Synthesis, structural and electrochemical study of graphene-based materials for lithium-oxygen batteries

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS, STRUCTURAL AND
ELECTROCHEMICAL STUDY OF
GRAPHENE-BASED MATERIALS
FOR LITHIUM-OXYGEN BATTERIES**

ZHANG WENYU

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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2014

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ABSTRACT

Due to the crisis of conventional fossil fuels, the need of new generation of green power sources is increasing nowadays. Graphene-based materials have been fervidly studied in the realm of energy storage systems because of its high flexibility, electrical conductivity and low cost. Li-O₂ batteries are attracting more and more interest around the world because of their high capacity. In this work, graphene-based materials is prepared and studied for LOBs.

First, a novel method is proposed to prepare bind-free graphene foams as O₂ electrodes for Li-O₂ batteries. The graphene foams are synthesized by electrochemical leavening of the graphite papers, followed by annealing in inert gas to control the amounts of the structural defects of the graphene foams. It was found that the structural defects were detrimental to the processes of the ORR and OER in Li-O₂ batteries. The round-trip efficiencies and the cycling stabilities of the graphene foams were undermined by the structural defects. For example, the as-prepared graphene foam with a high defect level ($I_D/I_G=0.71$) depicted a round-trip efficiency of only 0.51 and a 20th-cycle discharge capacity of only 340 mAh g⁻¹ at a current density of 100 mA g⁻¹. By contrast, the graphene foam electrode annealed at 800 °C with $I_D/I_G=0.07$ delivered a round-trip efficiency of up to 80 % with a stable discharge voltage at ~2.8 V and a stable charge voltage below 3.8 V for 20 cycles. According to the analysis on the electrodes after 20 cycles, the structural defects led to the quickened decay of the graphene foams and the boosted formation of the side products.

Besides, an electrochemical method is proposed to synthesize transition metal oxides/graphene composites. The method combines electrochemical deposition of redox active materials and exfoliation of graphene in one step. Fe₂O₃ nanoclusters decorated graphene (Fe₂O₃/graphene) hybrids with controlled contents of Fe₂O₃ were prepared by this

process. These $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrids were tested as O_2 electrodes for Li- O_2 batteries, which exhibited enhanced discharge capacities as compare that of pure graphene based O_2 electrode, e.g. the $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode with 29.0 wt% of Fe_2O_3 delivered a discharge capacity of 8290 mAh g^{-1} as compared to 5100 mA h g^{-1} for pure graphene electrode. The excellent electrochemical properties of $\text{Fe}_2\text{O}_3/\text{graphene}$ as O_2 electrodes is ascribed to the combination of the fast kinetics of electron transport provided by the graphene sheets and the high electrocatalytic activities for O_2 reduction provided by the Fe_2O_3 .

Finally, metallopolymer nanowalls were prepared through a simple wet-chemical process using reduced graphene oxides as heterogeneous nucleation aids, which also help to form conductive electron paths. The nanowalls grow vertically on graphene surface with 100-200 nm in widths and ~ 20 nm in thickness. The Fe-based metallopolymer nanowall based electrode shows best performance as O_2 cathode for Li- O_2 batteries exhibiting high round-trip efficiencies and stable cycling. The electrode delivers discharge-charge capacities of 1000 mAh/g for 40 cycles and maintains round-trip efficiencies $>78\%$ at 50 mA/g . The 1st-cycle round-trip efficiencies are 79 %, 72 % and 65 % at current densities of 50, 200 and 400 mA/g , respectively. The NMR analysis of the Fe-based metallopolymer based electrode after 40 cycles reveals slow formation of the side products of $\text{CH}_3\text{CO}_2\text{Li}$ and HCO_2Li .

The novelties and significant progress in terms of science and technologies in the main work (Chapter 4) of this thesis are summarized as the following. In the 1st section of Chapter 4, a novel electrochemical leavening strategy followed by annealing to produce graphene foams with small amounts of defects/functionalities is developed. The correlation between the amounts of defects/functionalities of graphene and the electrochemical performance of LOBs is studied and interpreted. In the 2nd part of Chapter 4, a novel electrochemical method to synthesize $\text{Fe}_2\text{O}_3/\text{graphene}$ composites is developed. This method exhibits much improved efficiencies to produce graphene-based composites in comparison to

the conventional approaches. Another original contribution in the field of LOBs is that the contents of Fe_2O_3 in the composites are studied and correlated to the electrochemical performance of LOBs. In the 3rd section of Chapter 4, metallopolymer/graphene composites with novel morphologies are synthesized. An original strategy to improve the performance of LOBs is proposed: altering the architecture/morphologies of the electrode materials. The above-mentioned materials exhibit outstanding properties as cathodes of LOBs in comparison to the conventional electrodes for air/oxygen batteries, e.g. precious metals/amorphous carbons, which are reported in the literatures. Therefore, the graphene-based composite materials are promising candidates for LOBs due to the low cost and high performance.

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CHAPTER 1: INTRODUCTION

1.1 Background

Most of human activities involve the usage of various energy resources. Fossil fuels, e.g. gasoline, coals and fuel gas, are still the most popular energy resources at present. The disadvantages of fossil fuels include low efficiency and heavy pollution. Hence electrical energy is going to replace fossil fuels gradually in future. Different types of energy have been converted to electricity, e.g. water power, wind power, thermal power, nuclear energy, solar power, etc. These different energy resources satisfy the daily need of our life. However, electrical devices must be connected to power grid to utilize electricity directly, e.g. industrial and domestic equipments. Therefore new portable energy storage and conversion systems have been developed for portable electrical devices, e.g. cell phones and laptops. In comparison to other new generation energy storage and conversion systems, e.g. fuel cells and supercapacitors, batteries prevail in terms of large specific capacities.

In 1859, lead-acid batteries were invented as the 1st battery system with PbO_2 and Pb electrodes. The specific gravimetric capacity of lead-acid batteries is ~ 50 Wh/kg with a discharge voltage of ~ 2 V. By contrast, the specific capacity of commercial Li-ion batteries is ~ 150 Wh/kg with a high voltage of ~ 3.6 V. The development of battery systems has experienced a sluggish advancement over the past 150 years with annual increase of ~ 0.735 % in specific capacities. However, lead-acid, Ni-Cd and Ni-MH batteries are still widely used in today's market. Moreover, there are some issues in the application of Li-ion batteries, e.g. safety concerns, poor performance at elevated/low temperatures, high cost, etc. Much effort is being made to solve these problems.

At the same time, researchers are searching for battery systems with high performance. Although the electrochemical potentials of all kinds of electrodes can be calculated based on electrochemistry, it is hard to realize all battery systems because of technological issues, e.g. the limited electrochemical windows of electrolytes. With the breakthrough on the electrolytes improvement, recent studies show that Li-S and Li-O₂ batteries (LOBs) exhibit ultrahigh theoretical specific capacities of ~ 2500 and ~ 3500 Wh/kg, respectively. [1] It is worth noting that the theoretical energy capacity of LOBs is almost identical to gasoline, enabling them to be promising candidates as the next generation of power sources. Nevertheless, there are still many problems for the industrialization of these new systems, e.g. the dissolution of polysulfides in Li-S batteries and the byproducts in LOBs. More details about LOBs will be covered in later discussions.

1.2 Literature Review

1.2.1 The fundamentals of Li-O₂ batteries

A typical battery consists of an anode, an electrolyte and a cathode. When a reaction takes place at the interface between an electrolyte and an electrode, the free energy decrease can be expressed as

$$\Delta G^0 = -nFE^0$$

where F is Faraday constant (~ 96500 C/mol), n is the number of electrons involved in the reaction and E^0 is the standard potential. The voltage of a battery is the difference between the potentials of the anode and the cathode.

Another important equation in electrochemistry is the well-known Nernst equation:

$$E_{red} = E_{red}^* - \frac{RT}{zF} \ln \frac{a_{Red}}{a_{Ox}}$$

where E_{red} is the actual reduction potential, E_{red}^* is the standard reduction potential, R is the gas constant ($\sim 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), F is the Faraday constant ($\sim 96500 \text{ C mol}^{-1}$), z is the number of electrons transferred in mole, a_{Red} is the activity of the reductant and a_{Ox} is the activity of the oxidant.

An LOB is comprised of a lithium metal anode, an electrolyte or hybrid electrolytes and an O_2 cathode. For now, LOBs can be divided into three categories in terms of electrolytes: aprotic LOBs with organic electrolytes, aqueous LOBs with special protection on the anode and aqueous electrolytes on the cathode and solid state LOBs with solid electrolytes.

As one lithium atom can give one electron (96500 C/mol), the theoretical capacity of lithium metal is

$$\frac{96500 \text{ C/mol}}{7 \text{ g/mol}} = \frac{96500 \text{ C}}{7 \text{ g}} = \frac{96500 \text{ A.s}}{7 \text{ g}} = \frac{96500 * 1000 \text{ mA} * \frac{1}{3600} \text{ h}}{7 \text{ g}} = 3830 \text{ mAh/g}$$

During the discharge process of LOBs, oxygen diffuses to the cathode first through the electrolyte. Then oxygen is adsorbed by the cathode and reduced. Li ions react with desorbed reduced oxygen to form the discharge products. During the charge process, the discharge products are oxidized to evolve oxygen. Then oxygen is desorbed and diffuses to environment.

In electrochemistry, the Butler-Volmer equation is often used to describe the electrocatalysis process:

$$i = i_0 \left[e^{\frac{\overleftarrow{\gamma} F \eta}{RT}} - e^{\frac{\overrightarrow{\gamma} F \eta}{RT}} \right]$$

where i_0 is the exchange current density (10^{-9} - 10^{-11} A cm⁻² for oxygen reduction reaction and oxygen evolution reaction), η is the overpotential, $\frac{\leftarrow}{\gamma}$ is the backward charge transfer coefficient and $\frac{\rightarrow}{\gamma}$ is the forward charge transfer coefficient. The exchange current density is the current in the absence of net electrolysis and at zero overpotential. It depends on the electrode, e.g. the structure and the physical parameters (e.g. surface roughness). In addition, the adsorbed species on the electrode surface also affect the exchange current density. [2] This explains why the exchange current density covers a range of values instead of a specific number.

The overpotential in the Butler-Volmer equation can be caused by the charge transfer process (at low current densities) or by the mass transfer process (at high current densities). It is critical to note that the exchange current density of oxygen reduction reaction and oxygen evolution reaction is very small. The overpotential is caused by the sluggish charge transfer for LOBs. Therefore catalysts are employed to enhance the exchange current density. The π orbital in oxygen overlaps with the empty orbital of the center of the catalysts, leading to the weakened O=O bond in oxygen. The occupied orbital of the catalysts interacts with the π^* orbital in oxygen, resulting in the adsorption of oxygen. [2]

The effects of the electrocatalysts include two aspects. One is the heat of adsorption, e.g. the bonding energy between the electrocatalysts and oxygen. If the bonding strength is high, oxygen can be easily adsorbed. But the following desorption will be hard. On the contrary, if the bonding strength is low, the adsorption process can be hard and the desorption can be easy. [3] Therefore, the bonding energy of the catalysts with oxygen must be balanced. The other effect is that the catalysts will affect the double layer structure of the electrodes.

There is a voltage drop on the catalysts and the potential at the interface between the catalysts and oxygen will be changed in comparison to that without the catalysts.

For LOBs, the discharge voltage and the charge voltage are

$$U_D = E - \eta_D$$

$$U_C = E - \eta_C$$

, respectively, where U_D is the discharge voltage, U_C is the charge voltage, E is the electromotive force (theoretical voltage), η_D is the overpotential during discharge and η_C is the overpotential during charge.

The testing protocols of LOBs include two models. One model is the discharge depth of 100% at ~2 V (vs. Li). This protocol leads to the formation of a large amount of discharge products. In this circumstance, the cathode covered with discharge products will be nearly electrically insulating. Thus the charge voltage will be elevated significantly due to the high resistance overpotential and the components inside LOBs will be damaged or destroyed under high anodic voltages. The other model is to limit the discharge capacity. A small amount of discharge products can be formed in this case and the cathode can be recharged with moderate overpotentials.

1.2.2 Configurations and stability issues

At present, there are four kinds of architectures of LOBs with the use of lithium metal anode. [1] Today's anode materials for Li-ion batteries (LIBs) can be used as anodes for LOBs. Lithium-free anodes for LIBs must be lithiated before used for LOBs. Moreover, to provide plenty Li ions for battery cycling, the anodes must be used in large quantity. Although the presence of lithium metal arouses the safety concern of industrial applications

of LOBs, this simplifies the assembly of LOBs in scientific labs. The four types of constructions are aprotic, aqueous, solid state and mixed aqueous/aprotic LOBs (**Figure 1. 1**). The aprotic LOB uses aprotic electrolyte, e.g. ethylene carbonate, propylene carbonate, tetrahydrofuran, dimethylether. [4] Another possible model of LOBs consists of lithium metal anode with artificial interface, aqueous electrolyte and O₂ cathode. The artificial interface on lithium metal prevents contamination of O₂. However, no reports have been published using this model. The other two configurations both apply solid state electrolytes, i.e. glass ceramic and gel electrolytes. Examples of glass ceramic and gel electrolytes are the LISICON made by Ohara, Japan [5] and Zhou et al. [6] Glass ceramic makes it feasible to use aqueous electrolytes, which can dissolve discharge products and increase the specific capacity of LOBs. But the poor mechanical properties and high cost remain as key challenges. Especially, the high brittleness adds to the safety concern because the contact between lithium metal and water could cause unexpected incidents. In addition, gel electrolytes shrink after evaporation of solvents and lead to handling issues. Therefore, aprotic LOBs are the most popular due to their simple constructions, high safety and low cost.

Figure 1. 1 Four types of Li-air batteries with the use of lithium metal anode.[1] *Reprinted with permission from Ref. 1. Copyright 2010, American Chemical Society.*

The choice of electrolytes for the aprotic LOBs has been a major issue for a long time. The works at the early stage of LOBs used carbonate-based electrolytes (ethylene carbonate, propylene carbonate and dimethyl carbonate). [7-10] The skeletal formulas of the three compounds are shown in **Figure 1. 2**. But the highly oxidative environment of LOBs makes these electrolytes unstable. During discharge/charge processes, they decompose to generate much lithium-contained carbonate, which deposits on the oxygen electrode. **Figure 1. 3** shows the proposed process of the decomposition of alkyl carbonate electrolytes. [11, 12] Ether-based electrolytes have been proved to be more stable than carbonate-based electrolytes. [13] The discharge product, Li_2O_2 , is confirmed by the XRD patterns and

lithium carbonate is not detected. The ether-based electrolytes are demonstrated to be stable below 4.38 V (versus Li).

Figure 1. 2 Skeletal formula of (a) ethylene carbonate, (b) propylene carbonate and (c) dimethyl carbonate.

