct;160(2):1487-94.
- [187] Jin X, Zhou W, Zhang S, Chen GZ. Nanoscale microelectrochemical cells on carbon nanotubes. *Small*. 2007 Sep;3(9):1513-7.
- [188] Jurewicz K, Delpeux S, Bertagna V, Beguin F, Frackowiak E. Supercapacitors from nanotubes/polypyrrole composites. *Chemical Physics Letters*. 2001 Oct;347(1-3):36-40.
- [189] Pantea D, Darmstadt H, Kaliaguine S, Blacher S, Roy C. Surface morphology of thermal, furnace and pyrolytic carbon blacks by nitrogen adsorption - Relation to the electrical conductivity. *Rubber Chem Technol*. 2002 Sep-Oct;75(4):691-700.
- [190] Pantea D, Darmstadt H, Kaliaguine S, Summchen L, Roy C. Electrical conductivity of thermal carbon blacks - Influence of surface chemistry. *Carbon*. 2001;39(8):1147-58.
- [191] Ruiz V, Blanco C, Raymundo-Pinero E, Khomenko V, Beguin F, Santamaria R. Effects of thermal treatment of activated carbon on the electrochemical behaviour in supercapacitors. *Electrochimica Acta*. 2007 Apr 20;52(15):4969-73.
- [192] Frackowiak E, Lota G, Machnikowski J, Vix-Guterl C, Beguin F. Optimisation of supercapacitors using carbons with controlled nanotexture and nitrogen content. *Electrochim Acta*. 2006 Feb;51(11):2209-14.
- [193] Shrestha S, Mustain WE. Properties of Nitrogen-Functionalized Ordered Mesoporous Carbon Prepared Using Polypyrrole Precursor. *J Electrochem Soc*. 2010;157(11):B1665-B72.
- [194] Hulicova-Jurcakova D, Seredych M, Lu GQ, Kodiweera N, Stallworth PE, Greenbaum S, et al. Effect of surface phosphorus functionalities of activated carbons containing oxygen and nitrogen on electrochemical capacitance. *Carbon*. 2009 May;47(6):1576-84.
- [195] Pognon G, Brousse T, Demarconnay L, Belanger D. Performance and stability of electrochemical capacitor based on anthraquinone modified activated carbon. *J Power Sources*. 2011 Apr;196(8):4117-22.
- [196] Lin ZY, Liu Y, Yao YG, Hildreth OJ, Li Z, Moon K, et al. Superior Capacitance of Functionalized Graphene. *J Phys Chem C*. 2011 Apr;115(14):7120-5.
- [197] Portet C, Taberna PL, Simon P, Laberty-Robert C. Modification of Al current collector surface by sol-gel deposit for carbon-carbon supercapacitor applications. *Electrochim Acta*. 2004 Mar 1;49(6):905-12.
- [198] Darling RM, Meyers JP. Kinetic model of platinum dissolution in PEMFCs. *Journal of the Electrochemical Society*. 2003 Nov;150(11):A1523-A7.
- [199] Greeley J, Stephens IEL, Bondarenko AS, Johansson TP, Hansen HA, Jaramillo TF, et al. Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. *Nature Chemistry*. 2009 Oct;1(7):552-6.
- [200] Zhang L, Zhang JJ, Wilkinson DP, Wang HJ. Progress in preparation of non-noble electrocatalysts for PEM fuel cell reactions. *Journal of Power Sources*. 2006 Jun;156(2):171-82.
- [201] Maldonado S, Stevenson KJ. Influence of nitrogen doping on oxygen reduction electrocatalysis at carbon nanofiber electrodes. *Journal of Physical Chemistry B*. 2005 Mar;109(10):4707-16.

