Graphene-based composites for electrochemical energy storage

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**GRAPHENE-BASED COMPOSITES FOR
ELECTROCHEMICAL ENERGY STORAGE**

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**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

2015

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ELECTROCHEMICAL ENERGY STORAGE**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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PhD is a journey filled with hardships, lessons, celebrations, enjoys and special moments that ultimately lead me to the new stage in life. The road is not always smooth. In fact, throughout the whole travel, I encountered many challenges, and luckily, learned, gained a lot from them. At the moment, it is the time to say goodbye to this wonderful journey and it is the time to say thanks to everyone accompanying with me.

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Summary

Achieving secure, clean and sustainable energy production, storage, and consumption are, perhaps, the greatest technical and social challenge that the world are facing. The key achievement is not only to explore renewable and sustainable energy sources but also, perhaps even more importantly, to store energy efficiently and deliver on demand. The realization of high performance electrochemical energy storage devices is no doubt strongly dependent on the achievements of multidisciplinary sciences, including materials sciences, chemistry sciences and physical sciences etc. Graphene, a single atomic layer of sp^2 -bonded carbon atoms, has attracted worldwide interest because of its intrinsic difference from other forms of carbon allotropes. Graphene is particularly suitable for the implementation in electrochemical applications due to its remarkable electrical conductivity, large specific surface area, unique heterogeneous electron transfer and charge carrier rates, and good electrochemical stability. This thesis focuses on the synthesis and characterization of low-dimensional carbon materials, including graphene oxide/graphene, graphene foam (GF), GF/carbon nanotubes (CNTs) hybrids, and their composites with nanostructured metal oxides. The application of these graphene-based materials in electrochemical energy storage devices is also explored. The thesis consists of three parts: Introduction (chapter 1), Main text (chapters 2-5), and Conclusion, Comments and Future Work (chapter 6).

Specifically, chapter 1 describes the energy demand and challenges, introduces the basic principles and working mechanism of capacitors, supercapacitors and rechargeable batteries from the thermodynamic and kinetic

aspects, and retrospects previous works on the synthesis of graphene/graphene oxide and their applications in flexible energy storage devices.

The synthesis of graphene/graphene oxide in both high-quality and large-quantity *via* an economic and environmentally-friendly way is highly desirable but still challengeable. In Chapter 2, a novel and facile electrochemical exfoliation approach has been developed and proposed for the synthesis of high-quality graphene flakes. The corresponding process mechanism is proposed. The optimized synthesis conditions were explored. The electrochemical performance of as-resulted graphene flakes for oxygen reduction reaction (ORR) was evaluated. The results presented here could provide deep understanding of the underlying mechanism for electrochemical exfoliation of graphite, effective guides for optimized/controlled synthesis of graphene, and promising approaches for graphene commercialization in future.

The development of deformable electrodes with high energy density and good mechanical integrity is one key challenge in flexible electrochemical energy storage. Graphene foam (GF) grown from chemical vapour deposition using Ni foam as template is a three-dimensional (3D) interconnected network of high-quality graphene. It processes high porosity, good electric conductivity and excellent mechanical integrity, and is a good scaffold for flexible electrodes. In chapter 3, GF is employed as a 3D interconnected current collector for nanostructured Fe_3O_4 electrode, because it can provide highly conductive pathway for electrons and ions. The bottom-up strategy assisted by atomic layer deposition approach has been proposed for grafting mesoporous Fe_3O_4 nanostrucutre onto 3D graphene foam. The resulting GF/ Fe_3O_4 electrode demonstrates high reversible capacity and fast charging and discharging

capability, in addition to its thin, lightweight, and flexible features. The unique and rational design we proposed here successfully overcome the bottleneck of poor cyclability and low rate capability of Fe_3O_4 , and provide effective guides for optimized electrodes in flexible energy storage devices.

To achieve high gravimetric and volumetric energy density for flexible energy storage devices, it is critically important to increase the areal loading of electroactive materials on truly flexible electrode supports. In chapter 4 a facile approach is developed to fabricate a novel electrode support (GF/CNTs) consisting of carbon nanotubes supported on graphene foam (GF) with covalent bonding. The densely grown CNTs extend the 3D architecture of GF without sacrificing the good ohmic and mechanical contact between them, which provides a high surface-to-volume ratio that allows high mass loading of active materials. The GF/CNTs hybrid films show several critical merits, including: (i) good electric conductivity; (ii) large specific surface area; (iii) high active materials mass loading, which could be 4-5 folds higher than pure GF ($3\text{-}8\text{ mg/cm}^2$); (iv) Ultrathin and Lightweight with thickness range from 30 to 100 μm ; (v) large size, good flexibility and mechanical integrity; and (vi) excellent electrochemical stability. These features provide GF/CNTs hybrid film with great potential for applications in next-generation flexible energy storage devices. GF/CNTs/ MnO_2 and GF/CNTs/Ppy composites with excellent electrochemical performance were fabricated based on GF/CNTs hybrid films. They were further assembled into asymmetric supercapacitors (ASCs) (GF/CNTs/ MnO_2 // GF/CNTs/Ppy) that show high energy/power density and are capable of repeated bending without structure failure and degradation in

performance. These results presented in this work would no doubt provide a promising approach for flexible electrode design in future.

Nickel/Iron battery is century-old and well developed in the past decades. However, there is less reports on its application in modern power-stationary systems, particularly in flexible energy storage devices. To explore its promising potential in modern flexible power source system is therefore challengeable and meaningful. In chapter 5, flexible rechargeable Ni/Fe batteries are constructed by direct growth of $\text{Ni}(\text{OH})_2$ nanosheets (cathode material) and mesoporous Fe_2O_3 nanroods (anode material) on the GF/CNTs hybrid films. The assembled f-Ni/Fe cells are able to deliver high energy/power densities (100.7 Wh/kg at 287 W/kg and 70.9 Wh/kg at 1.4 kW/kg, based on the total mass of active materials) and outstanding cycling stability (retention 89.1% after 1,000 charge/discharge cycles). Benefiting from the ultrathin and lightweight features of GF/CNTs hybrid films, our f-Ni/Fe cell can exhibit a volumetric energy density of 16.6 Wh/l (based on the total volume of full cell), which is comparable to that of thin film battery and better than that of typical commercial supercapacitors. Our present results make it possible to explore the promising applications of traditional energy storage devices into modern, flexible energy storage systems via employing novel materials and device deign. These results would no doubt provide a novel direction for the development of flexible energy storage devices.

Chapter 6 summarizes the achievements in each chapter, discuss the challenges, and propose plans for further studies.

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Chapter 1

Introduction and Literature Background

1.1 Energy demands and challenges

Energy is no doubt the engine for the car of Human civilization and development. Achieving secure, clean and sustainable energy production, storage, and consumption are, perhaps, the greatest technical and social challenge that the world are facing.^[1-6] Generally, energy sources could be divided into two categories based on their intrinsic nature: non-renewable sources and renewable sources. Non-renewable energies include fossil fuels, nature gas, oil and coal, are available in limited quantity on the earth and could not be re-generated within a short span of time. Renewable energies are the energies that are inexhaustible, and could be generated repeatedly when required, such as solar, wind, geothermal, tide and biomass. It is projected by the U.S. Energy Information Administration that the world energy consumption will grow from 524 quadrillion British thermal units (Btu) in 2010 to 820 quadrillion Btu in 2040, a 56 percent increase between 2010 and 2040 (Figure 1.1, reference case).^[7]

Figure 1.1. World energy consumption in 2010 and 2040 (quadrillion Btu) with three economic growth cases.^[7]

With rapidly growing energy demand and concerns over energy security and local pollution, it is highly desirable to explore renewable and sustainable energy sources. It is anticipated by Russia International Energy Agency that the share of renewable energies in primary energy consumption would rise from 13% in 2011 to 18% in 2035 (Figure 1.2), resulting from rapidly increasing demand for modern renewable society to produce heat, generate power, and make transport fuels^[8].