Figure 1. 3 Proposed process of the decomposition of alkyl carbonate electrolytes. [10]

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Apart from the decomposition of carbonate-based electrolytes, carbon in oxygen electrodes also causes stability concern for non-aqueous LOBs. A study using dimethyl sulphoxide (DMSO, boiling point: 189 °C **Figure 1. 4a**) and tetraethylene glycol dimethyl ether (TEGDME, boiling point: 275 °C, **Figure 1. 4b**) as the electrolytes showed that carbon decomposed above 3.5 V to form lithium carbonate. [14]

Figure 1. 4 Skeletal formulas of (a) DMSO and (b) TEGDME.

There are two sources of oxygen: pure oxygen and air. Pure oxygen is now widely used because air can lead to the formation of side products, e.g. carbonates, hydroxides or basic carbonates, which is caused by moisture and carbon dioxide in air. These side products are not electrochemically reversible and impair the electrochemical performance of LOBs or lithium-air batteries (LABs). However, researchers have found that some organic membranes can successfully eliminate moisture and carbon dioxide from air and let oxygen pass through. [15]

1.2.3 Electrochemistry

For aqueous and mixed aqueous/aprotic LOBs, the reaction takes place at the cathode is

For aprotic LOBs, the reaction is

Some studies have consented that the reaction consists of some steps [16]

In this case, LiO_2 is the first reduction product and quickly decomposes to form Li_2O_2 by self-disproportionation due to its high instability.

Other studies suggest different steps [16]

Some researchers think that further reduction of Li_2O_2 to LiO_2 can occur. But there is little support on the formation of LiO_2 .

In summary, oxygen is reduced to form LiO_2 , which is converted to Li_2O_2 via self-disproportionation or further reduction.

1.2.4 Challenges

LOBs are still on their preliminary stage although Li-ion batteries have been commercialized for more than 30 years. To fabricate LOBs that can be industrialized for wide applications, scientists have to overcome many problems, some of which are inevitable and terribly serious.

For the non-aqueous LOBs, the use of lithium metal anode adds problems, e.g. lithium dendrite and safety issues. The requirements of the electrolytes include stability, conductivity, volatility and oxygen solubility, diffusivity. The cathodes should be highly catalytic to oxygen reactions.

For the aqueous LOBs, the requirements of the anodes and the cathodes are the same as the non-aqueous LOBs. The aqueous LOBs apply mixed electrolytes, i.e. aqueous and solid state electrolytes. The solubility of LiOH in water is limited and excessive LiOH can precipitate on the cathode and block the pores of electrodes. In addition, LiOH can also

deposit on the LISICON glass ceramics. Besides, poor mechanical properties and instability in the electrolytes of LISICON require improvement.

1.2.5 The oxygen electrode materials

Although LOBs are just on their incipient stage, the oxygen electrode materials should meet the following requirements as other energy storage systems:

- 1) Low/high intercalation potentials for anodes/cathodes to get high voltages.
- 2) Large amount of Li ions can be reversibly stored/extracted into electrodes to get high capacities.
- 3) Minimal crystal structure change to get good cyclability.
- 4) Smooth conversion potentials during charge and discharge.
- 5) Good electrical and ionic conductivity for low polarization and high performance.
- 6) Low cost and environmentally friendly.

Unlike other energy storage systems, there are some new concepts for LOBs. The round-trip efficiency, which is also called the energy efficiency, is introduced to evaluate the electrochemical performance of oxygen electrodes. The round-trip efficiency is defined as the ratio between the discharge energy and the charge energy and sometimes can be calculated simply as the ratio between the discharge voltage and the charge voltage. The round-trip efficiency shows how much energy is effectively released and how much is wasted during battery performance test. Normally, the round-trip efficiency of LOBs is 60-70 %. In comparison, commercial LIBs always deliver a high energy efficiency of higher than 99 %. It is known that small currents can be used for charging to avoid high overpotentials. Even though small currents are used for LOBs, the round-trip efficiency is still very low. The low

energy efficiency of LOBs can be explained in terms of the sluggish kinetics of oxygen reactions. During a typical discharge process, electrons are transferred to the oxygen electrode and accepted by oxygen. But the rate of electron transfer is much higher than that of oxygen reception to electrons. So electrons accumulate on the electrode and lower the potential of the electrode. Thus the discharge voltage of LOBs is reduced. During the charge process, electrons are quickly transferred to the anode once released from Li_2O_2 . Therefore the accumulation of Li^+ ions increases the electrode potential and the overall charging voltage. In addition, the low conductivity of Li_2O_2 adds to the internal impedance of LOBs, which also elevates the charging overpotential.

During the discharge processes of the non-aqueous LOBs, oxygen is reduced to form Li_2O_2 , which deposits on the oxygen electrodes and slows the further discharge reaction due to its low electrical conductivity. For both the non-aqueous and the aqueous LOBs, the oxygen electrodes need to provide a convenient path for electron transfer, Li ion transfer, O_2 diffusion and buffer space for $\text{Li}_2\text{O}_2(\text{solid})/\text{O}_2(\text{gas})$ conversion. To facilitate the discharge reaction, materials with high conductivity and surface area are always adopted as the oxygen electrodes. Carbon-based materials are widely studied due to their low mass density. Therefore the oxygen electrodes are usually prepared by mixing catalysts with carbon, e.g. super-p, Vulcan or carbon nanotubes. In LOBs, carbon works as a conductive additive (**Figure 1. 5**).

Figure 1. 5 The construction of a Li-O₂ battery. [9] *Reprinted with permission from Ref. 9. Copyright 2008, John Wiley & Sons, Inc.*

Noble metal-based electrodes without carbon have been also applied and depicted high catalytic performance for LOBs [17] although the capacities are much lower than carbon-based electrodes due to the high mass density. The addition of mediators in electrolytes [18] have also been studied and improved the battery performance. However, a detailed study on the mechanism of mediators should be performed. The carbon-free noble metal-based electrodes and mediators remain yet to be accepted and investigated by scientists around the world.

So far, the popular catalysts for LOBs are transition metal oxides [8-10], spinels [19, 20], perovskites [21, 22], and noble metals[23, 24]. Other kinds of catalysts have also been tried out on LOBs.[25]

1.2.5.1 Transition metal oxides

The transition metals and their compounds have catalytic activities due to their multiple oxidation states and their ability to form complexes. They can chemically adsorb

oxygen with the formation of chemical bonds and weaken the bonds inside oxygen, which lowers the activation energy.

The first work on LOBs within the last decade used commercial MnO_2 as the catalyst. [7] The oxygen electrode with the catalyst exhibited better performance than the pure carbon electrode. The LOB could be cycled for 50 cycles although the discharge capacity faded fast from 1000 mAh/g to ~600 mAh/g at 70 mA/g. This is the first time an LOB can deliver much higher capacity than LIBs. Not too long after this work, the researchers from the same group studied the electrochemical performance of MnO_2 with various phases and morphologies (**Figure 1. 6**). [9] They compared bulk and nanowire-shaped MnO_2 with α , β and γ phases. The α - MnO_2 nanowires were prepared by acid treatment of LiMn_2O_4 . The α - MnO_2 nanowires exhibited highest discharge capacity and best cycling performance. The discharge capacity was up to 3000 mAh/g in the 1st cycle and decreased to ~1500 mAh/g in the 10th cycle. The discharge voltage was ~2.75 V and the charge voltage was ~4 V with a round-trip efficiency of ~68.8 %. To improve the cycling performance, the cycling capacities were restricted at certain values. For example, the discharge capacity could be steadily delivered when cycling capacity was fixed at 1980 mAh/g. This is because a deep discharge generated much discharge products (Li_2O_2), which increased the electrical impedance of the electrodes and so elevated the overpotential during the following charging process. The restriction on the cycling capacity reduced the formation of Li_2O_2 and the charging overpotential. The low charging overpotential reduced the possibility of the decomposition of the electrolytes. Therefore the cycling stability was improved.

Figure 1. 6 The TEM and SEM images of α -MnO₂ wires, α -MnO₂ bulk, β -MnO₂ wires and β -MnO₂ bulk. [9] Reprinted with permission from Ref. 9. Copyright 2008, John Wiley & Sons, Inc.

Ti containing MnO₂ hollow structures were studied and tested for Li-air batteries in a previous study (**Figure 1. 7**). [10] The samples were prepared in a precipitation method. Ti existed in the MnO₂ structures in the form of simple substance. No titanium oxides were detected in the Raman spectra and the XRD patterns. The sample electrodes delivered a discharge capacity of 1800-2400 mAh/g. This work provided a convenient method to synthesized MnO₂ hollow structures. However, it didn't provide sufficient information about the electrochemical characterization of the samples. The catalytic activity of the samples couldn't be testified.

Figure 1. 7 SEM image of Ti containing MnO₂ hollow structures. [8] *Reprinted with permission from Ref. 8. Copyright 2010, John Wiley & Sons, Inc.*

RuO₂ is another popular catalyst for oxygen reactions. RuO₂/reduced graphene oxide (rGO) [26] and RuO₂/CNT [27] exhibited very low charge voltage of ~3.5 V even at a current density of 100 mA/g (**Figure 1. 8**). The NMR spectra showed no indication of side products. This was because the electrolyte was very stable under the low charge voltage. Moreover, the RuO₂ coating layer with a thickness of ~4 nm on CNTs separated CNTs from the electrolyte and hence suppressed the generation of side products, which were deemed to be relevant to the oxidation of carbon in the electrode. In addition, RuO₂/rGO presented superior properties than Ru/rGO and pure rGO, indicating the oxidation states of Ru affected the catalytic activity.

Figure 1. 8 (a) Schematic diagram of a CNT@RuO₂ nanowire. (b) Electrochemical performance of the CNT@RuO₂ nanowire electrode. [27] *Reprinted with permission from Ref. 27. Copyright 2013, John Wiley & Sons, Inc.*

1.2.5.2 Metal-N composites

Metallopolymers are promising catalysts for ORR. Metallopolymers consist of metal ions or complexes linked by organic ligands. The metal-N bonding is considered to be the active site. Co-polypyrrole composite was prepared for fuel cells. [28] The material was synthesized by wet chemistry at low temperature. Co ions were linked with N in the pyrrole structure. Polypyrrole was a one dimensional chain. A two dimensional network formed with the incorporation of Co. The oxidation state of Co was between 0 to +2. Fuel cell tests exhibited that the cell voltage with Co-polypyrrole was much higher than Co metal catalyst, indicating the high catalytic activity of Co-polypyrrole. Other studies have been carried out on different molecules. [29-32]

1.2.5.3 Graphene-based materials

Graphene has been widely investigated as one of the most promising materials in many fields due to its high electrical conductivity (10^3 - 10^4 S m⁻¹), large surface area (2630 m² g⁻¹), high thermal conductivity (~ 5000 W m⁻¹ K⁻¹), high flexibility and low toxicity.

Graphene is a single layer sp^2 hybridized carbon sheet with six member rings. The bond length between adjacent carbon atoms is 0.142 nm. The high electrical conductivity of graphene is ascribed to the π bond which is vertical to the crystal plane. The thickness of single layer graphene is ~ 0.35 nm. The graphene structure is very stable and flexible. When an external force is applied on graphene, the graphene plane will be bent to adapt the external force and the carbon atoms don't have to rearrange. This guarantees the structural stability of graphene.

Graphene is fervidly incorporated with transition metal oxides. This is because transition metal oxides experience large volume swing during discharge and charge processes and result in pulverization. The pulverized particles in the batteries lose effective electrical contact with current collectors and undermine the cycling stability of the electrodes. Graphene has high mechanical performance, e.g. flexibility and tensile strength. The large volume swing of transition metal oxides during battery cycling can be partially alleviated by graphene and so the internal stress of the transition metal oxides is reduced. Moreover, graphene can form a network in the electrodes. Even though some of the active materials are pulverized, graphene is able to hold them and keep the electrical contact with them. Some of the graphene-based hybrids in previous works are listed in Table 1.1.

Table 1. 1 Summary of graphene-based materials for energy storage, where G is short for graphene, r for reduced and m for mildly oxidized.

Materials	Preparation routes	References
TiO ₂ /rGO	GO→TiO ₂ /rGO (Chemical co-reduction)	[33, 34]
Fe ₂ O ₃ /rGO	GO→Fe ₂ O ₃ /rGO (Chemical co-reduction)	[35, 36]
Mn ₃ O ₄ /rGO	GO→Mn ₃ O ₄ /rGO (Chemical co-reduction)	[37]

$\text{Co}_3\text{O}_4/\text{rGO}$	$\text{GO} \rightarrow \text{Co}_3\text{O}_4/\text{rGO}$ (Chemical co-reduction)	[38]
CoO/rGO	$\text{GO} \rightarrow \text{CoO}/\text{rGO}$ (Chemical co-reduction)	[36]
MnO_2/rGO	$\text{GO} \rightarrow \text{MnO}_2/\text{rGO}$ (Chemical co-reduction)	[39]
$\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{rmGO}$	$\text{mGO} \rightarrow (\text{Mn}_{0.75}\text{Fe}_{0.25})_3\text{O}_4/\text{mGO} \rightarrow$ $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{rmGO}$ (Chemical co-reduction)	[40]
$\text{LiFePO}_4/\text{rGO}$	$\text{GO} \rightarrow \text{LiFePO}_4 \rightarrow \text{LiFePO}_4/\text{rGO}$ (Spray drying)	[41]
$\text{V}_2\text{O}_5/\text{rGO}$	$\text{GO} \rightarrow \text{rGO} \rightarrow \text{V}_2\text{O}_5 \rightarrow \text{V}_2\text{O}_5/\text{rGO}$ (Physical mixing)	[42]
$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{rGO}$	$\text{GO} \rightarrow \text{rGO} \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{rGO}$ (Physical mixing)	[43]
$\text{LiMn}_2\text{O}_4/\text{rGO}$	$\text{GO} \rightarrow \text{rGO} \rightarrow \text{MnO}_2/\text{rGO} \rightarrow \text{LiMn}_2\text{O}_4/\text{rGO}$ (Chemical lithiation)	[44, 45]

In typical discharge/charge processes, Li_2O_2 deposits and vanishes on the oxygen electrodes, leading to the large volume change of the oxygen electrodes. The strong cyclic stress caused by the volume change can damage the integrity of the oxygen electrodes and so undermine the cycling performance of LOBs. The situation is the same as the transition metal oxides for LIBs and even more terrible. Graphene is prone to form a network in the electrodes with the assistance of binders. The graphene network is flexible and conductive. This enables graphene to be a promising material for LOBs.

Pure graphene was applied for aqueous LOBs in a previous study. [5] Graphene was prepared using a conventional method. The discharge voltage of the graphene electrode was higher than the carbon black electrode by 250 mV and slight lower than the Pt-contained electrode by 50 mV only. The high catalytic activity of graphene was thought to be related to the defects and edges of graphene. In addition, hierarchically porous graphene was synthesized using surfactant-assisted sonication for primary LOBs. [46] The discharge

capacity of the sample electrode was ~ 15000 mAh/g. The authors claimed that the defects and functionalities on graphene were in favor of ORR. Moreover, the discharge product grew on the functionalities and the pore clogging effect was avoided. However, this statement needs experimental data support.

Wu et al prepared N-doped graphene catalysts for LOBs (**Figure 1. 9**). [47] The samples were synthesized by polymerization of polyaniline with multiwall carbon nanotubes as templates. The sample electrodes exhibited a descending discharge voltage plateau between 3-2.7 V with a capacity of ~ 4000 mAh/g. The sample electrodes were stable for 50 cycles with a narrowed cycling voltage range (2.4-4.2 V).