- [202] Sheng ZH, Shao L, Chen JJ, Bao WJ, Wang FB, Xia XH. Catalyst-Free Synthesis of Nitrogen-Doped Graphene via Thermal Annealing Graphite Oxide with Melamine and Its Excellent Electrocatalysis. *Acs Nano*. 2011 Jun;5(6):4350-8.
- [203] Nallathambi V, Lee JW, Kumaraguru SP, Wu G, Popov BN. Development of high performance carbon composite catalyst for oxygen reduction reaction in PEM Proton Exchange Membrane fuel cells. *J Power Sources*. 2008 Aug;183(1):34-42.
- [204] Biddinger EJ, von Deak D, Ozkan US. Nitrogen-Containing Carbon Nanostructures as Oxygen-Reduction Catalysts. *Topics in Catalysis*. 2009 Oct;52(11):1566-74.
- [205] Kurak KA, Anderson AB. Nitrogen-Treated Graphite and Oxygen Electroreduction on Pyridinic Edge Sites. *Journal of Physical Chemistry C*. 2009 Apr;113(16):6730-4.
- [206] Rao CV, Cabrera CR, Ishikawa Y. In Search of the Active Site in Nitrogen-Doped Carbon Nanotube Electrodes for the Oxygen Reduction Reaction. *Journal of Physical Chemistry Letters*. 2010 Sep;1(18):2622-7.
- [207] Gong KP, Du F, Xia ZH, Durstock M, Dai LM. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science*. 2009 Feb;323(5915):760-4.
- [208] Feng LY, Yan YY, Chen YG, Wang LJ. Nitrogen-doped carbon nanotubes as efficient and durable metal-free cathodic catalysts for oxygen reduction in microbial fuel cells. *Energy & Environmental Science*. 2011 May;4(5):1892-9.
- [209] Byon HR, Suntivich J, Shao-Horn Y. Graphene-Based Non-Noble-Metal Catalysts for Oxygen Reduction Reaction in Acid. *Chemistry of Materials*. 2011 Aug;23(15):3421-8.
- [210] Subramanian NP, Li XG, Nallathambi V, Kumaraguru SP, Colon-Mercado H, Wu G, et al. Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells. *Journal of Power Sources*. 2009 Mar 1;188(1):38-44.
- [211] Luo ZQ, Lim SH, Tian ZQ, Shang JZ, Lai LF, MacDonald B, et al. Pyridinic N doped graphene: synthesis, electronic structure, and electrocatalytic property. *Journal of Materials Chemistry*. 2011;21(22):8038-44.
- [212] Wang P, Wang ZK, Jia LX, Xiao ZL. Origin of the catalytic activity of graphite nitride for the electrochemical reduction of oxygen: geometric factors vs. electronic factors. *Physical Chemistry Chemical Physics*. 2009 Apr;11(15):2730-40.
- [213] Kim H, Lee K, Woo SI, Jung Y. On the mechanism of enhanced oxygen reduction reaction in nitrogen-doped graphene nanoribbons. *Physical Chemistry Chemical Physics*. 2011;13(39):17505-10.
- [214] Jaouen F, Charretier F, Dodelet JP. Fe-based catalysts for oxygen reduction in PEMFCs - Importance of the disordered phase of the carbon support. *Journal of the Electrochemical Society*. 2006;153(4):A689-A98.
- [215] Bagri A, Mattevi C, Acik M, Chabal YJ, Chhowalla M, Shenoy VB. Structural evolution during the reduction of chemically derived graphene oxide. *Nature Chemistry*. 2010 Jul;2(7):581-7.
- [216] Boukhvalov DW, Katsnelson MI. Enhancement of Chemical Activity in Corrugated Graphene. *Journal of Physical Chemistry C*. 2009 Aug;113(32):14176-8.
- [217] Chen Z, Higgins D, Chen ZW. Nitrogen doped carbon nanotubes and their impact on the oxygen reduction reaction in fuel cells. *Carbon*. 2010 Sep;48(11):3057-65.
- [218] Biddinger EJ, Ozkan US. Role of Graphitic Edge Plane Exposure in Carbon Nanostructures for Oxygen Reduction Reaction. *Journal of Physical Chemistry C*. 2010 Sep;114(36):15306-14.
- [219] Ikeda T, Boero M, Huang SF, Terakura K, Oshima M, Ozaki J, et al. Enhanced Catalytic Activity of Carbon Alloy Catalysts Codoped with Boron and Nitrogen for Oxygen Reduction Reaction. *Journal of Physical Chemistry C*. 2010 May;114(19):8933-7.
- [220] Huang SF, Terakura K, Ozaki T, Ikeda T, Boero M, Oshima M, et al. First-principles calculation of the electronic properties of graphene clusters doped with nitrogen and boron:

Analysis of catalytic activity for the oxygen reduction reaction. *Physical Review B*. 2009 Dec;80(23).