Figure 1.2. Renewable energy share in total primary energy sources, demand by category and region (New Policies Scenario), 2011 and 2035.^[8]

Wind power and solar photovoltaics (PV) are the world's fastest-growing renewable energy. Wind and solar would account for about 19% of global installed power capacity, and reach almost 35% of that of the European Union in 2035 (Figure 1.3) according to the New Policies Scenario.^[8]

Figure 1.3. Shares of wind and solar power capacity and generation in the New Policies scenario^[8].

However, unlike dispatchable power generation technologies (fossil fuel-fired, geothermal, hydropower with reservoir and bio-energy), which may be ramped up or down to match demand, the output from wind power and solar PV is only intermittently available and is strongly dependent on the availability of the sources including the time, weather, season and location, while the demands and consumption of electric energy are relatively constant.^[8] Wind power and solar PV are also characterized as variable renewable energies because of their typical properties, such as variability, uncertainty, modularity, low operation cost and non-synchronous generation. Although quite attractive, the variable nature of variable renewable sources present great challenge for energy storage and transmission. The key success lies in exploring renewable and sustainable energy sources, particularly, storing energy efficiently, and delivering on

demand. Consequently, large-scale stationary energy storage systems (ESSs) connected to renewable power plants have become key enablers of improving power reliability and quality as well as taking full advantages of high penetration of renewable energy sources.^[6, 9, 10] To be highly efficient, energy storage technologies are required to be adapted for various applications types. EESs that are available for large-scale applications by far could be categorized into four types, mechanical, chemical, electrical and electrochemical (Figure 1.4).^[6, 9, 11-13] Although mechanical energy storage via pumped hydroelectricity is dominating current energy storage, electrochemical energy storage in the form of electrochemical capacitors and batteries has by far found their wide application in powering portable electronics and electrification of the transportation sector because of their desirable characteristic such as high round-trip efficiency, controllable power and energy, long cycle life, environmental-friendly feature and low costs.^[6, 9, 11] However, there are several challenges that rooted primarily in materials and technologies for coupling electrochemical energy storage with renewable energy sources including wind and solar for powering the electric grid. The realization of high performance electrochemical energy storage devices is strongly dependent on the achievements of multidisciplinary sciences, including materials sciences, chemistry sciences and physical sciences etc.^[6, 9, 14]

Figure 1.4. Ranges of application of storage technologies.^[13]

1.2 Electrochemical Energy Storage Systems

1.2.1 Electrochemical Capacitors (ECs)

Since the first patent was released by General Electric on 1957^[15], electrochemical capacitors (ECs) have attracted considerable attention due to their promising applications in various areas including power storage and supply, power quality applications and backup etc,^[16] since ECs have high power capability, efficiency and long life span^[16-18] (Figure 1.5). ECs are energy storage devices that are capable of storing and releasing electric charge in a faster way than electrochemical cells.^[17] Based on different underlying mechanisms, ECs are classified into two categories: (i) Electrochemical Double Layer Capacitors (EDLCs) and (ii) Pseudocapacitors.^[16-20] The so-called EDLCs are based on electrostatic charge separation at the electrochemical interface between an electrode and electrolyte, creating two electrostatic capacitors connected in series in electrolyte. The so-called pseudocapacitors are based on faradaic pseudocapacitance, that associated with electrosorption or

surface/near-surface electrochemical redox processes involving in pseudocapacitive materials such as transition metal oxides and conducting polymers.^[14, 18, 19, 21]

Figure 1.5. (a) Ragone Plot and (b) Fundamental mechanisms of different energy storage technologies, include double-layer capacitor, pseudocapacitor and batteries.

1.2.1.1 Thermodynamic Principles of Electrochemical Capacitors (ECs)

Double Layer Capacitance. Different from traditional electrostatic capacitors, EDLCs store and release energy at the interface between electrolyte and electrode, where two capacitors are formed resulting from the reversible adsorption of solvated ions at the electrode surface, and connected in series by electrolyte (Figure 1.5).^[19, 21] This type of charge storage is electrostatic, potential dependent, physicochemical nature of the electrode surface dependent, and no redox reactions are involved.^[14, 18, 19, 21] The current during charge storage/release process is essentially a displacement current due to the rearrangement of charges. Therefore, the process is no-faradaic in nature and the response to changes in potential without diffusion limitations is rapid and lead to high power.^[20, 22] Inversely, the energy density of EDLCs is lower than that of battery because the charge is confined to the surface. The individual

“double-layer capacitance” of each electrode could be described as follows:^[14, 16, 17, 19, 21, 23]

$$C_{dl} = \frac{Q}{V} = \frac{\epsilon_r \epsilon_o A}{d} \quad (1)$$

where C_{dl} is the double layer capacitance (F) of a single electrode, Q is the total charge transferred at potential V , ϵ_r is electrolyte dielectric constant, ϵ_o is the vacuum dielectric constant, d is the charge separation distance, and A is electrode surface area.

When considering that C is a constant for double layer capacitors, another equation could be derived from (1):

$$I = \frac{dQ}{dt} = \frac{d(CV)}{dt} = C \frac{dV}{dt} + V \frac{dC}{dt} = C \frac{dV}{dt} \quad (2)$$

where I is the response current, t is the charge time.

If the applied voltage V varies with time t in a linear way, i.e. $V = V_0 + vt$ (V_0 is the initial voltage; v is the scan rate (V/s)), the relationship could be given as:

$$I = Cv \quad (3)$$

It is found from Eq. (3) that the current responses linearly with the scan rate. This feature translates into a well-defined rectangular current (I)-voltage (V) plot or cyclic voltammogram (CV) at different scan rates (Figure 1.6a).

Figure 1.6. (a) Cyclic Voltammogram (CV) curves at different scan rates, and (b) Galvanostatic Charge/Discharge curves at various currents for a 50 mF capacitor.^[24]

Based on eqs. (2) and (3), if a constant current is applied for charging/discharging a capacitor, the voltage would increase/decrease in a constant rate $v = dV/dt$. This feature would translate into a well-defined triangular galvanostatic charge/discharge curves (Figure 1.6b).

The energy stored in such a capacitor is given by:^[14, 16, 17, 19, 21, 25]

$$E = \int_0^Q V(q) dQ = \int_0^Q \frac{Q}{C} dQ = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} CV^2 \quad (4)$$

$$Q = \int_0^{\Delta t} I dt = \int_0^q dq \quad (5)$$

where V is nominal voltage (volts) and q is the state of charge.