Figure 1. 9 Synthesis route of N-doped graphene sheet. [47] *Reprinted with permission from Ref. 47. Copyright 2012, American Chemical Society.*

The defects in graphene include 3 types: zero-dimensional defects (point defects), one-dimensional defects (dislocations), two-dimensional defects (grain boundaries and stacking faults). There are three mechanisms of the formation of these defects: Crystal growth (CVD), particle irradiation and chemical treatment.[48] Electrochemical exfoliation of graphene can also lead to the formation of the defects, in which the mechanism is similar to the chemical treatment. During electrochemical exfoliation, graphene is oxidized by the

anodic voltage and attached with hydroxyl and carboxyl groups. The electronic structures of graphene can be definitely changed in the presence of the defects. In particular, hydroxyl and carboxyl groups lower the conductivity of graphene and lead to high overpotential when graphene is adopted as the electrodes in energy storage systems.

1.2.5.4 Other materials

The common chemical formula of perovskites is ABO_3 , in which A atoms occupy the corner positions of the unit cell, B atoms occupy the center positions and oxygen atoms occupy the face center positions. The perovskites possess high catalytic activity to the oxygen reduction reaction (ORR) and high conductivity. [49] Porous $La_{0.75}Sr_{0.25}MnO_3$ nanotubes were prepared by electrospinning (**Figure 1. 10**). [22] The sample electrodes exhibited stable cycling performance with discharge/charge capacity of 1000 mAh/g. The one dimensional structure was likely ascribed to the good electrochemical properties of LOBs because it provided a convenient path for oxygen and charge transport.

Figure 1. 10 (a,b) FESEM images of as-electrospun $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ fibers. (c,d) FESEM images of porous $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanotubes. (e,f) TEM images of porous $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ nanotubes. [22] *Reprinted with permission from Ref. 22. Copyright 2013, John Wiley & Sons, Inc.*

In another work, mesoporous $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ nanowires were synthesized and applied for primary LOBs. [50] The discharge capacity of the sample was ~ 11600 mAh/g while the discharge capacity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ nanoparticles was only ~ 5300 mAh/g. Besides, the discharge capacity was ~ 1450 mAh/g without catalysts. The results revealed that the morphology of catalysts played an important role on the electrochemical performance of LOBs.

Spinels are another group of catalysts for LOBs. CoMn_2O_4 /graphene was used for LOBs by the Goodenough's group. [19] CoMn_2O_4 has high catalytic activity to oxygen reactions but the conductivity is very low. Therefore CoMn_2O_4 was grown on graphene to enhance the electrical conductivity. The sample electrode showed very small gap (0.3 V) between the discharge and charge voltages for aqueous LOBs. Besides, mesoporous NiCo_2O_4 nanoflakes were also applied for LOBs (**Figure 1. 11**). [20]

Figure 1. 11 TEM image of mesoporous NiCo_2O_4 nanoflakes. [20] *Reprinted with permission from Ref. 20. Copyright 2013, Royal Society of Chemistry.*

Nitrides are another option as LOBs catalysts. The advantages of nitrides include high chemical stability, high mechanical strength and low cost. Some kinds of nitrides have high electronic conductivity. TiN showed improved ORR activity that was only slightly worse than Pt and the discharge voltage of aqueous LOBs was ~ 3.7 V (**Figure 1. 12a**). [51] MoN/graphene delivered a discharge voltage of ~ 3.2 V for non-aqueous LOBs (**Figure 1. 12b**). [52]

Figure 1. 12 Voltage profiles of (a) TiN for aqueous LOBs [51] and (b) MoN/graphene for non-aqueous LOBs [52]. *Reprinted with permission from Ref. 50 and 51, Copyright 2011, Royal Society of Chemistry.*

Noble metals were also tried out for LOBs. PtAu nanoparticles were shown to exhibit high catalytic activity to elevate the energy efficiencies of LOBs as bifunctional catalysts (**Figure 1. 13**). [23] In comparison to the amorphous carbon, the sample electrode with PtAu nanoparticles increased the discharge voltage by ~ 0.2 V and decreased the charge voltage by ~ 0.6 V at 0.04 mA/cm^2 . The electrodes with pure Pt improved the charge voltage and the ones with pure Au improved the discharge voltage, respectively. The PtAu alloy particles possessed both the advantages of Pt and Au and were named as bifunctional catalysts.

Figure 1. 13 (a) TEM image and (b) cyclic voltammograms of PtAu/C. [23] *Reprinted with permission from Ref. 23. Copyright 2010, American Chemical Society.*

This conclusion was also supported by another work employing pure Au as the catalyst to enhance the discharge voltage of LOBs (**Figure 1. 14**). [24] The discharge voltages were elevated by 0.04 V at 0.1 A/g, 0.07 V at 0.25 A/g and 0.05 V at 0.5 A/g, respectively.

Figure 1. 14 TEM images of (a,b) Au/Vulcan carbon and (c) pure Vulcan carbon (VC). [24]

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Based on the calculation method and the experimental results, some noble metals were compared in terms of catalytic activities for LOBs. [53] The order of different noble metals' electrochemical performance for LOBs is Pd, Pt, Ru and Au at 100 mA/g (**Figure 1. 15**). The discharge voltage of Pd was between 2.90-2.93 V, which was quite close to the standard potential of the discharge reaction.

Figure 1. 15 Discharge profiles of Pd/C, Pt/C, Ru/C, Au/C and Vulcan carbon (VC) electrodes for LOBs. [53] *Reprinted with permission from Ref. 52. Copyright 2010, American Chemical Society.*

Another work employed nanoporous gold electrodes for non-aqueous LOBs. [17] The nanoporous gold electrode exhibited much improved cycling stability in comparison to the conventional carbon electrodes. For example, the sample electrodes retained 95 % capacity from the 1st cycle to the 100th cycle although the discharge/charge capacities at each cycle were limited to 320-330 mAh/g. The discharge/charge capacities were low due to the elevated lower limit on the cell voltage. Besides, the high gravimetric density of gold also contributed to the low capacities because the surface area of the gold electrode cannot be as

high as that of the conventional carbon materials. The charge transfer process during the oxidation of the discharge product was promoted in the presence of the sample electrodes.

Hollow carbon fibers binder-free electrodes were also prepared via chemical vapor deposition method on anodized aluminum oxide substrates (**Figure 1. 16**). [54] These electrodes delivered ~56% energy efficiency at 578 mA/g and ~64% energy efficiency at 43 mA/g. The energy efficiencies didn't increase much at high current densities.

Figure 1. 16 SEM images of (a) Al_2O_3 substrate and (b) hollow carbon fibers growing on the Al_2O_3 substrate. [54] *Reprinted with permission from Ref. 53, Copyright 2011, Royal Society of Chemistry.*

Metallic mesoporous pyrochlore was prepared as the catalysts for LOBs (**Figure 1. 17**). [55] The sample electrode exhibited a largest discharge capacity higher than 10000 mAh/g and the subsequent charge voltage was lower than 4.5 V. The sample electrodes showed much improved electrochemical properties than pure carbon electrodes.

Figure 1. 17 TEM image of Nanocrystalline lead ruthenate pyrochlore $\text{Pb}_2[\text{Ru}_{1.73}\text{Pb}_{0.27}]\text{O}_{6.5}$.

[55] *Reprinted with permission from Ref. 54, Copyright 2012, Nature Publishing Group.*

1.3 Synthesis methods

There are many synthesis methods for electrode materials, e.g. hydrothermal/solvothermal, chemical vapor deposition (CVD), electrochemical deposition and etc.

Although much research has been done on the synthesis and electrochemical tests of graphene-based composites for energy storage systems, the synthesis strategies are limited because a preparation of graphene is inevitable, which elongates and complicates the entire synthesis processes. Therefore a novel and efficient synthesis approach is a key challenge for the wide applications of graphene-based materials.

1.3.1 Hydrothermal/solvothermal synthesis

Hydrothermal/solvothermal synthesis is carried out in airtight autoclaves at high temperatures and pressures. The reaction medium could be water or organic solvents. Reactants with low solubility can be dissolved easily in hydrothermal/solvothermal synthesis and chemical reactions can happen quickly. One critical advantage of this method is that powder products can be obtained without high temperature annealing. Other advantages include high crystallinity, high purity, narrow size distribution and easy controllability of morphologies. Hydrated ruthenium oxide/reduced graphene oxide was synthesized for Li-air batteries by hydrothermal method. [26] Other examples include LiMn_2O_4 for LIBs [56], CuO nanobelts [57], V_2O_5 nanowire/graphene [58].

1.3.2 Chemical vapor deposition

CVD employs the chemical reactions happening between one or multiple gases reactants under heat, laser or plasma radiation. The advantages of CVD include narrow size distribution, high specific surface area, high flexibility and high purity. MnO_2 /carbon nanotube was prepared by CVD using alumina templates. [39] Graphene networks grown by CVD exhibited high mechanical and electrochemical properties. [59, 60] Besides, CVD was also used to synthesize carbon nanofibre [54], nitrogen-doped graphene quantum dots [61]

1.3.3 Electrochemical synthesis

Electrochemical deposition (ECD) possesses the following outstanding advantages: low cost, low toxicity and controllability. [62] Generally, a three-electrode ECD system contains a working electrode, a counter electrode and an electrolyte. When a certain voltage or current is applied between the working and counter electrodes, redox reactions happen in the double layer on the working electrode. The product forms on the surface of the electrode. Aimed materials can be obtained by tuning the voltage and current or the electrolyte composition. Products that chemical methods fail to synthesize can be obtained via ECD.

However there are some disadvantages as follows:

- 1) Products can only form on conducting substrates. That means when depositing insulating or semiconducting materials electrochemically, the deposition wouldn't continue due to the decreasing conductivity.
- 2) The products are often poorly crystallized due to the low temperature synthesis. A subsequent heat treatment is often necessary to improve the crystallinity.

Nevertheless ECD is still attractive as a soft chemistry technique due to the following advantages:

- 1) Low temperature synthesis. The residual thermal stress is minimal between the substrates and products, which assures the good adhesion.
- 2) Products can be deposited on the substrates with complex shapes.
- 3) Large scale production.
- 4) Low cost of the instruments and raw materials.

The electrolyte composition determines the products. In addition, the products are also affected by the depositing current and voltage. Depositing current influences the kinetics and the voltage exercises the thermodynamics. Two techniques are always adopted:

- 1) Galvanostatic mode. In this mode, a uniform morphology and a good adhesion can be obtained. However impurities form during the process.
- 2) Potentiostatic mode. Since the potential is precisely controlled, no impurities grow on the electrode in most cases.

In addition to plate metal films [63-65], ECD is capable of growing products with more complex compositions on conductive substrates.

Wu synthesized Fe_2O_3 nanowires on vapor-grown carbon nanofiber (VGCN).[66] After heating in air, the nanowires with a diameter of 30 nm were uniformly dispersed on the substrate. Li grew MnO_2 nanowires with controllable diameters of 40-150 nm by electrochemical deposition. [67] Hu electrochemically deposited V_2O_5 network on graphite substrates. [68] Li found that the morphologies of anodically deposited V_2O_5 are dependent on the PH values of the electrolyte and depositing potentials.[69]

Electrochemical exfoliation is a newly developed method to produce graphene. [70, 71] Ions in electrolytes are inserted into graphene interlayers of graphite paper and result in graphene exfoliation. The products consist of few graphene layers. Electrochemical exfoliation is an efficient method to produce graphene. In addition, electrochemical exfoliation can also be used to synthesize graphene quantum dots. [72] In this method, an

anodic voltage applied on graphite electrode leads to the oxidation and damage to the graphene structure. This results in the pulverization of graphene sheets. However, the most popular synthesis method is Hummers method. [73-85] In Hummers method, graphite is oxidized to weaken the π - π bonding, followed by sonication to exfoliate graphene layers.

1.3.4 Other methods

Precipitation is a widely accepted method to synthesize nanomaterials with high purity. Insoluble resultants can be formed by mixing soluble reactants at specific temperatures directly or followed by annealing. The sizes of the resultants are relevant to the concentrations of the reactants. The higher the concentration, the bigger the size of the resultant will have.

In the sol-gel method, metal organic or inorganic compounds are first dissolved in solvents and undergo hydrolysis or condensation in the presence of catalysts or additives. Then dispersions of particles or clusters, which are the so-called 'sol' can be obtained afterwards. Solid gel can be formed after annealing, stirring, hydrolysis or electrochemical reactions of the sols. Nanomaterials can be prepared by further treatment of the gels, e.g. annealing or drying. The advantages of the sol-gel method include low processing temperatures and small sizes of the products.

The microemulsion method employs two immiscible solvents with surfactants. Solid phases nucleate and grow into particles in the small sphere emulsion. Agglomeration can be avoided with this method. The microemulsions include surfactants, surfactant auxiliary additives, oils and aqueous solutions. They are a transparent, uniform, thermodynamically stable system. Nanoparticles can exist steadily in the microemulsions for a long term without agglomeration. In addition, nanoparticles modified with organic molecules can be obtained using this method.

1.4 Summary

LOBs are promising candidates as the next generation of energy storage and conversion systems. The theoretical energy density of LOBs is five to six times higher than LIBs. A typical LOB is comprised of a lithium metal anode, an electrolyte/mixed electrolytes and an oxygen electrode (cathode). LOBs can be categorized into two types in terms of electrolytes: aqueous and non-aqueous LOBs. Aqueous LOBs use mixed electrolytes to protect lithium anode from being oxidized by aqueous electrolytes. Non-aqueous LOBs employ organic electrolytes. Many investigations have been done on the electrochemical stability of non-aqueous LOBs' electrolytes. So far, TEGDME is the best electrolyte for non-aqueous LOBs although it still decomposes during battery test. In general, there are two important requirements for the oxygen electrodes. First, the oxygen electrodes must meet the basic needs for battery systems, e.g. high conductivity, high surface area and good mechanical properties (to weather the large volume swing caused by the formation and decomposition of discharge products). Second, the oxygen electrodes should possess high catalytic activities to oxygen reactions.

Graphene is an attractive candidate for LOBs. The high mechanical properties of graphene can alleviate the negative effect from large volume change during discharge/charge. The high electrical conductivity can help reduce the overpotentials of LOBs. Besides, the stable chemical properties of sp^2 hybridized carbon can elongate the lifetime of LOBs by avoiding decomposition to some extent during battery cycling. This is because localized high overpotentials cannot be predicted or avoided. Localized overpotentials exist due to the fact that the electrodes are not absolutely uniform in terms of physical structures. So when the current flows through the electrodes, some spots on the electrodes undergo high potentials and are likely to be oxidized. However, the stability of graphene is yet theoretically higher

than the amorphous carbons, which are widely used as the conductive additives of the electrodes.

Various catalysts have been synthesized for non-aqueous LOBs. Some of them exhibit high electrochemical performance as the cathodes for non-aqueous LOBs, e.g. transition metal oxides, noble metals, perovskites and chemically modified graphene. However, the catalytic activities of these materials are not high enough for LOBs to be industrialized. Moreover, the high cost of some of these materials, e.g. noble metals and perovskites, limit their wide applications.