[221] Ozaki J, Kimura N, Anahara T, Oya A. Preparation and oxygen reduction activity of BN-doped carbons. *Carbon*. 2007 Aug;45(9):1847-53.

[222] Deng DH, Pan XL, Yu LA, Cui Y, Jiang YP, Qi J, et al. Toward N-Doped Graphene via Solvothermal Synthesis. *Chemistry of Materials*. 2011 Mar;23(5):1188-93.

[223] Gochi-Ponce Y, Alonso-Nunez G, Alonso-Vante N. Synthesis and electrochemical characterization of a novel platinum chalcogenide electrocatalyst with an enhanced tolerance to methanol in the oxygen reduction reaction. *Electrochemistry Communications*. 2006 Sep;8(9):1487-91.

[224] Pattabi M, Castellanos RH, Castillo R, Ocampo AL, Moreira J, Sebastian PJ, et al. Electrochemical characterization of tungsten carbonyl compound for oxygen reduction reaction. *International Journal of Hydrogen Energy*. 2001 Feb;26(2):171-4.

[225] Liu RL, Wu DQ, Feng XL, Mullen K. Nitrogen-Doped Ordered Mesoporous Graphitic Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Angewandte Chemie-International Edition*. 2010;49(14):2565-9.

[226] Jain M, Chou SH, Siedle A. In search for structure of active site in iron-based oxygen reduction electrocatalysts. *J Phys Chem B*. 2006 Mar;110(9):4179-85.

[227] Higgins DHD, Chen Z, Chen ZW. Nitrogen doped carbon nanotubes synthesized from aliphatic diamines for oxygen reduction reaction. *Electrochimica Acta*. 2011 Jan;56(3):1570-5.

[228] Sidik RA, Anderson AB, Subramanian NP, Kumaraguru SP, Popov BN. O₂ reduction on graphite and nitrogen-doped graphite: Experiment and theory. *Journal of Physical Chemistry B*. 2006 Feb 2;110(4):1787-93.

[229] Gasteiger HA, Markovic NM. Just a Dream-or Future Reality? *Science*. 2009 Apr 3;324(5923):48-9.

[230] Ladouceur M, Lalande G, Guay D, Dodelet JP, Dignardbailey L, Trudeau ML, et al. PYROLYZED COBALT PHTHALOCYANINE AS ELECTROCATALYST FOR OXYGEN REDUCTION. *J Electrochem Soc*. 1993 Jul;140(7):1974-81.

[231] Matter PH, Wang E, Ozkan US. Preparation of nanostructured nitrogen-containing carbon catalysts for the oxygen reduction reaction from SiO₂- and MgO-supported metal particles. *Journal of Catalysis*. 2006 Oct;243(2):395-403.

[232] Lefevre M, Proietti E, Jaouen F, Dodelet JP. Iron-Based Catalysts with Improved Oxygen Reduction Activity in Polymer Electrolyte Fuel Cells. *Science*. 2009 Apr;324(5923):71-4.

[233] Choi JY, Hsu RS, Chen ZW. Highly Active Porous Carbon-Supported Nonprecious Metal-N Electrocatalyst for Oxygen Reduction Reaction in PEM Fuel Cells. *Journal of Physical Chemistry C*. 2010 May;114(17):8048-53.

[234] Pietron JJ, Biffinger JC, Qadri SB, Rolison DR. Electrocatalysis at Copoly(difluoropyrrole) electrodeposited on Vulcan carbon supports: demonstration of halogenated polypyrrole as an electrocatalytic material. *Journal of Materials Chemistry*. 2011;21(21):7668-77.