The power is thus described by the equation:

$$P = \frac{E}{t} = \frac{1}{2} \frac{CV^2}{t} \quad (6)$$

Pseudocapacitive Capacitance. Pseudocapacitive processes are, ideally, two-dimensional (2D) or Quasi-two-dimensional, and based on fast and

reversible faradaic redox process in which a monolayer or quasi-monolayer of electrochemical reactive species could be electrosorbed/electrodesorbed with charge transfer.^[18, 19, 26, 27] The charge-discharge mechanism involves the transfer of electric charge between the phases but without any bulk phase transformation. The state of charge/discharge (q) is a function of the electrode potential with the extent of faradaic charge/discharge (Q) passed.^[19] The change of charge (Q) with respect to the potential gives rise to the derivative, dQ/dV , corresponds to pseudocapacitance.^[18] This kind of pseudocapacitance is faradaic in nature, which is different from the double layer capacitance that associated with potential-dependent accumulation of electrostatic charge,^[18, 19] and the ideal Nernstian processes involved in a battery-type materials where faradaic reactions occurs at a constant potential.^[28]

$$C_{\phi} \sim \frac{dQ}{dV} \quad (7)$$

There are several faradic processes that can result in pseudocapacitance according to Conway's comments: (i) under-potential deposition (UPD) (two-dimensional, 2D), (ii) surface redox system, and (iii) intercalation system (quasi-2D) (Figure 1.7).^[18, 19]

Figure 1.7 Different faradaic processes that give rise to pseudocapacitance.

*Note: X is two-dimensional site occupancy fraction for UPD, $[O_x]/([O_x] + [Red])$ for redox systems and occupancy fraction of layer lattice for intercalation systems, respectively.

The deposition of metal ions well above their redox potential at a different metal surface to form an adsorbed monolayer is called under-potential deposition (UPD).^[29, 30] Well-known cases of UPD is that of H on Pt or Pb on Au.^[26, 27, 29, 30] Redox processes take place when electroactive species are electrochemically adsorbed onto the surface or near surface of electrode materials with a concomitant faradaic charge-transfer. Redox systems exhibiting pseudocapacitance consist of electrochemical oxidation/reduction of transition metal oxides and electrochemical generation of conducting polymer (polyaniline, polypyrrole, polythiophene etc.).^[14, 18, 21] Intercalation pseudocapacitance arises when the intercalation sorption of electroactive species takes place quasi-two-dimensionally accompanied with faradaic charge-transfer without crystallographic phase change. Intercalation systems include the

intercalation of Li into hosts such as TiS_2 , MnO_2 or MoS_2 , or the intercalation of H into Pd and Pd-Ag alloys.^[14, 19, 26, 27] Although these three mechanisms take places based on different faradaic process and different types of electrode materials, they exhibit similarity in electrochemical and thermodynamic feature with logarithmic relationship between electrode potential and the extent of charge/discharge^[14, 19, 31] (Figure 1.7 & Table 1.1):

$$E = E^0 + \frac{RT}{nF} \ln \frac{X}{1-X} \quad (8)$$

where E is the electrode potential (V), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), n is the number of electrons, F is the Faraday constant (96485 C mol^{-1}), and X is the occupancy fraction of surface or layer lattice.

If the electrochemical sorption of electroactive species follows an electrochemical Lagmuir isotherm^[27, 32]:

$$\frac{X}{1-X} = k \cdot \exp\left(\frac{VF}{RT}\right) \quad (9)$$

a capacitor could be defined as^[19]:

$$C_\phi = q^* \cdot \frac{dX}{dV} \quad (10)$$

where q^* is the charge required for completion of monolayer sorption.

Applying eq (9) into (10) leads to :

$$C_\phi = \frac{q^*F}{RT} \cdot \frac{k \cdot \exp[VF/RT]}{(1 + k \cdot \exp[VF/RT])^2} = \frac{q^*F}{RT} \cdot X \cdot (1-X) \quad (11)$$

which indicates that the capacitance C_θ is not constant and has a maximum value at $X = 0.5$. The C_θ is called pseudocapacitance.^[19]

Table 1.1. Different systems that give rise to pseudocapacitances.^[18, 31]

Pseudocapacitive System Types	Essential Relations
(a) Under-potential deposition of metal atoms: $M^{Z+} + S + Ze^- \rightleftharpoons SM$ or $H^+e^- + S \rightleftharpoons SH$	$E = E^0 + \frac{RT}{ZF} \ln \frac{\theta}{1 - \theta}$ (θ two-dimensional site occupancy fraction)
(b) Redox system: $Ox + Ze^- \rightleftharpoons Red$ and $O^{2-} + H^+ \rightleftharpoons$ in lattice	$E = E^0 + \frac{RT}{ZF} \ln \frac{R}{1 - R}$ $R = [O_x]/([O_x] + [Red])$; $R/(1 - R) = [O_x]/[Red]$
(c) Intercalation system: “Li ⁺ ” into “MA ₂ ”	$E = E^0 + \frac{RT}{ZF} \ln \frac{X}{1 - X}$ $X =$ Occupancy fraction of layer lattice sites (e.g. Li ⁺ into TiS ₂)

1.2.1.2 Kinetic Electrochemical Features of ECs

While thermodynamic aspects for ECs have been described above, the practical application of ECs is strongly related to their kinetic behaviour. It should be stated that all electrochemical reactions are subjected to polarization effects that would sacrifice working voltage and reversible capacity.^[14, 19] Therefore, although electrochemical capacitances could result from various electrochemical processes as mentioned above, they suffer from polarization effects and the ideal complete reversibility is not practical from a kinetic viewpoint. Indeed, there is an internal resistance, known as equivalent series resistance (R_{ESR}), for any electric power sources. Here we try to introduce the kinetic electrochemical features of ECs from the point of R_{ESR} firstly, and then

illustrate electrochemical features of pseudocapacitive via their responses to (i) potentiodynamic sweep (in cyclic voltammetry); (ii) constant current (galvanostatic charge/discharge curves), and (iii) alternating current (impedance spectroscopy).^[14, 19]

1.2.1.2.1 Equivalent Series Resistance (R_{ESR})

Just as mentioned above, package electric power sources process intrinsic internal resistance (R_{ESR}), which is an important parameter that determines their power performance (Figure 1.8).

Figure 1.8. (a) Typical electric circuit that a power source (V_W) with a load of (R_L) and an equivalent series resistance (R_{ESR}). (b) Constant current discharge curves for a EC (where V_W is working voltage, Capacitive is the voltage drop due to discharge of the capacitor (eq2), V_{drop} is the voltage drop due to R_{ESR} (eq13), V_{min} is the minimum voltage allowed by power system; t_d is the discharge time.).(c) Idealized voltage waveform during current interrupt event.(d) Typical Nyquist Plot for a pseudocapacitor.