In this thesis, graphene-based materials, including pure graphene foams and graphene-based composites, are synthesized with high catalytic activity and high electrochemical properties for LOBs.

CHAPTER 2: AIMS AND MOTIVATION

2.1 Objectives

The climate anomaly, the air pollution and the shortage of fossil fuels trigger the interest of exploring environmentally friendly energy storage systems. For example, the market of electric vehicles (EVs) is undergoing a fast development all over the world. Scientists apply high power Li-ion batteries on EVs. Although the technology of EVs' batteries is relatively mature and the market share of EVs is increasing quickly, solutions are needed to solve the problems of the batteries such as high cost, short lifetime and safety issues. LOBs are brought into the eyesight of scientists due to their high theoretical energy density.

A typical LOB consists of an anode, an electrolyte and a cathode. The configuration of LOBs is basically the same as LIBs, except that the cathodes of LIBs are solid species, e.g. lithium manganese oxide, lithium cobalt oxide and lithium phosphate, while the cathode of LOBs is oxygen gas. The cycling stability of non-aqueous LOBs is affected by the formation of side products. Much research has been done on the electrochemical stability of various organic electrolytes. Tetraethylene glycol dimethyl ether (TEGDME) is proved to be relatively stable in the discharge and charge processes of LOBs. Therefore TEGDME is used as the electrolyte in this thesis.

The electrochemistry on the LOB cathode is related to the oxygen reduction reaction and oxygen evolution reaction. Therefore the catalytic activity of the LOB cathode is taken into consideration when the electrochemical performance of the LOB cathode is examined. Various LOB cathodes have been studied, e.g. noble metals, transition metal oxides, metal-

organic frameworks, perovskites and spinels. Some progress has been made to improve the catalytic activities. However, it is still a challenge to prepare LOB cathodes with high performance. This is because LOB performance is dependent on not only the catalytic effect but also the architecture of the electrodes.

The materials selection and processing steps are chosen because of the following reasons. The graphene support is anticipated to facilitate the charge transport of LOBs and to endure the large volume swing during discharge/charge. The catalysts are expected to distribute homogeneously on graphene support. The materials selection is based on the catalytic properties of the materials and the processing steps selection are based on the efficiencies of the approaches. In particular, the selected materials have been proved to exhibit excellent catalytic properties to oxygen related reactions. But they haven't be applied or studied for LOBs. In addition, the electrochemical method to produce graphene-based materials is chosen in Section 4.2 due to its high efficiency.

Based on the previous studies and the status quo of the development of energy storage and conversion systems, the objectives of this thesis are to explore graphene-based electrodes for non-aqueous LOBs with high electrochemical performance. In particular, a novel electrochemical method to prepare graphene foams and Fe_2O_3 /graphene composites is proposed and a Fe-based metallopolymer/graphene composite is synthesized. These products exhibit high energy efficiencies and high stability as the O_2 electrodes for LOBs.

The following contents will be investigated in this thesis:

- 1) Synthesis, materials characterization, electrochemical characterization and analysis following battery tests of graphene-based materials;
- 2) The catalytic effect of graphene-based materials on the redox reactions (ORR/OER) in the non-aqueous LOBs;

- 3) The effect of graphene-based materials on the electrochemical performance of the non-aqueous LOBs.

According to the results of the above studies, new strategies about the synthesis of the electrode materials for the non-aqueous LOBs with high electrochemical performance will be proposed.

2.2 Hypothesis

Some hypotheses are made before the works of this thesis are carried out:

- 1) The LOB performance can be improved by decreasing the defects of graphene;
- 2) The loading of the second phase should be balanced between the catalytic effect and the overall conductivity;
- 3) The formation of the byproducts can affect the electrochemical performance of LOBs.

The above hypotheses are made based on the electrochemical process of LOBs during discharge/charge. First, the carbon electrodes are experiencing oxidation during charge. This leads to the abatement of active materials. Graphene oxide is usually prepared by strong oxidation of graphite. There are many defects on graphene. These defects make carbon atoms active and undermine the stability of carbon during discharge and charge. Second, as LOB electrodes, the second phase in graphene-based materials can enhance the catalytic effect but compromise the overall conductivity. Third, the oxygen electrodes experience the formation and vanishment of the discharge products, in which the byproducts are electrochemically irreversible. The byproducts form and grow on the electrodes, leading to deterioration of the

conductivity of the electrodes. Therefore, depression on the formation of the byproducts will result in the enhancement of the electrochemical performance of LOBs.

CHAPTER 3: EXPERIMENTAL DETAILS

3.1 Preparation and electrochemical characterization of binder-free graphene foams

3.1.1 Preparation of binder-free graphene foams

The electrochemical synthesis of the graphene foams was performed on a potentiostat/galvanostat system (CH instruments, Models1200A). A modified two-electrode electrochemical cell was used consisting of a graphite paper (1.5 cm × 1.5 cm × 0.3 mm) as the working electrode, two graphite papers as the counter electrodes and an aqueous solution of Na₂SO₄ (1 M) as the electrolyte. A constant current of 200 mA cm⁻² was applied for 6 hours at room temperature. Without washing, the products were annealed in Ar at 400, 600 and 800 °C for 30 min, respectively.

3.1.2 Electrochemical measurements of binder-free graphene foams

The LOB cells were assembled for electrochemical characterization with graphene foams as the working electrodes, lithium foils as the reference and counter electrodes and 1 M LiCF₃SO₃ in tetra(ethylene) glycol dimethyl ether (TEGDME) as the electrolytes. All cells were assembled in a glove box system filled with argon (MBraun UniLAB). The concentrations of moisture and oxygen were both below 0.1 ppm. The LOB cells were tested on a NEWARE system. All samples were immersed in electrolytes overnight before testing. LOBs cells were aerated with O₂ and sealed afterwards.

3.2 Preparation and electrochemical characterization of Fe₂O₃/graphene composites

3.2.1 Preparation of Fe₂O₃/graphene composites

Fe₂O₃/graphene was produced in an electrochemical approach. In a typical process, the electrochemical cell comprises of a highly oriented pyrolytic graphite (HOPG) sheet as the working electrode and a Pt wire as the counter electrode. The electrolyte consisting of 0.1 M FeSO₄ and 0.9 M Na₂SO₄ in deionized water was used. Step voltages with 0 V (10 seconds) and 10 V (10 seconds) were applied between the working and counter electrodes. The precipitates were collected via vacuum filtration and washed with deionized water for several times. The products were subsequently sintered in argon gas at 400 °C for one hour.

Another two electrolytes with different concentrations (0.03 M FeSO₄ + 0.97 M Na₂SO₄ and 0.15 M FeSO₄ + 0.85 M Na₂SO₄) were also used to prepare Fe₂O₃/graphene with different contents of Fe₂O₃.

3.2.2 Electrochemical characterization of Fe₂O₃/graphene composites

The electrochemical performance of the samples was examined on a Li-O₂ cell. The O₂ electrodes were fabricated by mixing the samples (90 wt%) and poly(vinylidene fluoride) (10 wt%) in N-methyl-2-pyrrolidone. Then the slurry was stirred overnight and cast onto a separator (Whatman GF/D microfiber filter paper), followed by vacuum-drying at 50 °C for 24 h. The Li-O₂ cell configuration was designed in a way proposed in a previous report.[86] Typically, a lithium metal foil as the counter and reference electrode was placed on a stainless steel current collector. Then a separator (Whatman GF/D microfiber filter paper) was put on top of the lithium foil, followed by adding 20 μL electrolyte (0.1 M LiClO₄ in 1, 2-Dimethoxyethane). The O₂ electrode was then put on top with a stainless steel mesh and a

stainless steel spring as the current collectors. The cells were assembled in a glove box. After assembly, the cells were sealed and tested on a NEWARE system between 2-4.5 V under pure O₂ flow of 1 mL min⁻¹.

3.3 Preparation and electrochemical characterization of transition metal-polypyrrole metallopolymer /graphene composites

3.3.1 Synthesis of reduced graphene oxide (rGO)

Graphite oxide was prepared by a modified Hummer's method. [36, 87, 88] The aqueous solution of concentrated H₂SO₄ (12 g), K₂S₂O₈ (2.5 g) and P₂O₅ (2.5 g) was heated to 80 °C, followed by the addition of graphite powder (3 g). The mixture was kept at 80 °C for 4.5 h. The pre-oxidized product was washed with de-ionized water and dried in a vacuum oven for overnight. Then the graphite powder was added into concentrated H₂SO₄ (120 mL) in ice bath, followed by slow addition of KMnO₄ (15 g). After the mixture was kept at 35 °C for 2 h, de-ionized water (250 mL) was put into the mixture and stirred for 2 h. Then de-ionized water (0.7 L) and 30 % H₂O₂ (20 mL) was added. The mixture was washed with diluted HCl aqueous solution and de-ionized water. The product (graphite oxide) was dried in vacuum oven for overnight.

The graphite oxide (100 mg) was dispersed in de-ionized water (100 mL) and sonicated for 1 h. An aqueous solution of cetrimonium bromide (4 mL, 0.5 wt %) and NaBH₄ (2 g) were added and kept at 100 °C for 4 h. The final product was washed dried in vacuum oven.

3.3.2 Synthesis of polypyrrole/rGO

An aqueous solution of rGO (100 mL, 1mg/mL) was prepared and mixed with pyrrole (20 mg). 10 % H_2O_2 (100 μL) was added into the solution and stirred at room temperature for 3 h. Then the product was washed with de-ionized water and dried in vacuum.

3.3.3 Synthesis of Fe-polypyrrole/rGO (FPG)

The polypyrrole/rGO composite (45 mg) was mixed with de-ionized water (10 mL) and heated under reflux for 30 min. $\text{Fe}(\text{NO}_3)_3$ (24.7 mg in 250 μL de-ionized water) was added into the solution and kept at 80 °C for 30 min, followed by the addition of the aqueous solution (12.5 mL) of NaBH_4 (130 mg) and NaOH (9.2 mg), which was heated to 80 °C beforehand. Then the mixture was kept at 80 °C for 30 min. The product was washed and dried in vacuum. The amount of Fe in the composite can be calculated to be ~ 8.2 wt % by the weight of the composite.

In the synthesis of Co-polypyrrole/rGO (CPG) and Mn-polypyrrole/rGO (MPG), $\text{Co}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ (24.7 mg in 250 μL de-ionized water) were used to replace $\text{Fe}(\text{NO}_3)_3$, respectively.

3.3.4 Electrochemical characterization

The electrodes slurry was prepared by mixing the samples (90 wt %) and poly(vinylidene fluoride) (10 wt%) in N-methyl-2-pyrrolidone. After stirring for one day, the slurry was coated onto microfiber filter paper (Whatman GF/D) and dried in a vacuum oven for overnight. In a typical LOB cell, Li metal foil was used as the counter and reference electrode. A microfiber filter paper (Whatman GF/D) was applied as the separator and 1 M LiCF_3SO_3 in tetra(ethylene) glycol dimethyl ether (TEGDME) as the electrolytes. The electrochemical properties of the samples were studied using NEWARE system. All discharge/charge capacities are calculated on the total weight of the composites.

3.3.5 Calculation of specific capacity

The specific capacity of the products are calculated according to the equation below:

$$Q = It / M,$$

where Q is the specific capacity, I is the discharge/charge current, t is the time of discharge/charge and M is the mass of the active materials.

3.4 Physical characterizations

The morphological information of the products was collected with transmission electron microscopy (TEM) (JEOL, Model JEM-2100) operating at 200 kV and field-emission scanning electron microscopy (FESEM) (JEOL, Model JSM-7600F) with 5 kV accelerating voltage. In particular, TEM samples were prepared by dropping the sample dispersion in ethanol onto the copper grids with amorphous carbon films on it. Then they were dried in normal oven for 5 minutes. Similarly, FESEM samples were prepared by dropping the samples dispersion in ethanol onto the copper tapes and then dried naturally.

Crystal phases were detected by the Powder X-ray diffraction (Shimadzu XRD-6000, Japan) with Cu K α irradiation with $\lambda=1.5406$ Å). The samples were mounted in a sample holder prior to the X-ray diffraction (XRD) test. In addition, the electrodes were cleaned with 1, 2-Dimethoxyethane in a glove box with contents of moisture and O₂ below 0.1 ppm. The the electrodes were sealed with parafilms in the glove box and tested by XRD after drying in vacuum for several hours.

Raman spectra were collected using a WITec CRM 200 confocal Raman microscope with a wavelength of 488 nm and a spot size of 0.5 mm. Wave number calibration was performed with the Si peak at 520 cm⁻¹ as the reference.

Nitrogen adsorption/desorption isotherms were carried out on a Micromeritics ASAP2020 at 77 K. The samples were degassed at 100 °C for 4 hours and the specific

surface areas were calculated in the Brunauer-Emmett-Teller (BET) method. Prior to the test, the samples were dried in normal oven at 70 °C for 12 hours.

The X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a VG ESCA 220i-XL using aluminium K α (1486.6 eV). Calibration was performed using the C1s peak (284.5 eV) as the reference.

The nuclear magnetic resonance (NMR) analysis was carried out on a Bruker 300 NMR spectrometer. Prior to the test, the sample electrodes were extracted from the cells and immersed in D₂O for 4 hours.

Thermogravimetry analysis (TGA) was performed using TGA Q500 at a heating rate of 10 K min⁻¹ in air in the range of 25-800 °C. Prior to the test, the samples were dried in oven at 70 °C overnight.

Atomic Force Microscopy (AFM) results were obtained on a DI-3100. A Si tip was used in the tapping mode and images were collected in ambient under 1 Hz scanning rate.

CHAPTER 4: RESULTS AND DISCUSSION

Work presented in this chapter has been published. In particular, Sections 4.1 and 4.2 are reprinted with permission from the journals of ‘Nanoscale’ and ‘RSC advances’, respectively. (Copyright (2013 & 2012) Royal Society of Chemistry). Section 4.3 is reprinted with permission from the journal of ‘ACS Applied Materials & Interfaces’. (Copyright (2014) American Chemical Society).

4.1 Binder-free graphene foams as O₂ electrodes for Li-O₂ batteries

1. Introduction

Li-O₂ batteries (LOBs) are considered to be one of the most promising candidates as the next generation of the energy storage system due to their high theoretical specific energy (~3500 Wh kg⁻¹), which is almost an order of magnitude higher than today’s Li-ion batteries (~380 Wh kg⁻¹). [1, 16, 89] Precious metals[17, 23, 53] and transition metal oxides[7, 9, 22, 50, 90] have been widely investigated to enhance the electrochemical properties of LOBs. A typical prototype of LOBs contains a Li metal anode, an electrolyte and an O₂ electrode. The requirements of an O₂ electrode include high surface area, high electrical conductivity and strong electrocatalytic activity to the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER).[29]

However, recent studies show that the amorphous carbon, which is frequently used as conductive agents in LOBs, exhibit triggered electrochemical activity in the highly oxidizing environments of LOBs, especially at high potentials [14, 17] [18]. This would result in the decomposition of the conductive agents and so compromise the electrochemical performance of LOBs. Thus it is a key challenge to search for the alternative to the conventional conductive agents. Graphene, a monolayer of honeycombed carbon rings, possesses attractive

features as good mechanical properties, high surface area, high electrical conductivity and thermal conductivity.[91-95] Recently, intensive studies have been carried out on graphene-based materials for energy storage systems, e. g. electrochemical capacitors[96], Li-S batteries[97, 98] and Li-ion batteries[35, 99-101]. In comparison to the large amount of sp^3 hybridized carbon atoms in the amorphous carbons, the graphitic sp^2 bonds with higher bonding energy in graphene enable it to be a reasonable conductive agent due to its high chemical stability. Although graphene-based materials have been proved to be feasible electrodes for LOBs,[5, 46, 47] little study has been reported on the effect of its structural defects on the electrochemical performance.