[235] Schulenburg H, Stankov S, Schunemann V, Radnik J, Dorbandt I, Fiechter S, et al. Catalysts for the oxygen reduction from heat-treated iron(III) tetramethoxyphenylporphyrin chloride: Structure and stability of active sites. *J Phys Chem B*. 2003 Aug 28;107(34):9034-41.

[236] Zhang L, Lee K, Bezerra CWB, Zhang JL, Zhang JJ. Fe loading of a carbon-supported Fe-N electrocatalyst and its effect on the oxygen reduction reaction. *Electrochim Acta*. 2009 Nov;54(26):6631-6.

[237] Liang YY, Li YG, Wang HL, Zhou JG, Wang J, Regier T, et al. Co₃O₄ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nature Materials*. 2011 Oct;10(10):780-6.

- [238] Wang X, Zheng WT, Tian HW, Yu SS, Xu W, Meng SH, et al. Growth, structural, and magnetic properties of iron nitride thin films deposited by dc magnetron sputtering. *Appl Surf Sci.* 2003 Dec 30;220(1-4):30-9.
- [239] Raghavan V. C-Fe-N (carbon-iron-nitrogen) *J Phase Equilibria.* 1993;14(5):620-1.
- [240] Y. Ohshima YW, N. Tsubouchi, Y. Ohtsuka. Approach to the iron-catalyzed formation process of N₂ from heterocyclic nitrogen in carbon by use of XRD and XPS methods. *ACS Fuel* 2000 (San Francisco). 2000(45(2)).
- [241] Shi YF, Wan Y, Zhang RY, Zhao DY. Synthesis of self-supported ordered mesoporous cobalt and chromium nitrides. *Advanced Functional Materials.* 2008 Aug 22;18(16):2436-43.
- [242] Shin C, Lee W, Suh Y, Yoon H, Lee Y, Woo W. CAMAR 2.0: Future Direction of Context-Aware Mobile Augmented Reality. 2009 International Symposium on Ubiquitous Virtual Reality (Isuvr 2009). 2009:21-4.
- [243] Lee SH, Kim HW, Hwang JO, Lee WJ, Kwon J, Bielawski CW, et al. Three-Dimensional Self-Assembly of Graphene Oxide Platelets into Mechanically Flexible Macroporous Carbon Films. *Angewandte Chemie-International Edition.* 2010;49(52):10084-8.
- [244] Wu G, Johnston CM, Mack NH, Artyushkova K, Ferrandon M, Nelson M, et al. Synthesis-structure-performance correlation for polyaniline-Me-C non-precious metal cathode catalysts for oxygen reduction in fuel cells. *Journal of Materials Chemistry.* 2011;21(30):11392-405.