For a power source with working voltage (V_w), current (I) flows through the circuit with a load (R_L) on discharge could be given as^[24, 33]:

$$I = \frac{V_w}{(R_L + R_{ESR})} \quad (12)$$

Accordingly, there is an resistance component in addition to the capacitive component described in eqs (2) and (3). The resistance component is governed as:

$$V_{drop} = IR_{ESR} \quad (13)$$

And then, the eqs (4) and (6) were modified, and new derivations are described as:

$$E = \int_0^Q V(q)dQ = \int_0^Q \frac{Q}{C}dQ \quad (14)$$

$$P = IV = I(V_w - V_{OFF}) = I^2 R_L = \left(\frac{V_w}{R_L + R_{ESR}}\right)^2 R_L \quad (15)$$

From eq (15), the maximum power, P_{max} , could be derived at $R_L = R_{ESR}$ ^[34] and given as:

$$P_{max} = \left(\frac{V_w}{R_L + R_{ESR}}\right)^2 R_L = \frac{1}{4} \frac{V_w^2}{R_{ESR}} \quad (16)$$

By combing eqs (6) and (12), the shortest discharging time, t_{min} , can be derived and given as^[24]:

$$t_{min} = \frac{1}{2} \frac{C V_w^2}{P_{max}} = 2 C R_{ESR} \quad (17)$$

1.2.1.2.2 Determination of Equivalent Series Resistance (R_{ESR})

Several methods could be used to determine R_{ESR} , such as i) measuring the iR drop at the initiation of a constant current discharge, ii) measuring the bounce back of voltage at the end of a constant current discharge, or iii) using AC impedance spectroscopy (often at 1000Hz).^[35]

iR drop. The R_{ESR} is usually determined from the galvanostatic discharge tests using iR drop for practical packed cell and testing cells in lab. In this case, R_{ESR} is defined as the voltage change that occurs nearly instantaneously upon application of current^[34]. A change in the form of eq (13) could define the R_{ESR} as:

$$R_{ESR} = V_{drop}/I \quad (18)$$

This method is somewhat subjective because the data cannot be accurately described by an instantaneous drop followed by a perfectly linear discharge (Figure 1.8b). In practical, the discharge curve is smooth with a gradual transitions. Nevertheless, this method does provide useful information for internal resistance of the cell from a first-order approximation. The results calculated from iR drop is inversely proportional to cell size.^[21, 34]

Current Interrupt Steps. The R_{ESR} could also be measured via constant current interrupt steps (<5 sec) at a specified voltage. In this case, R_{ESR} is defined as the voltage change that occurs nearly instantaneously upon application of current^[34, 35](Figure 1.8c):

$$R_{ESR} = \Delta V/\Delta I \quad (19)$$

It should be stated that this method is dependent on the methodology used, including the data sampling rate, electrode geometry, etc.^[34] Special caution should be given for porous electrode-based electrochemical systems, where the overestimation of the ohmic voltage change and the R_{ESR} of the cell would be collected *via* the interrupt method.

Electrochemical Impedance Spectroscopy (EIS). In EIS testing, a sinusoidal voltage perturbation at a well-defined frequency is applied to the cell with the desired state of charge. The resulting variation in current is recorded which provides information about the electrochemical response of the system over a wide range of frequencies (typically 10kHz to 1Hz or lower).^[34, 36, 37] The resistance of a cell, solution resistance, electrode properties in terms of ohmic resistance and activation polarization resistance, EDL capacitance, and transport or diffusion properties,^[38-41] could be therefore characterized as shown in Figure 1.8d.

Typical Nyquist plot (Figure 1.8d) shows a semicircle in the high-frequency region, followed by a Warburg and linear part in the low frequency region. The first crossover point on the Nyquist plot, R_s , is generally considered as the resistance associated with electrolyte resistance and the external contact resistance. R_f is the charge transfer resistance resulting from the EDL capacitance on the particle surface of the electrode, and/or the faradaic reactions. $R_s + R_f$ is the main contributor to R_{ESR} . It must be emphasized that the interpretation of the EIS data should be based on individual cases and different experimental configurations will lead to different data interpretation. In the case where pseudocapacitive materials are present, perfect semicircles generally

cannot be obtained. Rather, suppressed semicircles in high-frequency region with sloppy linear line in the low-frequency region might be obtained instead.

1.2.1.2.2 Kinetic Electrochemical Features for Pseudocapacitance

(a) Potentiodynamic sweep-cyclic voltammetry

Among various instrumental techniques for the study of electrochemical reactions, potential sweep method was one of widely used and powerful tool for the study of electrochemical reactions via modulating an electrochemical process by a potential varying in time. The potential varying in time is called sweep rate (v , V/s or mV/s).^[42, 43]

Figure 1.9. CV profiles of ideal double layer capacitor(a) and Reversible pseudocapacitor (b), (c) and (d) with different scan rate v . v_0 is the critical sweep rate^{[19] [44, 45]}

Sweep rate dependence of peak potential. One feature for pseudocapacitance is the relationship between peak potential (E_p) and sweep rate (v). In cyclic voltammetry experiments at various sweep rates, ideally, there is no or small potential difference between the anodic and cathodic peaks, and

the cyclic voltammograms are mirror particularly at slow sweep rates for capacitive system (Figure 1.9).^[14, 19]

However, except for air or vacuum dielectric capacitors, all ECs have effective R_{ESR} , which result in polarization effect and deviations from ideal capacitive behavior. The presence of the charge transfer resistance in pseudocapacitors imposes kinetic limitations. If the surface faradaic processes involved for pseudocapacitors are modulated by an increasing sweep rate (ν), the kinetic reversibility is lost gradually.^[19] This is manifested by the peak potential, E_p , which remains independent of ν until ν reaches critical sweep rate ν_o , and then increase with $\log \nu$.^[42] It indicates that there exists a critical sweep rate value ν_o from which the kinetic behavior is radically different.^[42] For example, the cyclic voltammograms would translate into non-mirror images with increase in the difference between the cathodic and anodic peak voltage ($\Delta E_{a,c}$) as $\nu > \nu_o$, indicating the transition from kinetic reversible process to an kinetic irreversible process (Figures 1.9c and 1.9d).^[44, 45] But the kinetic reversibility could be regained for pseudocapacitor by lowering the sweep rate, since there is no phase change occurs during the charge/discharge processes. The presence of kinetic limitation (characterized by the ν_o value) determines the effective charge/discharge rates or power performance of ECs.

Sweep rate dependence of response current. Another important and characteristic feature of the kinetic behavior for pseudocapacitance is the relationship between the response current (i) and sweep rate (ν). In cyclic voltammetry experiments, the total current measured under a potential sweep rate is the sum of the diffusion current (i_{diff}) and the current required to charge

the double layer at the electrolyte interface / ignite fast faradaic reactions on the exposed electrode surface (i_{cap}).^[46] It could be expressed as:

$$i(V) = i_{cap} + i_{diff} = av^b \quad (20)$$

where v is the scan rate, and both a and b are adjustable parameters.^[47-50] The parameter b -value is determined from the slope of the linear plot of $\log i$ versus $\log v$. There are two well-defined conditions in general: $b = 0.5$ and $b = 1$. The slope $b = 1$ is representative of a capacitive contribution that arises from surface redox reactions, thus $i_{cap} = av$. While the slope $b = 0.5$ is denoted for semi-infinite diffusion-controlled faradaic process.^[47-49, 51] The diffusion current (i_{diff}) could be described by the classical Sevcik equation^[52]:

$$i_{diff} = nFAC^*D^{1/2}v^{1/2}(\alpha nF/RT)^{1/2}\pi^{1/2}\chi(bt) \quad (21)$$

where n is the electron transfer number, F is the Faraday constant, A is the apparent surface area of the electrode materials, D is the diffusion coefficient of the rate limiting species, α is the transfer coefficient, R is the molar gas constant, T is the absolute temperature, and the $\chi(bt)$ functional part is the normalized current for a totally irreversible system as indicated by the cyclic voltammetric response.