Meanwhile, much effort has been made to study the electrochemistry of LOBs.[6, 14, 18, 102-105] However, most O_2 electrodes are typically fabricated using a conventional way by combining the conductive agents, the polymeric binders and the catalysts. The tedious preparation and multiple components of O_2 electrodes further complicate the electrochemistry and impose difficulties on the chemical analysis of LOBs.[11, 12, 14, 102, 106] Therefore the application of the binder-free graphene foams as the O_2 electrodes is promising for the characterization and the fundamental studies of LOBs. In other fields, in order to employ the superior properties of graphene for scalable sized devices, three dimensional (3D) freestanding graphene foams have attracted great attention.[59, 74, 88, 107-109] The polymeric binders, utilized in conventional electrode fabrication techniques, increase the resistance of electrodes and hence affect the electrochemical performance. Thus, effective and reliable preparation approaches to grow 3D graphene foams, which can be used to make binder-free electrodes, have been developed, e. g. template-assisted chemical vapor deposition (CVD) [59, 109], filtration of graphene oxide (GO) or reduced graphene oxide (rGO) [74, 88, 107] and graphene hydrogel [108]. However, the CVD process may be limited by the facts of high cost, template removal steps and low efficiency in large scale production;

the filtration and hydrogelation processes requires the pre-synthesis of graphene oxide, which includes different steps of oxidation and cleaning.

Electrochemical exfoliation (ECE) of graphite paper, a one-step approach based on ions insertion into graphitic structures, has been developed to prepare graphene sheets with high quality and high yield [70, 71], which inspires a novel scope of synthesis strategies of graphene. According to the previous studies [70, 110], during the electrochemical exfoliation process, ions intercalate into graphene interlayers and result in expansion of interlayer spacing. This can be described as a leavening process similar as what occurs during the preparation of rGO, in which the released gaseous species causes volume expansion.[111] Thus it is attractive to apply such strategy on the synthesis of 3D graphene foams. However, defects can be introduced during the electrochemical leavening (ECL) process.[70, 112] The presence of defects undermines the crystallinity of the graphitic structure and slows down the kinetics of charge transfer. Moreover, the hybridization of the stable sp^2 carbon atoms of graphene is changed by defects, leading to the activated chemical properties of graphene. This may affect their performance as O_2 electrode in the highly oxidative environment of the LOBs.

Here in this section, we report a facile and controllable method to synthesize freestanding graphene foams by the ECL process of graphite paper in aqueous solution of Na_2SO_4 . The sizes of graphene foams depend on the sizes of graphite papers. Such process is advantageous with high yield, environmentally friendliness, and low cost. A graphene foam of $6\text{ mm} \times 6\text{ mm} \times 3\text{ mm}$ can be fabricated by leavening at 200 mA cm^{-2} for 6 hours with BET surface area of $\sim 110\text{ m}^2\text{ g}^{-1}$. These graphene foams were studied as O_2 electrodes of LOBs. As annealing can remove the structural defects in the graphene sheets, we also investigated the performance of samples with different I_D/I_G ratios (I_D and I_G refer to the intensities of the D band and the G band in the Raman spectra, respectively). I_D/I_G is related to

the defect densities in the sample). It was found that the defects were detrimental to the electrochemical performance of the graphene foam electrodes in the LOBs. The samples exhibited weakened round-trip efficiencies (the ratio between the discharge energies and the charge energies), cycling stabilities and generated more side products for samples with higher I_D/I_G values. For example, the as-prepared graphene foam with a high I_D/I_G value of 0.71 depicted a round-trip efficiency of only 0.51 and a 20th-cycle discharge capacity of only 340 mAh g⁻¹ at a current density of 100 mA g⁻¹. By contrast, the graphene foam electrode annealed at 800 °C with $I_D/I_G = 0.07$ delivered a round-trip efficiency of up to 80 % with a stable discharge voltage at ~2.8 V and a stable charge voltage below 3.8 V for 20 cycles.

2. Results & Discussion

The as-purchased graphite papers are used in this work (Figure 4. 1). The graphite paper consists of highly oriented graphite sheets stacked together. The effect of applied anodic currents on graphite papers have been investigated (see

Table 4. 1). An aqueous electrolyte containing 1 M Na₂SO₄ is applied and the duration is limited to 1 hour. Under low current densities, e. g. 0-100 mA cm⁻², the graphite paper expands mildly and no graphene sheets are exfoliated. When the anodic currents are adjusted to 100-300 mA cm⁻², separated graphene sheets form and remain interconnected without peeling-off within 1 hour. This range of anodic currents is adopted for the leavening synthesis of graphene foams. Higher current densities (>300 mA cm⁻²) result in fast and thorough exfoliation of graphene sheets, which is consistent with previous reports [70, 71]. These effects can be interpreted as the applied electric fields weaken the van der Waals' force bonding among graphene layers. The anions in the electrolytes (inclusive of those solvated anions) are driven by the electric fields to the interlayer space of graphite structures. Besides, O₂ evolves and graphite is inevitably oxidized. These lead to the weakening of the van der Waals' force. Therefore, the final products are determined by the competition between the applied electric fields and the van der Waals' force. At 100-300 mA cm⁻², the electric field

cannot provide enough energy to the anions, which results in partially exfoliated graphite paper with interconnected graphene sheets (e.g. graphene foam). The graphene foam can be considered as a transient state between the graphite paper and fully exfoliated graphene sheets. Based on the above results, we carried out the electrochemical leavening process of graphite paper at a moderate current (200 mA cm^{-2}) with duration of up to 6 hours.

Figure 4. 1 (a) The optical and (b) SEM images of the pristine graphite paper.

Table 4. 1 Effects of anodic currents on graphite electrodes. The aqueous electrolyte consists of 1 M Na_2SO_4 . Anodic currents duration is limited within one hour.

Current range (mA cm ⁻²)	Phenomena	Schematic demonstration
0 - 100	Mild expansion and no exfoliation.
100 - 300	Moderate expansion and slow exfoliation. (Electrochemical leavening of graphene foams)
> 300	Intense expansion and fast exfoliation. (Electrochemical exfoliation of graphene sheets)

To leaven the graphite papers homogeneously and efficiently, a modified electrochemical cell is employed (Figure 4. 2a). Two graphite papers, which are the counter electrodes, are placed at both sides of the working electrode. The electrochemical leavening mechanism of graphene foam is illustrated in Figure 4. 2b. As is described above, since it is a transient state with partially exfoliated graphene sheets, the graphene foam contains a large amount of unexfoliated graphite joints, which can maintain the physical stability and electrical continuity of the graphene foam.

Figure 4. 2 (a) The cell and (b) schematic illustration for the electrochemical leavening synthesis of graphene foams. The red circles indicate the structural connection between graphene sheets. These connecting kinks maintain both the structural stability and electrical continuity of graphene foams.

The morphology evolution of the graphite paper leavened at 200 mA cm^{-2} is shown in Figure 4. 3. The surface of the pristine graphite paper (Figure 4. 3a) is flat and smooth and the graphene edges are invisible. After electrochemical leavening for 2 hours (Figure 4. 3b), the edges of graphene sheets start to roll up and become observable, which is related to the insertion of sulfate anions. This process continues after 4 hours (Figure 4. 3c) and the graphene foam comprising interconnected graphene networks forms with pores of $\sim 1 \text{ }\mu\text{m}$ after electrochemical leavening for 6 hours (Figure 4. 3d). The final products exhibit black fluffy surface, high robustness and high flexibility (Insets of Figure 4. 3d). The planar sizes of the graphene walls range from $1 \text{ }\mu\text{m}$ to tens of microns. The wrinkles of graphene walls are clearly observed in the low magnification TEM image (Figure 4. 3e). The HRTEM image shows that the trilayer graphene sheet has an interlayer spacing of $\sim 0.429 \text{ nm}$ (Figure 4. 3f), which is higher than that of graphite ($\sim 0.335 \text{ nm}$) due to the intercalation of SO_4^{2-} . The volume and morphology of the graphene foams (Figure 4. 4) shows no obvious change after annealing because the presence of SO_4^{2-} between graphene sheets prevents the recovery of the van der Waals' force between the graphene layers.

Figure 4. 3 SEM images of the graphite paper after electrochemical leavening for (a) 0, (b) 2, (c) 4 and (d) 6 hours in 1 M Na_2SO_4 at 200 mA cm^{-2} , (e) TEM and (f) HRTEM images of the graphene foam. The insets of (d) show the optical photograph of the graphene foam.

Figure 4. 4 The SEM image of the graphene foam after annealing in Ar.

To further study the formation of the graphene foams, the volumetric expanding behavior of the graphite paper is recorded (Figure 4. 5a). After two hours of electrochemical leavening, the graphite paper quickly swells by ~ 7 times. The expansion increases to ~ 16 times after 6 hours, in which the planar area (length $\times$ width) expands by ~ 0.6 times and the thickness by ~ 9 times. The vast volume expansion indicates the formation of large amounts of pores inside the graphene foams. The BET analysis (Figure 4. 5b) indicates the specific surface area of the graphene foams is $\sim 110 \text{ m}^2 \text{ g}^{-1}$.

Figure 4. 5 (a) Volume expansion versus leavening duration and (b) Nitrogen adsorption and desorption isotherms measured at 77 K of the graphene foam.

The graphene foams are inevitably oxidized due to the anodic current applied and the functionalities of C-O-C, C=O and C-OH form during the ECL process[70]. The presence of these deficiencies undermines the electrical conductivities and the electrochemical properties of the graphene foams as the O_2 electrodes in LOBs.[14] Therefore the as-prepared graphene

foams are annealed in Ar to remove the defects. The Raman spectra (Figure 4. 6) reveal that the ratios of I_D/I_G are 0.71, 0.35, 0.23 and 0.07 for as-prepared, H400, H600 and H800 samples, respectively. The decreased values of I_D/I_G confirm the successful removal of the deficiencies of the graphene foams.

Figure 4. 6 Raman spectra of graphene foams after annealed at 400, 600 and 800 °C in Ar.

The electrochemical characterization is performed on the LOB cells with modified Swagelok configurations[113], in which Li foils are used as the reference and counter electrodes and the graphene foams as the working electrodes. The specific discharge/charge capacities are limited to 1000 mAh g⁻¹. During the discharge process, O₂ is reduced to form Li₂O₂ with a theoretical potential at ~3 V (vs. Li). Li₂O₂ deposits on the electrodes and is converted back to O₂ during the charge process with a high overpotential (above 4 V vs. Li in most cases [90, 114]) due to the slow kinetics of charge transfer in Li₂O₂. [55, 115-117] Therefore the round-trip efficiency is introduced to evaluate the performance of the O₂ electrodes.[23] The round-trip efficiencies (the discharging specific energies/the charging specific energies) of the as-prepared, H400, H600 and H800 electrodes (Figure 4. 7a), in

selected representative cycles at a current density of 100 mA g^{-1} , are calculated to be 51 %, 60 %, 67 % and 80 %, respectively. The annealed samples exhibit the improved round-trip efficiencies in comparison to the as-prepared graphene foam. This can be related to the less amounts of defects in these graphene foams. The defects slow down the charge transfer during the discharge and charge processes and so suppress the ORR and OER. Hence the sample electrodes with fewer defects depict higher round-trip efficiencies. Moreover, the round-trip efficiency of the H800 is higher than the other carbon-based electrodes, e. g. Vulcan XC-72, reduced graphene oxide [118] and the woven carbon nanotubes [119]. The cycling performance of the sample electrodes are examined at 100 mA g^{-1} for 20 cycles (Figure 4. 7b and Figure 4. 8). The as-prepared graphene foam delivers a 20th-cycle discharge capacity of only 340 mAh g^{-1} with a charge voltage of $\sim 4.7 \text{ V}$ while the annealed electrodes are all capable of delivering discharge capacities of 1000 mAh g^{-1} for 20 cycles. The H800 electrode exhibits stable discharge voltages at $\sim 2.8 \text{ V}$ and charge voltages below $\sim 3.7 \text{ V}$ for 20 cycles while the other graphene foam electrodes depict decreasing discharge voltages and increasing charge voltages. The discharge and charge voltages reflect the process of the ORR and OER, respectively. High charge voltages will lead to the decomposition of the carbon electrodes.[14] Thus the low charge voltages of the H800 are beneficial to the electrochemical performance of LOBs. In addition, the H800 electrodes also exhibit excellent cycling stability at current densities of 200 and 300 mA g^{-1} (Figure 4. 7c and d). The discharge voltage at 200 mA g^{-1} is at $\sim 2.75 \text{ V}$ and the charge voltage is at $\sim 3.75 \text{ V}$ with a round-trip efficiency of 79 % (Figure 4. 7c) while the values are 2.7 V , 3.85 V and 78 % at 300 mA g^{-1} . The slight increase of the discharge/charge voltages at higher current densities indicates the excellent high-rate performance of the H800 electrode. The improved cycling performance of the graphene foams can be attributed to the fewer amounts of the defects. Some carbon atoms comprising graphene are connected to the functional groups of C-O-C,

C=O and C-OH. In comparison to the graphitic carbon atoms, these atoms tend to be oxidized and converted to carbonates or other compounds [14, 102] during the charge process. This leads to the irreversible loss of the active carbons and to the increase of the charge overpotential due to the insulating nature of those compounds.

Figure 4. 7 Electrochemical performance of the graphene foams as O₂ electrode for Li-O₂ batteries. (a) Presentative voltage profiles of the graphene foams at 100 mA/g. Cycling performance of the graphene foam annealed at 800 °C at (b) 100, (c) 200, (d) 300 mA/g.

Figure 4. 8 Cycling performance of the graphene foams (a) without annealing and after annealing in Ar at (b) 400 and (c) 600 °C at 100 mA/g.

To examine the structures of the electrode materials after 20 discharge/charge cycles, the electrodes after recharge are washed with deionized water and diluted HCl aqueous solution to get rid of Li_2O_2 . The Raman spectra of all graphene foam electrodes after 20 cycles (Figure 4. 9) show that the values of I_D'/I_G' (the intensity ratio of the D band and the G band for samples after cycling) are 1.17, 0.70, 0.42 and 0.11, corresponding to as-prepared, H400, H600 and H800 samples, respectively. Accordingly, the differences between I_D'/I_G' and I_D/I_G (pristine electrodes) are 0.46, 0.35, 0.19 and 0.04, indicating the structural defects generation is faster in the samples already with more defects.