- [245] Diekmann W, Panzner G, Grabke HJ. THE BONDING STATE OF NITROGEN SEGREGATED ON Fe(100) AND ON IRON NITRIDES Fe₄N AND Fe₂N. *Surface Science.* 1989 Aug;218(2-3):507-18.
- [246] Souto S, Pickholz M, dos Santos MC, Alvarez F. Electronic structure of nitrogen-carbon alloys (a-CN_x) determined by photoelectron spectroscopy. *Physical Review B.* 1998 Jan;57(4):2536-40.
- [247] Miola EJ, de Souza SD, Nascente PAP, Olzon-Dionysio M, Olivieri CA, Spinelli D. Surface characterisation of plasma-nitrided iron by X-ray photoelectron spectroscopy. *Appl Surf Sci.* 1999 Apr;144-45:272-7.
- [248] Shao YY, Zhang S, Engelhard MH, Li GS, Shao GC, Wang Y, et al. Nitrogen-doped graphene and its electrochemical applications. *Journal of Materials Chemistry.* 2010;20(35):7491-6.
- [249] Ikeda T, Boero M, Huang SF, Terakura K, Oshima M, Ozaki J. Carbon alloy catalysts: Active sites for oxygen reduction reaction. *Journal of Physical Chemistry C.* 2008 Sep 25;112(38):14706-9.
- [250] Zhang JL, Vukmirovic MB, Xu Y, Mavrikakis M, Adzic RR. Controlling the catalytic activity of platinum-monolayer electrocatalysts for oxygen reduction with different substrates. *Angewandte Chemie-International Edition.* 2005;44(14):2132-5.
- [251] Yang SB, Feng XL, Wang XC, Mullen K. Graphene-Based Carbon Nitride Nanosheets as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reactions. *Angewandte Chemie-International Edition.* 2011;50(23):5339-43.
- [252] Jafri RI, Rajalakshmi N, Ramaprabhu S. Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell. *Journal of Materials Chemistry.* 2010;20(34):7114-7.
- [253] Garsuch A, d'Eon R, Dahn T, Klepel O, Garsuch RR, Dahn JR. Oxygen reduction behavior of highly porous non-noble metal catalysts prepared by a template-assisted synthesis route. *J Electrochem Soc.* 2008;155(3):B236-B43.
- [254] Li YG, Tan B, Wu YY. Mesoporous CO₃O₄ nanowire arrays for lithium ion batteries with high capacity and rate capability. *Nano Letters.* 2008 Jan;8(1):265-70.
- [255] Lou XW, Deng D, Lee JY, Feng J, Archer LA. Self-supported formation of needlelike Co₃O₄ nanotubes and their application as lithium-ion battery electrodes. *Advanced Materials.* 2008 Jan;20(2):258-+.