It is derived from eqs (20), and (21) that the current response to sweep-rate varies depending on whether the reaction process involved is a surface mechanism (capacitive) or a diffusion-controlled mechanism. If the reaction process is controlled by surface mechanism, current varies linearly with v ($di/dv = \text{constant} = \text{the capacitance}$); for a faradaic process limited by semi-infinite linear diffusion, the current varies with $v^{1/2}$ ($di/dv^{1/2} = \text{constant}$).^[43, 46] Taking

into account all cases, a general expression for current at a certain potential could be given^[43, 46]:

$$i(V) = i_{cap} + i_{diff} = k_1 v + k_2 v^{1/2} \quad (22)$$

or it could be changed as:

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \quad (23)$$

from eq(23) values of k_1 and k_2 could be evaluated from the slop and intercept, respectively, if $i(V)/v^{1/2}$ plotted vs. $v^{1/2}$ give a straight line. Consequently, it becomes possible to separate the capacitive contribution from diffusion-controlled intercalation processes, and quantify the current or capacitance fraction related to each of these contributions. This technique has been utilized to evaluate the electrochemical performance of nanostructures materials (Figure 1.10)^[47, 53-56]. It is interestingly found that the contribution fraction of each parts is strongly dependent on materials crystalline,^[56] structure or morphology,^[53, 57] particle size,^[47] electrolyte^[54] and sweep rate.^[55]

Figure 1.10. CV curves of Au/MnO₂ core-shell nanowires at scan rates of 5 mV/s (a) and 100 mV/s (b): capacitive current ($i \propto v$, blue part) was separated from diffusion current ($i \propto v^{1/2}$, yellow part).^[53]

Sweep rate dependence of capacitance. The variation of voltammetric surface charge q^* with the sweep rate s has been described by Trasatti et al. at RuO₂ electrodes via a linear function^[58]:

$$q^* = q_s^* + q_d^* \quad (24)$$

The maximum charge density q^* is considered to consist of two fractions, q_s^* and q_d^* , representing the charge related to outer (capacitive contribution) surface and inner (diffusion-controlled contribution) surface. The q_s^* that corresponds to outer surface could be obtained at infinite potential sweep rate ($v \rightarrow \infty$),

$$q^* \rightarrow q_s^* \quad (25)$$

The maximum charge density (q_m^*) could be obtained when at the scan rate ($v \rightarrow 0$),

$$q^* \rightarrow q_m^* \quad (26)$$

Particularly, q^* is expected to be limited by $v^{-1/2}$ if semi-infinite linear diffusion is involved whereas capacitive contributions are independent of the sweep rate, thus equation (24) could be expressed as:

$$q^*(v) = q_{v \rightarrow \infty}^* + q_d^* = q_{v \rightarrow \infty}^* + \text{const} (v^{-1/2})^* \quad (27)$$

from which, a basic amount of q_s^* could be collected *via* the extrapolation of linear diagram of q^* vs $v^{-1/2}$ to $v^{-1/2} = 0$ (Figure 1.11a).

Generally, q^* decreases as the potential sweep rate increases because of diffusion limitation.^[58] Since q_s^* increases linearly with $v^{-1/2}$, it is reasonable to expect that $1/q^*(v)$ decrease linearly with $v^{1/2}$:

$$1/q^*(v) = 1/q_m^* + \text{const} (v^{1/2})^* \quad (28)$$

where q_m^* is the maximum total charge. Extrapolation of liner plot of $1/q^*(v)$ vs. $v^{1/2}$ to $v^{1/2} = 0$ gives the basic amount of the maximum total charge q_m^* (Figure 1.11b).

Consequently, the difference between the total charge (q_m^*) and the surface charge ($q_{v \rightarrow \infty}^*$) give the charge associated to diffusion-controlled processes.

$$q_d^* = q_m^* - q_{v \rightarrow \infty}^* \quad (29)$$

Similarly, the ratio of capacitive contribution and semi-diffusion controlled contribution for the total capacity would be evaluated.

Figure 1.11. (a) Typical areal capacitance (C) vs $v^{-1/2}$ plots and (b) $1/C$ vs. $v^{1/2}$ plots for bare (blue circles) and hierarchical (black squares) MnO₂ nanowire arrays in aqueous LiClO₄ electrolyte.^[54]

Sweep rate dependence of double-layer capacitance and Pseudocapacitance. The separation of capacitive current/charge from diffusion-controlled current/charge has been well addressed in above via cyclic voltammetry. Capacitive charge storage consists of contributions from both double-layer capacitive and pseudocapacitive effects.

$$C = C_{dl} + C_{\phi} \quad (30)$$

Through proper design of experiment, CV can sometimes (not always) be used to differentiate EDL mechanism from fast surface redox reaction, as demonstrated by Dunn, et al.^[59] Mesoporous Nb₂O₅ with crystallographically orientated layered nanocrystalline walls shows typical intercalation pseudocapacitance through fast cation intercalation into layered gaps (van der Waal gaps) of Nb₂O₅ (the third type of pseudocapacitive that is fundamentally different from the diffusion-controlled intercalation process in a battery where change in crystallographic phase takes place). When mesoporous Nb₂O₅ with crystalline walls was used as the electrode, the use of different electrolyte (and thus different cations) determines different charge storage mechanism. When tetrabutylammonium (TBA⁺) perchlorate in propylene carbonate is used as the electrolyte, the total charge storage shown in the CV curve (very small response current) (Figure 1.12a) is based on EDL mechanism only since the bulky TBA⁺ cations cannot be intercalated into the layered Nb₂O₅ quickly; Whereas in LiClO₄ electrolyte, both EDL and intercalation pseudocapacitive process contribute to the total charge storage (as evidenced by the much larger response current in Figure 1.12a). The ratio of the EDL capacitance/pseudocapacitance could therefore be estimated from the CV results. A small fraction (~10%) of

the total charge storage stems from EDL capacitance while most of the charge is stored through a surface-confined faradaic charge-transfer process. This is further confirmed by broad peaks in the voltages profiles in Figure 1.12b, which is characteristic of a surface-confined charge-transfer process.^[59] It must be emphasized that the method discussed here must be used with great care and it can only provide a rough estimation of the contribution from the EDL process and the surface redox processes. In addition, it is limited to certain types of electrodes only and the method will not work properly if highly porous electrodes containing pores much smaller than the size of the electrolyte ions are present in the system.

Figure 1.12 (a) Cyclic Voltammetry (CV) curves of amorphous and crystalline mesoporous $T-Nb_2O_5$ films in Lithium (Li^+) and tetrabutylammonium (TBA^+) electrolyte at a sweep rate of 10 mV/s.^[59] (b) Potential-dependant capacitance calculated from CV curves at sweep rate of 2 and 50 mV/s.

(b) Constant current-charge/discharge curve

As mentioned above, the profile of potential vs. capacitance for EDL capacitor is well-defined linear in shape as described by eqs (3) and (4) and is illustrated in Figure 1.13a. For pseudocapacitor, the electrode potential associated with the electrosorbed species is a continuous logarithmic function

of the extent of sorption (eq (8)), which is different from the linear function of that of EDL capacitor. In a constant current charge/discharge process, this translates into smooth charge/discharge profiles with small potential hysteresis (Figure 1.13b). On contrast, a battery electrode shows a potential plateau without a sloping line in potential vs capacity profile (Figure 1.13c).