Figure 4. 9 Raman spectra of the graphene foam electrodes after 20 cycles.

The nuclear magnetic resonance (NMR) analysis of the electrodes after 20 cycles was performed to identify the side products (Figure 4. 10). The peaks at 3.3 and 3.6 ppm can be indexed to the TEGDME and the peak at 4.7 ppm corresponds to the D₂O. The peaks at 1.8 ppm and 8.3 ppm represent the CH₃CO₂Li and HCO₂Li, respectively.[106] Those two compounds are the side products of the graphene foam electrodes and grow during the cycling of the LOBs. They can undermine the electrochemical performance of the LOBs due to their insulating and electrochemically irreversible properties. Because the amounts of the D₂O used in the NMR test are equivalent and the mass of the graphene foam electrodes is identical, the intensity ratios between the side products and the D₂O ($I_{\text{CH}_3\text{CO}_2\text{Li} + \text{HCO}_2\text{Li}}/I_{\text{D}_2\text{O}}$) are employed to estimate the contents of the side products generated in the electrodes. The values of $I_{\text{CH}_3\text{CO}_2\text{Li} + \text{HCO}_2\text{Li}}/I_{\text{D}_2\text{O}}$ are 0.0185, 0.0021, 0.0018 and 0.0003 corresponding to the as-prepared, H400, H600 and H800 samples, respectively. Therefore the side products form faster in the graphene foams with more defects.

Figure 4. $^{10} \text{H}$ NMR spectra of (a, b) as-prepared graphene foam, the graphene foam annealed at (c, d) 400 °C, (e, f) 600 °C and (g, h) 800 °C. (b, d, f, h) are the magnified spectra.

The superior electrochemical properties of the H800 graphene foams can be interpreted in terms of two aspects: the well prepared 3D structure and the successful

removal of the defects on the graphene foams. First, the micro-sized graphene sheets with large surface areas allow effective interaction between the O₂ and Li ions during cycling. Second, the fewer amount of defects in the H800 graphene foams enhance the charge transfer kinetics, which also facilitates the efficient oxygen reduction reactions and oxygen generation reactions. The defects hinder the charge transfer and the bonds of C-O-C, C=O and C-OH activate the carbon atoms, which make the graphene foams unstable and boost the generation of the side products during cycling.

3. Short summary

In this section, an electrochemical leavening strategy followed by annealing in inert gas to fabricate the defect-free graphene foams is developed in this work. The graphene foams consist of large and ultrathin graphene walls with 1-10 μm in plane and 1-2 nm in thickness. They are tested as the O₂ electrodes in LOBs. The round-trip efficiencies of the optimized graphene foams can reach up to 80 % and a stable discharge voltage of ~ 2.8 V is delivered for 20 cycles. The superior electrochemical properties of graphene foams can be ascribed to the 3D structure and the less amounts of structural defects. The structural defects in the graphene foam are detrimental to the structural stability of the O₂ electrode and can slow down the kinetics of charge transfer. This degrades the electrochemical performance of oxygen electrodes due to their slow kinetics of charge transfer and the more active chemical properties of the C-O-C, C=O and C-OH bonds in comparison to the sp^2 graphitic bonds. Moreover these defects lead to the faster growth of the side products of the LOBs during cycling, which further deteriorate the electrochemical performance. The strategy demonstrated in this work can be extended to fabricate 3D foam of other layer-structured materials.

4.2 Fe₂O₃/graphene composites as O₂ electrodes for Li-O₂ batteries

1. Introduction

Recently, lithium-O₂ batteries (LOBs) have attracted much attention due to their ultra-high theoretical specific energy of 3500 W h kg⁻¹, which is an order of magnitude higher than that of Li ion battery [120] currently used commercially.[1] At present, a prototype aprotic LOB includes Li metal, aqueous or non-aqueous electrolyte and an O₂ electrode.[5, 7, 23, 115, 121] In a typical discharge process of LOBs, two reduction reactions with O₂ have been suggested to take place at the O₂ electrode:[16, 24]

The discharge products, e.g. Li₂O₂ or/and Li₂O, precipitate on the surface of the O₂ electrode.

High catalytic activity of the O₂ electrodes is a critical factor to facilitate the O₂ reduction processes, which affects the overall performance of LOBs.[1, 16, 23] Transition metal oxides, e.g. MnO₂-based materials, have been investigated as O₂ electrodes in LOBs with carbonate-based electrolytes due to their low cost and low toxicity.[9, 10, 25, 122] However, a recent report has indicated that the usage of carbonate-based electrolytes in LOBs involves complex decomposition chemistry of the electrolytes, which influences the proper characterization of the specific capacities of the LOBs.[11] The ether-based electrolytes have been proved to be more suitable for LOBs as no obvious decomposition of the electrolytes takes place during the discharge process.[11] However, there are limited reports on transition metal oxide based O₂ electrode with ether-based electrolytes.

Apart from catalytic activity, it is also important for the O₂ electrodes to possess high surface area and high electrical conductivity to achieve large specific capacities of the LOBs.

Graphene-based materials have been extensively studied for applications in energy storage and conversion systems[34, 37, 43, 95, 100, 123-130] due to their promising properties, e.g. high electrical conductivity, high surface area, mechanical strength and high thermal conductivity.[92] Hierarchically porous graphene prepared with the Hummer's method has shown exciting performance as LOB O₂ electrodes.[131] Attaching transition metal oxides onto graphene could be a promising O₂ electrode for LOBs. This approach combines the catalytic effects from transition metal oxides with the high surface area and high electrical conductivity of graphene. As extensively studied electrode materials in Li ion batteries, the graphene based hybrid electrodes are typically prepared by Hummer's method,[37, 132] which is a multi-step process. It should be noted that different methods also exist for graphene preparation, e.g. chemical vapor deposition,[59, 133, 134] mechanical exfoliation[91] and electrochemical exfoliation,[70, 71] but some of these methods may not be easily adapted for large scale sample preparation.

Here, in this section, we carried out the study on using Fe₂O₃ nanoclusters-decorated graphene (Fe₂O₃/graphene) as the flexible O₂ electrode in LOBs. The Fe₂O₃/graphene samples are prepared by a facile electrochemical process, which combines the exfoliation of graphene and deposition of metal oxides in one step. It is shown in our study that the Fe₂O₃/graphene O₂ electrodes depicts higher discharge capacities as compared to that of O₂ electrodes made of pure graphene prepared by a similar electrochemical process. For example, the Fe₂O₃/graphene electrode with 29.0 wt% of Fe₂O₃ exhibits a discharge capacity of 8290 mA h g⁻¹ while pure graphene electrode delivers 5100 mA h g⁻¹. The discharge capacities of Fe₂O₃/graphene based O₂ electrodes with different Fe₂O₃ weight percentages (C_{Fe₂O₃}) were also examined. The increased discharge capacities for Fe₂O₃/graphene based O₂

electrodes are proposed to be related to the superior electron transporting properties of graphene and high electrocatalytic O₂ reduction activities of Fe₂O₃.

2. Results & Discussion

The Fe₂O₃/graphene hybrids were fabricated via an electrochemical method combining the deposition of metal oxides and the exfoliation of graphene sheets in a single process. Step voltages were applied in the process (**Figure 4. 11**). The first step with no voltage applied was set to eliminate the ion concentration gradient so as to obtain homogeneous deposits. A high voltage of 10 V (1A/cm²) was used. This led to the electrochemical deposition of metal oxides onto the graphite surface while sulfate ions were driven by electric field into the graphene layers, resulting in the expansion of graphene interspacing and the exfoliation of the outer graphene layers off the graphite surface. After cycling the above steps, the products were collected for further investigation. The amount of oxides in the hybrids can be easily tuned by varying the concentrations of FeSO₄ in the electrolyte.

Figure 4. 11 Applied step-voltage in the electrochemical preparation of Fe₂O₃/graphene hybrids.

The XRD pattern (**Figure 4. 12a**) of the sample prepared with a FeSO₄ concentration (I_{FeSO_4}) of 0.1 M can be indexed to the tetragonal Fe₂O₃ phase (JCPDS 25-1402). There is no crystalline impurity detected in the XRD pattern. The grain size of Fe₂O₃ is estimated to be 6.9 nm according to the Scherrer's equation. The FESEM and TEM images (**Figure 4. 12b** and **c**) show that the Fe₂O₃ nanoclusters with diameters of 30-40 nm are uniformly anchored onto the graphene surface. The high-magnification image (**Figure 4. 12d**) reveals that these Fe₂O₃ nanoclusters are composed of many crystallites with size in the range of 30-40 nm. Varying I_{FeSO_4} values to 0.03 M and 0.15 M resulted in hybrid samples with similar phases and morphology (**Figure 4. 13** and **Figure 4. 14**). Only the tetragonal Fe₂O₃ phase was detected in the XRD patterns while the size of the Fe₂O₃ nanoclusters is in the range of 20-50 nm for these hybrid samples.

Figure 4. 12 (a) XRD pattern, (b) SEM image, (c) TEM and (d) high magnification TEM image of the Fe₂O₃/graphene hybrid with $I_{\text{FeSO}_4}=0.1$ M.

Figure 4. 13 (a) XRD pattern, (b) SEM image and (c) TEM image of the $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrid with $I_{\text{FeSO}_4}=0.03$ M.

Figure 4. 14 (a) XRD pattern, (b) SEM image and (c) TEM image of the $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrid with $I_{\text{FeSO}_4}=0.15$ M.

The detailed structure of the graphene in the as-prepared samples was studied by HRTEM (**Figure 4. 15a**). The interlayer spacing of the graphene sheet with a trilayer structure is estimated to be ~ 0.49 nm, which is consistent with the AFM results (**Figure 4. 15b**).

Figure 4. 15 HRTEM image and AFM image of the $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrid with $I_{\text{FeSO}_4}=0.1$ M.

The quality of the as-prepared graphene sheets in the $\text{Fe}_2\text{O}_3/\text{graphene}$ samples was examined by Raman spectroscopy (**Figure 4. 16**). The intensity ratio $I_{2\text{D}:G}$ of the 2D band (located at 2720 cm^{-1}) to the G band (located at 1580 cm^{-1}) was estimated to be ~ 0.36 for the sample prepared with $I_{\text{FeSO}_4} = 0.1$ M. This $I_{2\text{D}:G}$ value is higher than that of reduced graphene oxide (~ 0.15).^[36] The $I_{2\text{D}:G}$ is proved to be relevant to the recovery for sp^2 C=C bonds in graphitic structures^[135] and higher $I_{2\text{D}:G}$ indicates fewer layers of graphene. In addition, the low intensity of D band indicates the small amount of defects. As a comparison, the reduced graphene oxides normally show a D band with higher intensities than those of 2D and G bands.^[38] Based on the results of the four-point probe measurements, the electrical

conductivity of $\text{Fe}_2\text{O}_3/\text{graphene}$ was calculated to be $\sim 250 \text{ S m}^{-1}$. Thermal gravimetric analysis (TGA) of the $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrids (**Figure 4. 17**) reveals that the weight percentages of Fe_2O_3 ($C_{\text{Fe}_2\text{O}_3}$), are 10.7, 29.0 and 52.1 wt% for samples prepared with $I_{\text{FeSO}_4} = 0.03, 0.1$ and 0.15 M , respectively. The Brunauer-Emmett-Teller (BET) analysis of the nitrogen absorption/desorption isotherm (**Figure 4. 18**) suggests that the specific surface areas of pure graphene and $\text{Fe}_2\text{O}_3/\text{graphene}$ electrodes with $C_{\text{Fe}_2\text{O}_3}=10.7, 29.0$ and $52.1 \text{ wt\%}$ are $218.1, 182.1, 145.2$ and $165.7 \text{ m}^2 \text{ g}^{-1}$, respectively.

Figure 4. 16 Raman spectrum of the $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrid with $I_{\text{FeSO}_4}=0.1 \text{ M}$.

Figure 4. 17 TGA results of Fe_2O_3 /graphene samples prepared with I_{FeSO_4} = (a) 0.03, (b) 0.1 and (c) 0.15 M, respectively. The corresponding contents of Fe_2O_3 , $C_{\text{Fe}_2\text{O}_3}$, are estimated to be (a) 10.7 wt%, (b) 29.0 wt% and (c) 52.1 wt%.

Figure 4. 18 Nitrogen adsorption and desorption isotherms measured at 77 K for (a) graphene and Fe₂O₃/graphene with $c(\text{Fe}_2\text{O}_3)$ = (b) 10.7 wt%, (c) 29.0 wt%, (d) 52.1 wt%.

The O₂ electrodes were fabricated by coating the Fe₂O₃/graphene hybrids on a pristine microfiber filter paper (MFFP). This type of filter paper is sponge-like (**Figure 4. 19a**) with good wettability with most liquid electrolytes and high mechanical flexibility, which makes it suitable as separator for LOBs. The Fe₂O₃/graphene-coated MFFP electrode remains robust and bendable (**Figure 4. 19b**). The LOB configuration is similar to the commonly used coin cells of Li-ion batteries[16] with some changes as shown in the scheme (**Figure 4. 19c**). First, according to previous reports on LOBs,[11] 1, 2-Dimethoxyethane (DME) was chosen as the electrolyte instead of using carbonate-based electrolytes (e.g. commonly used in Li ion batteries). The carbonate-based electrolytes are reported to be unstable in LOBs during discharge probably due to the presence of O₂ in the working environment. The DME remains stable without obvious decomposition during discharge due

to its chemical stability in the presence of superoxide ions and high O_2 solubility [24]. Secondly, $LiClO_4$ was chosen as the solute in the DME electrolyte instead of using $LiPF_6$ (e.g. commonly used in Li-ion batteries). The $LiPF_6$ is highly sensitive to the ambient moisture while $LiClO_4$ is more stable. The average ion mobility and dissociation constant that determine the ionic conductivity of $LiClO_4$ is almost identical to that of $LiPF_6$. [4] Additional information on the fabrication of the cells are provided as follows: 1) a stainless steel foil was used as the anode current collector with a lithium foil on top; 2) a MFFP was used as a separator and another MFFP with Fe_2O_3 /graphene was placed on the topside; 3) a stainless steel mesh and a spring were adopted as a cathode current collector; 4) pure O_2 gas was purged through a channel on top of the spring.

Figure 4. 19 (a) Pristine microfiber filter paper, (b) the Fe_2O_3 /graphene coated microfiber filter paper as O_2 electrode and (c) Li- O_2 cell construction.

The XRD patterns of the Fe_2O_3 /graphene electrode ($C_{\text{Fe}_2\text{O}_3}=29.0$ wt%) and pure graphene electrode before and after discharge are shown in **Figure 4. 20a** and b. It reveals that crystalline hexagonal Li_2O_2 (JCPDS 09-0355) forms during the discharge process. Due to the small amount of Fe_2O_3 in the electrode (~ 0.5 mg cm^{-2}), the peaks of Fe_2O_3 are not detectable in the XRD spectra. The observed peaks in the XRD pattern of electrode before discharge are originated from the microfiber filter paper (MFFP). The grain size of Li_2O_2 was estimated to be 6.4 nm according to the full width at half maximum (FWHM) of the peaks using Scherrer's equation. Fe_2O_3 /graphene electrodes with other $C_{\text{Fe}_2\text{O}_3}$ values show similar XRD patterns.