- [256] Li NC, Martin CR. A high-rate, high-capacity, nanostructured Sn-based anode prepared using sol-gel template synthesis. *Journal of the Electrochemical Society*. 2001 Feb;148(2):A164-A70.
- [257] Paek SM, Yoo E, Honma I. Enhanced Cyclic Performance and Lithium Storage Capacity of SnO(2)/Graphene Nanoporous Electrodes with Three-Dimensionally Delaminated Flexible Structure. *Nano Letters*. 2009 Jan;9(1):72-5.
- [258] Kang E, Jung YS, Cavanagh AS, Kim GH, George SM, Dillon AC, et al. Fe(3)O(4) Nanoparticles Confined in Mesocellular Carbon Foam for High Performance Anode Materials for Lithium-Ion Batteries. *Advanced Functional Materials*. 2011 Jul;21(13):2430-8.
- [259] Reddy MV, Yu T, Sow CH, Shen ZX, Lim CT, Rao GVS, et al. alpha-Fe2O3 nanoflakes as an anode material for Li-ion batteries. *Advanced Functional Materials*. 2007 Oct;17(15):2792-9.
- [260] Sun Q, Fu ZW. Vanadium nitride as a novel thin film anode material for rechargeable lithium batteries. *Electrochimica Acta*. 2008 Dec;54(2):403-9.
- [261] Sun Q, Fu ZW. Mn3N2 as a novel negative electrode material for rechargeable lithium batteries. *Applied Surface Science*. 2012 Jan;258(7):3197-201.
- [262] Gillot F, Oro-Sole J, Palacin MR. Nickel nitride as negative electrode material for lithium ion batteries. *Journal of Materials Chemistry*. 2011;21(27):9997-10002.
- [263] Fu ZW, Wang Y, Yue XL, Zhao SL, Qin QZ. Electrochemical reactions of lithium with transition metal nitride electrodes. *Journal of Physical Chemistry B*. 2004 Feb;108(7):2236-44.
- [264] S. H. Elder LHD, F. J. DiSalvo. LiMoN2: The First Metallic Layered Nitride Chemistry of Materials.4:928-37.
- [265] Rowsell JLC, Pralong V, Nazar LF. Layered lithium iron nitride: A promising anode material for Li-ion batteries. *Journal of the American Chemical Society*. 2001 Sep;123(35):8598-9.
- [266] Takeda Y, Nishijima M, Yamahata M, Takeda K, Imanishi N, Yamamoto O. Lithium secondary batteries using a lithium cobalt nitride, Li2.6Co0.4N, as the anode. *Solid State Ionics*. 2000 May;130(1-2):61-9.
- [267] Asahara H, Migita T, Tanaka T, Kawabata K. Microstructure and electrical properties of CoNX thin films deposited by unbalanced magnetron sputtering. *Vacuum*. 2001 Jun 15;62(2-3):293-6.
- [268] Nakatani I, Furubayashi T. Iron-Nitride Magnetic Fluids Prepared by Plasma Cvd Technique and Their Magnetic-Properties. *J Magn Magn Mater*. 1990 Apr;85(1-3):11-3.
- [269] Oda K, Yoshio T, Oda K. Preparation of Co-N Films by Rf-Sputtering. *J Mater Sci*. 1987 Aug;22(8):2729-33.
- [270] Chen D, Tang LH, Li JH. Graphene-based materials in electrochemistry. *Chemical Society Reviews*. 2010;39(8):3157-80.
- [271] Zhang KJ, Wang HB, He XQ, Liu ZH, Wang L, Gu L, et al. A hybrid material of vanadium nitride and nitrogen-doped graphene for lithium storage. *Journal of Materials Chemistry*. 2011;21(32):11916-22.
- [272] Das B, Reddy MV, Malar P, Osipowicz T, Rao GVS, Chowdari BVR. Nanoflake CoN as a high capacity anode for Li-ion batteries. *Solid State Ionics*. 2009 Jul;180(17-19):1061-8.
- [273] Wu YP, Jiang C, Wan C, Holze R. Modified natural graphite as anode material for lithium ion batteries. *Journal of Power Sources*. 2002 Sep;111(2):329-34.
- [274] Xifei Li JL, Yong Zhang, Yongliang Li, Hao Liu, Xiangbo Meng, Jinli Yang, Dongsheng Geng, Dongniu Wang, Ruying Li, Xuiliang Sun. High concentration nitrogen doped carbon nanotube anodes with superior Li+ storage performance for lithium rechargeable battery application. *Journal of Power Sources*. 2012;197:238-45.
- [275] Kim H, Seo DH, Kim SW, Kim J, Kang K. Highly reversible Co(3)O(4)/graphene hybrid anode for lithium rechargeable batteries. *Carbon*. 2011 Jan;49(1):326-32.