Figure 1.13. General electrochemical features of double-layer capacitor (a), pseudocapacitor (b) and battery (c).

(c) Alternating current - impedance spectroscopy

EIS is efficient tool for monitoring changes in ECs and determining their dynamic electrochemical behavior by applying a sinusoidal voltage perturbation to ECs at a well-defined frequency. The corresponding information regarding the electrochemical response of the system at that frequency is then derived from resulting current response. The equivalent electric circuit diagram is usually used to help to interpret the experimental data. If the behavior of an EC is purely capacitive, the R_{ESR} is frequency-independent with the real and imaginary components being out of phase by 90° , and the Nyquist plot is a vertical line with a resistive element R being connected in series with the capacitor C .^[14, 18, 21] The resistive element represents the resistance from the electrolyte solution and/or from the external contact. However, most practical ECs deviate from purely capacitive behavior because of kinetic limitations, and

therefore the equivalent circuit is more complex. The equivalent electric circuit model for EDL capacitor is generally approximated with the EDL capacitance (C_{dl}), being in parallel with a resistor R_f , and an additional resistance (R_s) that corresponds to electrolyte resistance and the external contact resistance. For pseudocapacitive system, faradaic resistance R_f and pseudocapacitance C_ϕ that associates with potential-dependent charge is connected in series, and being in parallel with EDL capacitance (C_{dl}) since pseudocapacitance arises from a potential dependent interfacial faradaic reaction. The practical impedance results for a solid electrode/electrolyte interface often display a frequency dispersion that cannot be described by simple elements such as capacitor, resistor, inductor or Warburg diffusion. Therefore, a constant phase element (CPE) which allows for a distribution of capacitance values is generally introduced in order to provide much better impedance fittings (Figure 1.14).^[60] The definition of constant phase element in the equivalent circuit is given by^[60, 61].

$$Z_{CPE} = \frac{1}{T(j\omega)^\alpha} \quad (31)$$

here, Z_{CPE} is the impedance, T is a constant in $F \text{ cm}^{-2} \text{ s}^{\alpha-1}$, ω is the frequency, α is an adjustable constant. When $\alpha = 1$, the CPE is regarded to represent an ideal capacitor. It would be a resistor for $\alpha = 0$, and an inductor for $\alpha = -1$. Particularly, the $\alpha=0.5$ indicates semi-infinite diffusion.

Figure 1.14. Equivalent circuits for: (a) double-layer capacitor, and (b) Pseudocapacitor. Corresponding electrochemical impedance spectroscopy results are listed in (c) and (d), respectively. ^[18]

Based on the equivalent electric circuit diagram (Figure 1.14), it is apparent that the separation of EDL contribution from pseudocapacitive contribution for certain types of electrodes is possible by fitting the AC impedance result appropriately. An example is shown in Figure 1.15, where the EDL and pseudocapacitive contributions in CeO_2 thin film electrodes are distinguished using AC impedance measurement at different applied potentials^[57]. For potential above 3 V, very small EDL capacitance was obtained due to the high electronic resistance of ceria when Ce is in its fully oxidized state. At lower potentials, a sizable fraction of Ce reduces to Ce^{3+} and the electronic conductivity increases, and thus, the film electrode revealed significant amounts of capacitance. It is noted that pseudocapacitive contributions increase with decreasing voltage while EDL contributions remain almost unchanged for applied potential less than 3V, suggesting different charge storage mechanisms are involved under different applied potentials.^[57]

Figure 1.15. Nyquist plot for KLE-template CeO_2 at the potential 3.5 V (a) and 2.0 V (b) (vs. Li/Li^+). (c) Equipment circuit model for impedance data fitting. (d) Separation of double layer capacitance and pseudocapacitance based on different applied potentials for CeO_2 films.^[57]

1.2.1.3 Symmetric and Asymmetric Supercapacitors

The well-known reciprocal relation between overall capacitance of the device (C) and that of each its two individual electrodes (C_1 and C_2) could be given as follows^[17, 18]:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (32)$$

If $C_1 = C_2$ (symmetric combination, for example, two same non-faradaic electrode work against with each other), the measured C would be half the value of individual electrode. This type of system is called as “symmetric capacitor”.^[18] If the capacitance of the cell is adjusted further via combining mass of two electrodes, a factor of “4” would introduce. For example, a single carbon electrode (with high surface area $1000 \text{ m}^2/\text{g}$) exhibits the capacitance of

$10 \mu\text{F}/\text{cm}^2$. This gives rise to a specific capacitance of 100 F/g for one electrode. For a symmetric capacitor, two electrodes with half the total capacitance (eq(32)) and doubled weight results in an 25 F/g active capacitor.^[17] The significant differences between single electrode and the complete is of significant importance and should be clarified when an EC is introduced.

If electrode “2” refers to faradaic electrode (or battery-type electrode), corresponding C_2 is essentially infinity. Thus $C \approx C_1$ is approximated according to equation (32) because of pseudocapacitance $C_2 \gg C_1$, and the full charge stored on C_1 (non-faradaic electrode) is hence available for discharge. This type of system is called as “asymmetric capacitor”.^[18]

The maximum energy stored in such a capacitor is given by^[14, 16, 17, 19, 21, 25].

$$E = \frac{1}{2} C V_w^2 \quad (8)$$

where V is nominal voltage (volts).

The maximum power is described by the equation:

$$P_{max} = \frac{1}{4} \frac{V_w^2}{R_{ESR}} \quad (16)$$

where R is equivalent series resistance (ESR) (Ω). For the packed cells, their ESR is typically determined via measuring the IR drop, the bounce back of voltage, or using AC impedance spectroscopy.^[21, 62]

1.2.1.4 Summary for Double-layer capacitance and Pseudocapacitance

Table 1.2. Separation of double-layer capacitance and Pseudocapacitance.

	Double-layer capacitance	Pseudocapacitance or supercapacitor
Mechanism	No-faradaic involved	Faradaic involved
Capacitance-Voltage	Capacitance constant (potential-independent)	Capacitance not constant (potential-dependent)
Phase angle-Frequency	90° phase angle	Phase angle function of frequency, but some embodiments have transmission-line behaviour
Kinetic aspect	High-power operation	Kinetic limitations for high charge/discharge rates
Reversible	Indefinitely reversible	Highly reversible
Electrode Material	Carbon allotropes	Transition metal oxides/hydroxides, conducting polymers, etc.

1.2.2 Lithium-ion Battery

1.2.2.1 Thermodynamic aspects of Battery

Similar to ECs, the energy and power features of battery follow directly from the thermodynamic principles for electrochemical reactions, which can be given as^[63]:

$$\Delta G = \Delta H - T\Delta S \text{ and } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (33)$$

where ΔG is the Gibbs free energy, ΔH is the enthalpy, ΔS is the entropy and T is the absolute temperature.