Figure 4. 20 The XRD patterns of (a) the Fe_2O_3 /graphene electrode with $C_{\text{Fe}_2\text{O}_3} = 29.0$ wt% and (b) pure graphene electrode before and after discharge. MFFP refers to microfiber filter paper.

The cathodic scan is carried out to study the catalytic properties of our samples (**Figure 4. 21a**). The Fe_2O_3 /graphene electrodes with $C_{\text{Fe}_2\text{O}_3}=10.7$, 29.0 and 52.1 wt% exhibit oxygen reduction reaction (ORR) onset potentials > 2.9 V, which is higher than pure graphene (~ 2.75 V). Moreover, the typical discharge/charge voltage profiles (**Figure 4. 21b**)

reveal that the round-trip efficiency, defined as discharge voltage/charge voltage, of $\text{Fe}_2\text{O}_3/\text{graphene}$ with $C_{\text{Fe}_2\text{O}_3}=29.0$ wt% is ~ 65.9 % while pure graphene exhibits only 57.5 %. These results indicate much improved catalytic properties of $\text{Fe}_2\text{O}_3/\text{graphene}$ electrodes.

Figure 4. 21 (a) Cathodic scan of $\text{Fe}_2\text{O}_3/\text{graphene}$ and graphene. (b) Typical voltage profiles of $\text{Fe}_2\text{O}_3/\text{graphene}$ (29.0 %) and graphene at a current density of $200 \text{ mA g}_{\text{carbon}}^{-1}$.

The discharge voltage profiles to 2 V (vs. Li) of $\text{Fe}_2\text{O}_3/\text{graphene}$ and pure graphene electrodes at a current density of 100 mA g^{-1} were evaluated (**Figure 4. 22**). The pure graphene electrode depicts a discharge capacity of 5100 mAh g^{-1} at a voltage of 2.5 V. However, the $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode with $C_{\text{Fe}_2\text{O}_3}=10.7$, 29.0 and 52.1 wt% are able to deliver much higher discharge capacities of 6420, 8290 and 7920 mAh g^{-1} at a voltage of ~ 2.7 V. The voltage increase of ~ 0.2 V with the addition of Fe_2O_3 , indicates the high electrocatalytic activities of Fe_2O_3 , which is comparable to that of gold.[24] The discharge capacity does not increase continuously with $C_{\text{Fe}_2\text{O}_3}$ because the excessive amounts of Fe_2O_3 impede the electron transfer in the electrodes, which compromises the electrochemical performance. The much improved properties enable the $\text{Fe}_2\text{O}_3/\text{graphene}$ composites to be promising O_2 electrodes for LOBs.

Figure 4. 22 Discharge voltage profiles of $\text{Fe}_2\text{O}_3/\text{graphene}$ and pure graphene electrodes at $100 \text{ mA g}_{\text{carbon}}^{-1}$.

We have noticed that the discharge curves of our samples are different from previous reports[5, 46, 114], which is probably due to the different measuring protocols and electrolytes. For example, hybrid electrolytes[5], carbonate-based electrolytes[114] and tri(ethylene glycol) dimethyl ether-based electrolytes[46] as well as confined discharge/charge capacities[5] may result in different voltage curves.

To further examine the electrochemical performance of our samples, we have modified the electrochemical measurement protocols. The voltage range is changed to 2.4-4.5 V and the discharge/charge capacities are confined to 1000 mAh g^{-1} (**Figure 4. 23**). All the $\text{Fe}_2\text{O}_3/\text{graphene}$ electrodes with $C_{\text{Fe}_2\text{O}_3}=10.7, 29.0$ and $52.1 \text{ wt\%}$ depict a stable discharge voltage at $\sim 2.7 \text{ V}$ for 30 cycles. However, the discharge voltage of pure graphene is $\sim 2.55 \text{ V}$ at the 1st cycle and gradually descends to $< 2.4 \text{ V}$ at the 30th cycle.

Figure 4.23 Voltage profiles of selected cycles at 200 mA g_{carbon}^{-1} of $\text{Fe}_2\text{O}_3/\text{graphene}$ with $C_{\text{Fe}_2\text{O}_3}$ = (a) 10.7 wt%, (b) 29.0 wt%, (c) 52.1 wt% and (d) graphene at 1000 mAh g_{carbon}^{-1} .

To study the electrochemical stability of Fe_2O_3 in the discharge process of LOBs, XPS was carried out on the pristine and discharged electrodes with $C_{\text{Fe}_2\text{O}_3}$ = 29.0 wt% (**Figure 4.24**). Before measurements, the discharged electrode was immersed in deionized water to remove Li_2O_2 that was formed on the electrode. The Fe $2p_{3/2}$ and Fe $2p_{1/2}$ bands show peaks at 711.4 and 724.8 eV, respectively, with the satellite peak at ~720 eV, which confirms the presence of Fe^{3+} [136, 137]. This indicates that Fe_2O_3 remains stable during the discharge process without change in the valence state.

Figure 4. 24 The XPS spectra of the pristine and discharged $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode with $C_{\text{Fe}_2\text{O}_3}=29.0$ wt%.

The superior performance of $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode can be explained in two aspects as shown in the scheme in **Figure 4. 25**. First, the incorporation of graphene with high surface area favors the electron transport. Second, Fe-based catalysts can exhibit efficient electrocatalytic activities towards O_2 reduction as demonstrated in polymer electrolyte fuel cells [138] and solid oxide fuel cells [137]. The iron-oxides-based catalysts can easily adsorb O_2 on their surface by forming a bond between Fe and O and thereby weakens the bonding inside the O_2 molecule, which leads to lower activation energy of O_2 . Therefore, the electrochemical process during discharge can be described as follows (**Figure 4. 26a** and **b**): the graphene facilitates the transport of charge electrons to the catalytic sites of Fe_2O_3 , on which the O_2^- is easily adsorbed. The O_2^- reacts with Li^+ to form a layer of LiO_2 on top of the $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode. LiO_2 is then quickly converted to Li_2O_2 via disproportionation and further reduction to generate a layer of Li_2O_2 . [16] Meanwhile, a new layer of LiO_2 forms between the $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode and the Li_2O_2 layer and quickly decomposes upon formation. Therefore, at the end of discharge, the electrode is coated with a

layer of Li_2O_2 (**Figure 4. 26b**). According to previous study,[139] the O_2 reduction process by lithium on discharge can be summarized as three steps:

Figure 4. 25 Proposed working mechanism of the Fe_2O_3 /graphene electrode.

Figure 4. 26 Proposed working mechanism of the $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode: (a) During discharge and (b) at the end of discharge.

The working mechanism of catalysts in Li-air and Li- O_2 batteries has been bewildering on account of the buildup of insoluble discharge products. The model proposed here may provide a reasonable explanation and support for further investigation on the role of catalysts in Li-air and Li- O_2 batteries.

3. Short summary

$\text{Fe}_2\text{O}_3/\text{graphene}$ composites with different contents of Fe_2O_3 are prepared electrochemically and investigated as O_2 electrode for Li- O_2 batteries. The $\text{Fe}_2\text{O}_3/\text{graphene}$ electrode with $C_{\text{Fe}_2\text{O}_3}=29.0$ wt% exhibits a discharge capacity of 8290 mAh g^{-1} while the pure graphene electrode delivers only a discharge capacity of 5100 mAh g^{-1} . The improved

performance is ascribed to the fast electron transport provided by the graphene sheets and the high electrocatalytic activities for O₂ reduction provided by the Fe₂O₃.

4.3 Transition metal-polypyrrole metallopolymers/graphene composites as O₂ electrodes for Li-O₂ batteries

1. Introduction

Rechargeable Li-ion batteries have been widely applied in the fields of electric vehicles and portable devices due to their high energy density.[89] Great efforts have been spent on further improving their electrochemical performances. Recently, new types of Li-based energy systems attracted large attentions. For example, Li-O₂ batteries (LOBs) are promising due to their ultrahigh theoretical energy densities.[1, 7, 12, 16-18, 23, 29, 53, 55, 113, 115, 140-142] A major challenge of O₂ electrodes in LOBs is to improve the sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) during cycling. Other requirements of O₂ electrodes include high specific surface area, high electrical conductivity and high electrochemical stability, which are beneficial to achieve excellent energy storage properties of LOBs.

To reinforce the ORR and the OER process of the LOBs, many research works have been done on precious metals, rare earth elements based materials and transition metal oxides.[7, 10, 22, 24] However, the high cost, the tedious synthesis procedures and toxicity of heavy metal-containing compounds limit their practical applications. The metallopolymers with the metal-N sites have been proved to be a new class of efficient catalysts for fuel cells.[28, 31, 32] Polypyrrole is prone to form metal-N bonding with the transition metal atoms. Such structures exhibit high catalytic activities to the oxygen related reactions in comparison to precious metals. Thus, it is attractive to apply such materials as oxygen cathode for the LOBs.

In this work, we synthesized metallopolymer catalysts for LOBs. To enhance the electrical conductivity of the O₂ electrodes, reduced graphene oxide [91, 96, 143-147] was incorporated as the support of the composite. The sample showed nanowall morphology with thickness of ~ 20 nm and grew uniformly on graphene sheets. This morphology is beneficial to the O₂ diffusion in LOBs [22, 139, 148] and to prevent graphene from restacking. Among the samples, the Fe-based metallopolymer composite exhibited better catalytic efficiency and excellent electrochemical stabilities for LOBs, e.g. delivering discharge/charge capacities of 1000 mAh/g for 40 cycles with energy efficiency (round-trip efficiency) of >78 %.

2. Results & Discussion

The schematic representation of metallopolymer structure shows the linkage of transition metal atoms and nitrogen atoms in pyrrole units (**Figure 4. 27**). [28] Prior to the microscopy characterization, the electron beam radiation from the transmission electron microscope (TEM) is used to exam the exact location of the metallopolymers (**Figure 4. 28a** and **b**). It shows that the nanowalls change to the nanoparticles after radiation. Therefore it is concluded that the nanowalls are the metallopolymers due to its poor stability upon electron beam radiation. [149] The scanning electron microscope (SEM) image (**Figure 4. 29a**) and the TEM image (**Figure 4. 29b**) show that the Fe-based metallopolymer nanowalls with 100 - 200 nm widths grow vertically on the graphene surface. The high-magnification TEM image (**Figure 4. 29c**) reveals that the thickness of the Fe-based metallopolymer nanowalls is ~ 20 nm. The crystal information of the composites is examined by X-ray diffraction patterns (**Figure 4. 30**). The peaks at ~ 26° and ~ 43° can be indexed to the (002) and (100) crystal planes of graphene, respectively. No peaks corresponding to impurities are detected.

Figure 4. 27 Schematic representation of the metallopolymer structure.

Figure 4. 28 Electron beam radiation of Fe-based metallopolymer/rGO: (a) Before radiation and (b) after radiation.

Figure 4. 29 (a) SEM image, (b, c) TEM images of Fe-based metallopolymer/reduced graphene oxide. (c) is the magnified area of the red square in (b).

Figure 4. 30 XRD patterns of Fe-based metallopolymer/rGO.

To study the metal-N sites with different metal species, Co-based metallopolymer/rGO (CMG) and Mn-based metallopolymer/rGO (MMG) are also prepared. The SEM images (**Figure 4. 31a** and **b**) show that Co-based metallopolymer and Mn-based metallopolymer nanowalls with widths of 200-300 nm are vertically attached on graphene. The morphologies of FMG, CMG and MMG are similar, indicating that the metal species don't affect the growth of metallopolymer.

Figure 4. 31 SEM images of (a) Co-based metallopolymer/rGO and (b) Mn-based metallopolymer/rGO.

From the Raman spectra shown in **Figure 4. 32**, typical peaks corresponding to the D and G band of graphene-based materials appear at around 1365 cm^{-1} and 1580 cm^{-1} , respectively for graphene oxide (GO), rGO and FMG. Two broad peaks at ~ 1200 and $\sim 1510\text{ cm}^{-1}$ in the spectrum, which is associated with integrated five-member rings or heteroatoms in graphene structures[32]. The intensities of these two broad peaks at ~ 1200 and $\sim 1510\text{ cm}^{-1}$ are increased for FMG. This indicates the incorporation of metallopolymer into the graphene structures. Besides, according to the previous studies, the intensity ratios of the D band and the G band, I_D/I_G , reflects the defect level of graphene-based materials. [70] Here, the I_D/I_G values for GO, rGO and FMG are 1.0, 1.1 and 1.1, respectively. The I_D/I_G of rGO and FMG

is slightly higher than that of GO because of the reduction process. [36] The X-ray photoelectron spectroscopy (XPS) is performed to investigate the valence state of the major elements in FMG (**Figure 4. 33a and b**). Peaks of the Fe 2p_{3/2} and Fe 2p_{1/2} locates at 711.5 and 724.8 eV, respectively, with a satellite peak at ~ 719.3 eV, indicating the presence of Fe²⁺. [87] Fe³⁺ is also detected in the FMG composite as evidenced by the peaks of the Fe 2p_{3/2} at 713.6 eV and the Fe 2p_{1/2} at 727.4 eV, respectively [21]. It is consistent with the previous study which shows that Fe²⁺ and Fe³⁺ normally coexist in such composite. [28] Presence of N is confirmed by XPS and the peak at 400.1 eV in the N 1s spectra corresponds to the pyrrolic N (Figure 3b). [47] The Fe-based metallopolymer without rGO is also prepared and examined (**Figure 4. 34a and b**). The X-ray diffraction patterns of Fe-based metallopolymer show no peaks. The XPS results confirm the presence of Fe²⁺ and Fe³⁺, which is similar to FMG. The BET analysis (**Figure 4. 35**) indicates the specific surface area of FMG is ~131 m²g⁻¹ and the average pore diameters of FMG is ~2.3 nm.

Figure 4. 32 The Raman spectra of (a) graphene oxide, (b) reduced graphene oxide and (c) Fe-based metallopolymer/reduced graphene oxide.

Figure 4. 33 The X-ray photoelectron spectra of the Fe-based metallopolymer/reduced graphene oxide: (a) Fe 2p and (b) N 1s spectra.

Figure 4. 34 (a) XRD and (b) XPS of the Fe-based metallopolymer.

Figure 4. 35 (a) Nitrogen adsorption and desorption isotherms measured at 77 K of the Fe-based metallopolymer/rGO and (b) pore size distribution.