- [276] Zhu XJ, Zhu YW, Murali S, Stollers MD, Ruoff RS. Nanostructured Reduced Graphene Oxide/Fe(2)O(3) Composite As a High-Performance Anode Material for Lithium Ion Batteries. *Acs Nano*. 2011 Apr;5(4):3333-8.
- [277] Wang DH, Kou R, Choi D, Yang ZG, Nie ZM, Li J, et al. Ternary Self-Assembly of Ordered Metal Oxide-Graphene Nanocomposites for Electrochemical Energy Storage. *Acs Nano*. 2010 Mar;4(3):1587-95.
- [278] Park S, Hu YC, Hwang JO, Lee ES, Casabianca LB, Cai WW, et al. Chemical structures of hydrazine-treated graphene oxide and generation of aromatic nitrogen doping. *Nat Commun*. 2012 Jan;3.
- [279] Xiang HF, Zhang K, Ji G, Lee JY, Zou CJ, Chen XD, et al. Graphene/nanosized silicon composites for lithium battery anodes with improved cycling stability. *Carbon*. 2011 Apr;49(5):1787-96.
- [280] Zhou GM, Wang DW, Li F, Zhang LL, Li N, Wu ZS, et al. Graphene-Wrapped Fe(3)O(4) Anode Material with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries. *Chem Mater*. 2010 Sep;22(18):5306-13.
- [281] Ji ZY, Shen XP, Song Y, Zhu GX. In situ synthesis of graphene/cobalt nanocomposites and their magnetic properties. *Materials Science and Engineering B-Advanced Functional Solid-State Materials*. 2011 May;176(9):711-5.
- [282] Bulusheva LG, Okotrub AV, Kurennya AG, Zhang HK, Zhang HJ, Chen XH, et al. Electrochemical properties of nitrogen-doped carbon nanotube anode in Li-ion batteries. *Carbon*. 2011 Oct;49(12):4013-23.
- [283] Tartaj P, Amarilla JM. Iron oxide porous nanorods with different textural properties and surface composition Preparation, characterization and electrochemical lithium storage capabilities. *Journal of Power Sources*. 2011 Feb;196(4):2164-70.
- [284] Zhu XJ, Zhu YW, Murali S, Stollers MD, Ruoff RS. Nanostructured Reduced Graphene Oxide/Fe₂O₃ Composite As a High-Performance Anode Material for Lithium Ion Batteries. *Acs Nano*. 2011 Apr;5(4):3333-8.
- [285] Zou YQ, Wang Y. NiO nanosheets grown on graphene nanosheets as superior anode materials for Li-ion batteries. *Nanoscale*. 2011;3(6):2615-20.
- [286] Xing LL, Cui CX, Ma CH, Xue XY. Facile synthesis of alpha-MnO₂/graphene nanocomposites and their high performance as lithium-ion battery anode. *Materials Letters*. 2011 Jul;65(14):2104-6.
- [287] Ding SJ, Chen JS, Luan DY, Boey FYC, Madhavi S, Lou XW. Graphene-supported anatase TiO₂ nanosheets for fast lithium storage. *Chem Commun*. 2011;47(20):5780-2.
- [288] Zhang HX, Feng C, Zhai YC, Jiang KL, Li QQ, Fan SS. Cross-Stacked Carbon Nanotube Sheets Uniformly Loaded with SnO₂ Nanoparticles: A Novel Binder-Free and High-Capacity Anode Material for Lithium-Ion Batteries. *Adv Mater*. 2009 Jun;21(22):2299-+.
- [289] Kang E, Jung YS, Kim GH, Chun J, Wiesner U, Dillon AC, et al. Highly Improved Rate Capability for a Lithium-Ion Battery Nano-Li₄Ti₅O₁₂ Negative Electrode via Carbon-Coated Mesoporous Uniform Pores with a Simple Self-Assembly Method. *Advanced Functional Materials*. 2011 Nov;21(22):4349-57.
- [290] Geim AK. Graphene: Status and Prospects. *Science*. 2009 Jun;324(5934):1530-4.
- [291] Shao YY, Wang J, Wu H, Liu J, Aksay IA, Lin YH. Graphene Based Electrochemical Sensors and Biosensors: A Review. *Electroanalysis*. 2010 May;22(10):1027-36.
- [292] Pumera M. Graphene-based nanomaterials for energy storage. *Energy & Environmental Science*. 2011 Mar;4(3):668-74.
- [293] Liu H, Huang J, Li X, Liu J, Zhang Y, Du K. Flower-like SnO₂/graphene composite for high-capacity lithium storage. *Appl Surf Sci*. 2012;258(11):4917-21.
- [294] Chen JS, Wang ZY, Dong XC, Chen P, Lou XW. Graphene-wrapped TiO(2) hollow structures with enhanced lithium storage capabilities. *Nanoscale*. 2011;3(5):2158-61.