It is noted that ΔG represent the net useful energy resulting from a given reaction, and it would be in terms of electrical energy for a battery/cell and expressed as follow:

$$\Delta G = -nFE \text{ and } \Delta G^\circ = -nFE^\circ \quad (34)$$

where n is the electron transfer number, F is the Faraday constant, E is the cell electromotive force (EMF). It should be stated here that the cell EMF is determined at some singular value by the Gibbs energies of pure, well-defined phases and is unique for each redox reaction couple. This is totally different from the continuous logarithmic-dependent electrode potential of ECs with the extent of sorption or conversion as mentioned above.

The free energy for bulk chemical reactions is given according to van't Hoff isotherm^[63-65]:

$$\Delta G = \Delta G^\circ + RT \ln(A_P/A_R) \quad (35)$$

Nernst equation for electrochemical reactions could be derived by combining eq (34) and eq (35)^[63-65]:

$$E = E^\circ + (RT/nF) \ln(A_R/A_P) \quad (36)$$

here, R is the gas constant, T is the absolute temperature, A_P is the activity of products and A_R is the activity of reactants.

The relationship between the current flow and the extent of reaction could be expressed as follow:

$$I = -nF \frac{m}{MW} / t \quad (37)$$

where I is the current flow, n is the number of electron involved in the reaction, m is the weight of active materials, MW is the molecular weight of active materials, and t is the time of current flow.

Based on these, the total charge (Q) could be given as^[64-66]:

$$Q = \int_0^{\Delta t} I dt = \int_0^Q dq \quad (38)$$

where q represents the state of charge. Q is the cell capacity that depending on I . In addition, changes in electrode volume, electrode decomposition and electrode-electrolyte chemical reactions result from charge/discharge cycling would cause an irreversible loss of capacity. Therefore, the Coulomb efficiency is one of important metric for a battery/cell, which can be described as follow^[64]:

$$\text{Coulom efficiency} = 100 \times Q_{dis}/Q_{ch} \quad (39)$$

The densities of stored energy and power are given as:

$$\text{Energy density} = \int_0^{\Delta t} IV(t)dt = \int_0^Q V(q)dq \quad (40)$$

$$\text{Power density} = V(q)I(q) \quad (41)$$

where Δt is the time required for complete discharge at a constant current $I_{dis} = dq/dt$. Based on eqs (38) and (40), it is apparent that the stored energy is strongly dependent on the average ($V(q)$) and the capacity (Q).

The electrochemical potential difference between anode (μ_a) and cathode (μ_c) gives rise to the open-circuit voltage (V_{oc}) of a cell^[65]:

$$V_{oc} = (\mu_a - \mu_c)/e \quad (42)$$

In practical batteries, the open-circuit voltage is also limited by the “working window” of the electrolyte. The electrolytes for practical rechargeable battery systems are crystalline solid, glass, polymer, or liquid. The working window is determined by the energy gap between the lowest unoccupied molecular orbital (LUMO) and the higher occupied molecular orbital (HOMO) for a liquid electrolyte (Figure 1.16) or the bottom of the conduction band and top of the valence band for a solid electrolyte.^[64, 67] For a thermodynamically stable cell, the electrochemical potentials of anode μ_a and cathode μ_c of a charged cell should be matched the LUMO and HOMO of the electrolyte for achieving maximum $V(q)$ of a stable and safety cell. That is because electrolyte would be reduced when the μ_a of anode is above its LUMO and would be oxidized when the μ_c of cathode is below its HOMO. Alternatively, the solid-electrolyte interphase (SEI) passivation layer that is electronically insulating but permeable to the working ion would form to stabilize a mismatched electrode system.^[64, 66]

Figure 1.16. (a) Relative energies of μ_a and μ_c versus the LUMO-HOMO window of the liquid electrolyte. (b) Voltage and capacity ranges for some cathode and anode materials.^[68]

1.2.2.2 Kinetic aspects of Battery

During discharge, the voltage drop off (electrode polarization) would occur when current flow across the battery. That results from kinetic limitations of reactions, in which an internal resistance R_b reduce the output voltage V_{dis} of a cell relative to the open-circuit voltage V_{oc} by a polarization $\eta = I_{dis}R_b$.^[63, 64] The polarization, η , is thus given as:

$$\eta(q, I_{dis}) = V_{oc} - V_{dis} \quad (43)$$

Reversely, the presence of R_b would increases the voltage required to reverse the chemical reaction on charge by an overpotential $\eta(q, I_{ch})$.^[65]

$$V_{ch} = V_{oc} + \eta(q, I_{ch}) \quad (44)$$

Generally, there are three different kinetics effects for polarization: (i) activation polarization, (ii) ohmic polarization, and (iii) concentration polarization (Figure 1.17a).^[63, 69, 70]

Figure 1.17. (a) Typical discharge curve of a battery, showing different types of polarization. (b) Simple battery circuit diagram (c) corresponding Nyquist plot for an idealized battery system, where characteristic behaviors of activation, ohmic, and concentration polarizations are distinguished. W_a and W_c are the Warburg impedances of diffusion processes for anode and cathode, respectively. R_a and R_c are the resistances of the anode reactions and cathode reactions. R_{inter} is the internal resistance of battery. CPE_{dl-a} and CPE_{dl-c} are the constant phase elements for anode and cathode, respectively.

Activation polarization arises from kinetics hindrances of the electrochemical redox (or charge-transfer) reactions taking place at the electrode/electrolyte interfaces of anode and cathode. For a charge-transfer-controlled battery reaction, the current flow i , could be given as^[63]:

$$i = i_0 \exp(\alpha F \eta / RT) - \exp((1 - \alpha) F \eta / RT) \quad (45)$$

where η is the polarization, α is the transfer coefficient. $i_0 = k_0 FA$ is the exchange current density (k_0 is the reaction rate constant for the electrode reaction, and A is the activity product of the reactants).

Derived from eq (45), the activation polarization following the Tafel equation was given as:

$$\eta(q, I_{dis}) = a - b \log(i/i_0) \quad (46)$$

Ohmic polarization consists of the resistance of individual cell components (electrodes, electrolyte, the conductive additive, binder, current collectors, terminals) and the contact resistance among various individual components. Ohm' Law is obeyed for ohmic resistance R :

$$\eta(q, I_{dis}) = IR \quad (47)$$

Concentration polarization results from mass transport limitations during cell operation, in which the availability of the active species at the electrode/electrolyte interface changes and becomes diffusion-limited. The concentration polarization for diffusion-controlled process can be expressed as

$$\eta(q, I_{dis}) = (RT/n) \ln(C/C_0) \quad (48)$$

where C is the concentration at the electrode/electrolyte interface, and C_0 is the concentration in the bulk of the solution.

In reality, the influence of the current rate on the cell voltage is controlled by all three types of polarizations. Similar to that of ECs, EIS is often used to access the kinetic behavior of a battery during the charge/discharge process. It is possible to distinguish different types of polarization by proper fitting of the impedance plot. The equivalent circuit model and the corresponding Nyquist diagram is shown in Figures 1.17b & 1.17c. The activation polarization is often reflected by two semicircles or arcs in Nyquist plot.^[71, 72] The first semicircle or arc at higher frequency is associated with the contact resistance between the electrode material and the metallic substrate coupled with a double layer capacitance,^[71] while the second semicircle or arc at lower frequency is associated with the charge transfer resistance between the electrode materials and the active species from the electrolyte coupled with a CPE element. In anode where there is an SEI layer, the contribution of the SEI resistance will come into the picture as well. Ohmic polarization has no capacitive character and is independent of frequency. It is represented as battery internal resistance R_{int} . The concentration effect is encapsulated as the Warburg element W . It reveals typical diffusion-controlled processes in the low frequency featured by 45° Warburg region, which is associated with the diffusion of the active species inside the solid electrode. A good battery cell should have small R_{int} , R_a , R_c and short Warburg region.