Prior to LOB test, the catalytic activities of CMG, MMG and FMG are examined by rotating-disk setup (**Figure 4. 36**). The onset potential of the FMG electrode (~ 0.04 V vs. HgO/Hg) is higher than CMG (~ -0.08 V vs. HgO/Hg) and MMG (~ -0.06 V vs. HgO/Hg), indicating the stronger catalytic activity of FMG. The electrochemical performance of the FMG composites is examined in LOBs at various current densities (**Figure 4. 37**). In a typical discharge process of LOBs, O₂ is reduced and reacts with Li ions to form Li₂O₂ at a theoretical potential of ~ 3 V (vs. Li), which is then reversibly oxidized and releases O₂ during charge process with high overpotentials (above 4 V vs. Li). It is noticed that the open circuit voltage (OCV) of Li-O₂ cells is higher than theoretical values (~ 3 V). OCV reflects a mixed potential effect due to the interaction between Li ions in the electrolytes and O₂.^[1] The activity of O₂ is enhanced by the catalysts in the electrodes and so the actual electrochemical potential of the electrodes is increased as well as OCV.^[23, 27] The round-trip efficiencies, defined as the ratio between the discharge energy and the charge energy, are introduced to evaluate the catalytic effect of the electrodes. The specific discharge-charge capacities of the samples are limited to 1000 mAh/g. The 1st-cycle round-trip efficiencies of the FMG electrodes at current densities of 50, 200 and 400 mA/g are 79 %, 72 % and 65 %, respectively.

respectively. In comparison, the 1st-cycle round-trip efficiencies of the CMG and MMG electrodes (**Figure 4. 38**) at 200 mA/g are 67 % and 65 %. Therefore, it is concluded that FMG exhibits higher catalytic activities than CMG and MMG. In addition, the round-trip efficiencies of the FMG electrodes are also higher than some of the reported oxygen cathodes including mesoporous NiCo₂O₄ nanoflakes[20], porous La_{0.75}Sr_{0.25}MnO₃ nanotubes [22] and CoMn₂O₄ nanoparticles [19]. On the other hand, the FMG electrodes deliver the discharge voltages of ~ 2.7 V and the charge voltages of ~ 3.5 V for 40 cycles at 50 mA/g (**Figure 4. 37a**). The low charge voltages of the FMG are beneficial to suppress the formation of the side products. [14] Moreover, after 40 cycles, the discharge voltages at 200 mA/g are ~ 2.65 V and the charge voltages are ~ 3.8 V with a round-trip efficiency of 72 % (**Figure 4. 37b**) while the values at 400 mA/g are ~ 2.6 V, ~ 4.1 V and 65 %, respectively (**Figure 4. 37c**). Such cycling performance under high current densities reveals the superior cathode performance of the FMG electrodes.

Figure 4.36 ORR polarization curves of (a) Co-based metallopolymer/rGO, (b) Mn-based metallopolymer/rGO and (c) Fe-based metallopolymer/rGO at different rotation rates.

Figure 4.37 Electrochemical performance of Fe-based metallopolymer/reduced graphene oxide electrodes for Li-O₂ batteries at (a) 50, (b) 200 and (c) 400 mA/g.

Figure 4.38 Electrochemical performance of (a) Co-based metallopolymer/rGO and (b) Mn-based metallopolymer/rGO at 200 mA/g.

To investigate the products after the charge-discharge process, nuclear magnetic resonance (NMR) analysis is performed on the electrodes after 40 cycles (**Figure 4.39**). The peaks at 3.3 and 3.6 ppm are generated by TEGDME and the peak at 4.7 ppm corresponds to

D₂O. The peaks at 1.8 ppm and 8.3 ppm symbolize CH₃CO₂Li and HCO₂Li, respectively. [106] The two compounds are the side products formed during the cycling process, which can decrease the electrical conductivity and impair the electrochemical properties of the O₂ electrodes. To study the side products quantitatively, equal amounts of D₂O and the sample electrodes are used in the NMR test. The intensity ratios between the side products and the D₂O ($I_{CH_3CO_2Li+HCO_2Li}/I_{D_2O}$) are employed to estimate the contents of the side products generated in the electrodes. The values of $I_{CH_3CO_2Li+HCO_2Li}/I_{D_2O}$ are 0.005, 0.003 and 0.001 as calculated from the CPG, MPG and FPG electrodes, respectively. Therefore the side products form most slowly in the FPG electrodes.

Figure 4. $^{39} \text{H}$ NMR spectra of (a, b) Co-based metallopolymer/rGO, (c, d) Mn-based metallopolymer/rGO and (e, f) Fe-based metallopolymer/rGO after 40 cycles. (b, d, f) are the magnified spectra.

The morphologies of the discharged products are also examined. The electrodes discharged to 1000 mAh/g are washed with TEGDME and handled with care to avoid prolonged exposure to the air. The SEM images of the electrodes show that the discharge

products of the CMG and MMG form thick and smooth coating layer on the surface of the electrodes (**Figure 4. 40a and b**). In comparison, the surface of the discharge products on the FMG electrode is rough with numerous bumps (**Figure 4. 40c**). The formation of the bumps on top of the Fe-based metallopolymer nanowalls may be due to the high catalytic activity of FMG, which induces faster growth of the discharge products near the Fe-based metallopolymer nanowalls (**Figure 4. 41a**). On the contrary, the growth rates of the discharge products near or far away from the Co-based metallopolymer and Mn-based metallopolymer nanowalls show no much difference due to their moderate catalytic activities (**Figure 4. 41b**). Hence no obvious bumps are formed on the surface of CMG and MMG. Besides, the rough surface of the discharge products on the FMG electrode enlarges the contact area of the discharged electrode with the electrolytes and thereby could further facilitate the subsequent charging process.

Figure 4. 40 SEM images of (a) Co-based metallopolymer/rGO, (b) Mn-based metallopolymer/rGO and (c) Fe-based metallopolymer/rGO electrodes discharged to 1000 mAh/g.

Figure 4. 41 Schematic growth of discharge products on metallopolymer/rGO electrodes with (a) high and (b) low catalytic effects.

3. Short summary

In conclusion, we have synthesized different metal-polypyrrole metallopolymer nanocomposites as O_2 electrodes for LOBs. The samples show interesting morphology as nanowalls grow vertically on the graphene surface, which is beneficial to achieve good performance as O_2 electrodes. The as-prepared Fe-polypyrrole metallopolymer sample exhibits better round-trip efficiencies and cycling performance. It can repeatedly deliver discharge-charge capacities of 1000 mAh/g for 40 cycles and maintain round-trip

efficiencies $> 78\%$. It also shows high 1st-cycle round-trip efficiencies of 79 %, 72 % and 65 % at current densities of 50, 200 and 400 mA/g, respectively.

CHAPTER 5: CONCLUSIONS

In this thesis, a systematic study on the graphene-based composite oxygen electrode (cathode) for LOBs is performed. A rational and convenient configuration of LOBs is established for electrochemical characterization. Battery testing protocols are optimized. Graphene-based composite materials are synthesized and applied for LOBs. In-depth investigation is carried out on the preparation processes, materials characterization and electrochemical characterization. Moreover, the effects of graphene-based composites are examined on the battery performance and the corresponding mechanisms are proposed.

Pure graphene foam is first prepared by a novel electrochemical method. Graphene sheets are incompletely exfoliated from graphite papers by ions that are driven by the applied electric field in the electrolytes. To some extent, the expansion of graphite papers is proportional to the duration of the applied current. However, the applied current must be optimized. This is because a high current leads to fast complete exfoliation of graphene sheets and a low current reduces the expanding rate. Then graphene foams are anneal in inert gas to decrease the defects of graphene. The effects of defects on the electrochemical performance of LOBs are studied. The results reveal the defects are harmful to battery performance. This is because the defects elevate the electrical resistance and so the overpotential during the charging process of LOBs. The high charging voltage results in the decomposition of electrolytes and graphene and much side products are generated. The side products are electrochemically irreversible and reduce the active materials. Therefore the cycling stability of LOBs is undermined. This implies graphene with high quality can be a promising candidate for LOBs. Moreover, the chemical/electrochemical stability of carbon electrodes is important for LOBs with high performance.

Besides, Fe_2O_3 /graphene composite is synthesized by one-step electrochemical method. The deposition of Fe_2O_3 and the exfoliation of graphene sheets are simultaneously realized in an electrochemical cell. The ratio of Fe_2O_3 and graphene can be adjusted by varying the concentrations of electrolytes. The composite exhibits improved electrochemical properties than pure graphene electrode. The loading of iron oxide as catalysts for LOBs is also investigated. The results show that there is an optimized content of the loading of iron oxide. This is because the high loading of iron oxide increases the electrical impedance of the oxygen electrodes while the low loading decreases the catalytic effect. Analysis of the electrodes after battery test shows no significant change on the oxidation states of iron, indicating a high durability of iron oxide as catalysts for LOBs.

Finally, metal-polypyrrole metallopolymer/reduced graphene oxide is prepared via a conventional wet chemistry method with multiple steps. First, reduced graphene oxide is synthesized by Hummers method. Then pyrrole units are polymerized on reduced graphene oxide, followed by coordination of metal ions via low temperature process. The synthesis strategy is simple and controllable. Three kinds of metallopolymer are prepared with Fe, Co and Mn, in which Fe-based metallopolymer/reduced graphene oxide exhibit highest electrochemical performance for LOBs. The ORR activity test shows that Fe-based composite possesses the highest catalytic property. Analysis of the electrodes after cycling reveals different morphologies of discharge products. The wrinkles of discharge products on Fe-based electrodes increase the contact area between the electrolytes and the electrodes, which is beneficial to the following charging process. The results indicate that the electrochemical performance of LOBs can be affected by the growth of discharge products.

Based on the results of the thesis, the hypotheses are listed and discussed as follows:

- 1) The LOB performance can be improved by decreasing the defects of graphene.

Discussion: This has been verified in Section 4.1. The structural defects in the graphene foam are detrimental to the structural stability of the O₂ electrode and can slow down the kinetics of charge transfer. This degrades the electrochemical performance of oxygen electrodes due to their slow kinetics of charge transfer and the more active chemical properties of the C-O-C, C=O and C-OH bonds in comparison to the sp² graphitic bonds. Moreover these defects lead to the faster growth of the side products of the LOBs during cycling, which further deteriorate the electrochemical performance.

- 2) The loading of the second phase should be balanced between the catalytic effect and the overall conductivity;

Discussion: This has been verified in Section 4.2. The Fe₂O₃/graphene with 29 wt% of Fe₂O₃ exhibits the best electrochemical performance in comparison to the other two samples with different contents of Fe₂O₃.

- 3) The formation of the byproducts can affect the electrochemical performance of LOBs.

Discussion: This has been verified in Section 4.1-4.3. The electrodes with fewer byproducts exhibit better electrochemical properties than those with more byproducts.

The novelties and significant progress in terms of science and technologies in the main work (Chapter 4) of this thesis are summarized as the following. In the 1st section of Chapter 4, a novel electrochemical leavening strategy followed by annealing to produce graphene foams with small amounts of defects/functionalities is developed. The correlation between the amounts of defects/functionalities of graphene and the electrochemical performance of LOBs is studied and interpreted. In the 2nd part of Chapter 4, a novel electrochemical method to synthesize Fe₂O₃/graphene composites is developed. This method

exhibits much improved efficiencies to produce graphene-based composites in comparison to the conventional approaches. Another original contribution in the field of LOBs is that the contents of Fe_2O_3 in the composites are studied and correlated to the electrochemical performance of LOBs. In the 3rd section of Chapter 4, metallopolymers/graphene composites with novel morphologies are synthesized. An original strategy to improve the performance of LOBs is proposed: altering the architecture/morphologies of the electrode materials. The above-mentioned materials exhibit outstanding properties as cathodes of LOBs in comparison to the conventional electrodes for air/oxygen batteries, e.g. precious metals/amorphous carbons, which are reported in the literatures. Therefore, the low cost and high performance of the graphene-based composite materials are promising candidates for LOBs.

CHAPTER 6: FUTURE WORK

Scientists' enthusiasm on LOBs has also aroused interests on other metal-air batteries, e.g. Na-air and Mg-air batteries. This is due to the similarity between those battery systems. The findings on LOBs are also contributing to the development of other metal-air batteries. As LOBs are still in the preliminary stage, the electrochemistry of LOBs is not quite clear yet. Much work is needed to be carried out to develop electrolytes and anode materials with high stability, high ionic/electronic conductivity and low cost. In addition, efforts are also needed to explore a simple and durable configuration of LOBs, which is dependent on the development of electrolytes and anodes. Besides, for industrial applications, the battery monitor system needs to be renovated. This is because conventional monitor system can judge the state of charge simply by measuring the voltages of batteries. However, the discharge/charge voltages of LOBs are very steady. It is impossible to cut down the discharge/charge process simply according to the voltages.

As for the oxygen electrodes (cathodes), the catalytic activity, electrochemical stability and specific capacity will still be the major challenges. Since one material cannot meet all the requirements, composite materials are more suitable for LOBs. Graphene possesses high electrical conductivity and high stability. Hence it is a promising candidate for LOBs as carriers of catalysts.

In addition, the redox reaction in LOBs may vary with different cell designs. Although the theory that LiO_2 forms in the first place and decomposes to Li_2O_2 has been well accepted, the detailed study on the redox reaction in the cell proposed in this thesis should be performed in future.

The study on graphene foam electrodes in the thesis shows that the quality of graphene can affect the electrochemical performance of LOBs. Thus it is a challenge how to

prepare high-quality graphene sheets. Annealing at high temperature in inert gas is effective, which is done in the thesis work, but costly. Other methods can be developed and tried out. For example, electrochemical reduction and microwave-assisted reduction have been reported. But the efficiencies of these methods should be examined. In addition, annealing composites may damage the quality of the materials other than graphene. Electrochemical reduction can help avoid this concern simply by controlling the reduction potentials out of the range that may harm the other materials. Moreover, it is also interesting to study how the defects and functionalities of graphene affect the LOB performance, e.g. the processes of the mass and charge transfer.

Fe_2O_3 /graphene is proved to exhibit high performance for LOBs. The samples are synthesized by a novel electrochemical method. This method can be extended to other kinds of graphene-based materials, e.g. noble metals and transition metal oxides. The exfoliation strategy is also applicable to produce two dimensional nanosheets from layered structures. It has been carried out on nanosized layered structures. But it failed because the nanosized particles are very durable to large volume expansion. So bulk counterparts can be tried out. Promising candidates can be layered transition metal oxides and hydroxides as these materials possess high catalytic activities, e.g. vanadium oxides, cobalt oxides and manganese oxides. In addition, it is attractive to study how the Fe_2O_3 /graphene catalyzes and improves the electrochemical performance.

Metallopolymers/graphene composites depict good electrochemical properties for LOBs. The growth of discharge products can be an important factor influencing the battery performance. The template effect of metallopolymers demonstrates that it is possible to improve the battery performance of LOBs by adjusting the morphologies/topographies of the oxygen electrode materials. Therefore, it is attractive to synthesize catalysts with controlled morphologies. In addition, other types of metallopolymers with different functionalities can

be prepared to study how the functionalities and metal-N bondings affect the performance of LOBs.

Besides, in this thesis, the discharge products and the undesired products over discharge process are mainly analyzed by ex-situ NMR method. Obviously, only NMR is not enough to characterize the discharge/charge products and undesired products over cycling. Therefore, other in-situ/ex-situ characterization methods, such as FT-IR, DEMS, XPS, TEM, SEM, etc., should also be employed in future work to analyze the charge/discharge process of LOBs.

Last but not least, the protection of Li-anode and exploration of electrolyte could also be considered in future work.

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