- [295] Tian L, Zhuang Q, Li J, Wu C, Shi Y, Sun S. The production of self-assembled Fe₂O₃-graphene hybrid materials by a hydrothermal process for improved Li-cycling. *Electrochim Acta*. 2012;65:153-8.
- [296] Wang HL, Cui LF, Yang YA, Casalongue HS, Robinson JT, Liang YY, et al. Mn(3)O(4)-Graphene Hybrid as a High-Capacity Anode Material for Lithium Ion Batteries. *J Am Chem Soc*. 2010 Oct;132(40):13978-80.
- [297] Mai YJ, Shi SJ, Zhang D, Lu Y, Gu CD, Tu JP. NiO-graphene hybrid as an anode material for lithium ion batteries. *J Power Sources*. 2012;204:155-61.
- [298] Kim H, Seo DH, Kim SW, Kim J, Kang K. Highly reversible Co₃O₄/graphene hybrid anode for lithium rechargeable batteries. *Carbon*. 2011 Jan;49(1):326-32.
- [299] Li BJ, Cao HQ, Shao J, Li GQ, Qu MZ, Yin G. Co₃O₄@graphene Composites as Anode Materials for High-Performance Lithium Ion Batteries. *Inorg Chem*. 2011 Mar 7;50(5):1628-32.
- [300] Tao L, Zai J, Wang K, Zhang H, Xu M, Shen J, et al. Co₃O₄ nanorods/graphene nanosheets nanocomposites for lithium ion batteries with improved reversible capacity and cycle stability. *J Power Sources*. 2012;202:230-5.
- [301] Wang B, Wang Y, Park J, Ahn H, Wang G. In situ synthesis of Co₃O₄/graphene nanocomposite material for lithium-ion batteries and supercapacitors with high capacity and supercapacitance. *Journal of Alloys and Compounds*. 2011;509(29):7778-83.
- [302] Zhang P, Guo ZP, Huang Y, Jia D, Liu HK. Synthesis of Co₃O₄/Carbon composite nanowires and their electrochemical properties. *J Power Sources*. 2011;196(16):6987-91.
- [303] Lian PC, Zhu XF, Liang SZ, Li Z, Yang WS, Wang HH. Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries. *Electrochim Acta*. 2010 Apr;55(12):3909-14.
- [304] Radhakrishnan G, Cardema JD, Adams PM, Kim HI, Foran B. Fabrication and Electrochemical Characterization of Single and Multi-Layer Graphene Anodes for Lithium-Ion Batteries. *J Electrochem Soc*. 2012;159(6):A752-A61.
- [305] Wu ZS, Ren WC, Xu L, Li F, Cheng HM. Doped Graphene Sheets As Anode Materials with Superhigh Rate and Large Capacity for Lithium Ion Batteries. *Acs Nano*. 2011 Jul;5(7):5463-71.
- [306] Wang XM, Naito H, Sone Y, Segami G, Kuwajima S. New additives to improve the first-cycle charge-discharge performance of a graphite anode for lithium-ion cells. *J Electrochem Soc*. 2005;152(10):A1996-A2001.
- [307] Yoon S, Kim H, Oh SM. Surface modification of graphite by coke coating for reduction of initial irreversible capacity in lithium secondary batteries. *Journal of Power Sources*. 2001 Feb;94(1):68-73.
- [308] Wang GX, Shen XP, Yao J, Park J. Graphene nanosheets for enhanced lithium storage in lithium ion batteries. *Carbon*. 2009 Jul;47(8):2049-53.
- [309] Bai S, Shen X. Graphene-inorganic nanocomposites. *Rsc Adv*. 2012;2(1):64.
- [310] Stoner BR, Raut AS, Brown B, Parker CB, Glass JT. Graphenated carbon nanotubes for enhanced electrochemical double layer capacitor performance. *Appl Phys Lett*. 2011 Oct 31;99(18).
- [311] Lai LF, Yang HP, Wang L, Teh BK, Zhong JQ, Chou H, et al. Preparation of Supercapacitor Electrodes through Selection of Graphene Surface Functionalities. *Acs Nano*. 2012 Jul;6(7):5941-51.
- [312] Yang DQ, Sacher E. A spectroscopic study of CN_x formation by the keV N-2(+) irradiation of highly oriented pyrolytic graphite surfaces. *Surf Sci*. 2003 May 20;531(2):185-98.
- [313] Li WY, Xu LN, Chen J. Co₃O₄ nanomaterials in lithium-ion batteries and gas sensors. *Adv Funct Mater*. 2005 May;15(5):851-7.

[314] Yang SB, Feng XL, Ivanovici S, Mullen K. Fabrication of Graphene-Encapsulated Oxide Nanoparticles: Towards High-Performance Anode Materials for Lithium Storage. *Angew Chem Int Edit*. 2010;49(45):8408-11.