1.2.3 Electrochemical Capacitor vs. Battery

In this section, the properties and differences of electrochemical capacitors and batteries are summarized in terms of electrochemical behavior and thermodynamic behaviour.

1.2.3.1 Thermodynamic Behavior

Table 1.3. Comparative Thermodynamic Behavior of Electrochemical Capacitor and Ideal Battery.^[19, 28, 31]

Electrochemical Capacitor		Battery
Double Layer Capacitor	Pseudocapacitor	
Free energies ΔG of the electroactive materials changes continuously with the extent of charge/discharge		Free energies ΔG of the electroactive phases involved is unique and single-valued during discharge/charge process $\Delta G \cong \text{Constant} = -nFE$
$G = 1/2 CV^2$	$\Delta G = \Delta G^0 + RT \ln(X/(1 - X))$	
Potential varies continuously with time	Potential varies continuously with the state of charge/discharge	Potential on discharge is single-valued
Behavior is capacitive		Behavior is non-capacitive
High degree of reversibility		Irreversibility

1.2.3.2 Electrochemical Properties

Table 1.4. Comparative Electrochemical Characteristics of Electrochemical Capacitor and Battery.^[14, 19, 31]

Electrochemical Capacitor		Battery
Double Layer Capacitor	Pseudocapacitor	
Potential is thermodynamically related to state of charge Q directly in a continuous manner	Potential is thermodynamically related to state of charge through $\log[X/1-X]$ factor in a continuous manner	Electromotive force (EMF) is ideally constant with degree of charge/discharge, except for nonthermodynamic incidental effects, or phase changes during discharge
Free energies varies	Free energies varies with	Free energies of components is

with extent of charge field in a continuous manner	degree of conversion in a continuous manner	single-valued
Galvanostatic discharge exhibits mainly linear decline of potential with time	Galvanostatic discharge exhibits mainly a “transition” from linear decline of potential to a more or less constant potential	Galvanostatic discharge arises at a more or less constant potential (except for intercalation Li batteries)
The linear modulation of potential exhibits more or less constant charge/discharge current profile (with some dependence on materials)		The linear modulation of potential displays irreversible i vs. V profile with non-constant currents
The cyclic voltammetry curves are mirror images	The cyclic voltammetry curves are mirror images until v reaches to v_o	The charge/discharge curves and cyclic voltammetry are not mirror images

Figure 1.18. Comparative electrochemical characteristics of double-layer capacitor, pseudocapacitor and battery.

1.2.3.3 Overall Comparison of Electrochemical Capacitor and Battery

Characteristics

Table 1.5. Overall Comparison of Electrochemical Capacitor and Ideal Battery.^[31]

Electrochemical Capacitor		Battery
Double Layer Capacitor	Pseudocapacitor	
Galvanostatic discharge exhibits mainly linear decline of potential with time (good intrinsic stage-of-charge indication)	Galvanostatic discharge exhibits mainly a “transition” from linear decline of potential to a more or less constant potential (relatively good intrinsic stage-of-charge indication)	Galvanostatic discharge arises at a more or less constant potential (poor intrinsic stage-of-charge indication) (except for intercalation Li batteries)
Relatively poor energy density	moderate energy density	moderate or good energy density (depending on active materials and battery types)
Good power density	Moderate power density	Moderate or poor power density
Excellent cyclability	Moderate cyclability	Poorer cycle life (due to irreversibility of redox and phase-change processes in 3D dimensions)
Internal iR drop (related to <i>high specific area</i> of electrodes and electrolyte and their surface chemistry)		Internal iR drop (due to surface chemistry of <i>electrolyte and active materials</i>)
No or little activation polarization (but C may be Temperature-dependent)		Significant Temperature-dependent activation polarization
Long life time (except for corrosion of current collector, etc.)	Moderate life time (due to degradation of active materials)	Poorer life time (due to degradation and reconstruction of active materials)

1.3 Introduction to Graphene

Graphene, a single atomic layer of sp^2 -bonded carbon atoms in a hexagonal lattice, has attracted unprecedented interest owing to its intrinsic difference from other forms of carbon allotropes (Figure 1.19).^[73] The excellent mechanical,^[74] electrical,^[75] thermal^[76] and optical properties^[77] ensures graphene is suitable for various applications, such as microelectronics, sensor, drug delivery, catalysis and energy storage/conversion.^[78] Graphene is particularly suitable for the implementation in electrochemical applications

because of extraordinary electrical conductivity (64 mS cm^{-1}),^[79] large specific surface area (theoretical surface area $\sim 2630 \text{ m}^2 \text{ g}^{-1}$),^[80] unique heterogeneous electron transfer and charge carrier rates, and good electrochemical stability.^[81] Indeed, Graphene/Graphene-based composites have been used as effective counter electrodes for dye-sensitized solar cells, photo-catalysts for water splitting, electrocatalysts for oxygen reduction/hydrogen evolution in fuel cells, high-performance electrodes in supercapacitors, ions (Li^+ , Na^+ , Al^{3+} , etc) batteries, lithium-sulfur batteries as and lithium- O_2 batteries.^[82] The synthesis of graphene in both high quality and quantity in a scalable and economical manner is therefore highly desirable.

Figure 1.19. (a) Graphene: the parent of all graphite forms & (b) their applications in Both Energy Conversion and Storage Devices.^[83]

1.3.1 Various Approaches Leading to Graphene Oxide/Graphene

Since the first fabrication of single-sheet graphene through micromechanical cleavage of bulk graphite was reported,^[84] a number of methods have been proposed for generating graphene with high quality and low cost, which can be classified into two categories: bottom-up approach and top-down approach (Figure 1.20).^[85] Bottom approaches, based on the catalytic decomposition of hydrocarbon gases, can provide large sized graphene with

high crystal nature *via* epitaxial growth^[86] or Chemical Vapour Deposition^[87] although their high cost and low production. Top-down approaches, consisting of the intercalation of additional elements between graphite layers to form graphite intercalation compound (GIC), and then followed by the exfoliation of GIC either by physical, chemical or electrochemical methods, have received intense interest due to their scalability and low production cost.^[88-91]

Chemical exfoliation of graphene based on Brodie, Staudenmaier and Hummers methods, which involves the oxidation of graphite with strong acids and oxidants, and subsequent chemical or thermal reduction, is particularly favorable due to easy-processing and scalability.^[88] Unfortunately, the use of strong acids and oxidants severely damages the sp^2 -bonded of graphene and deteriorates its performance in various applications even though these damages could be recovered partly by subsequent reduction process.^[89]

Figure 1.20. All roads lead to Graphene or Graphene oxide (GO).

Ultrasonic cleavage was also used to prepare graphene.^[90, 92] However, the success of ultrasonic cleavage is strongly dependent on the proper choice of solvents and surfactants as well as the sonication frequency amplitude and time, which thus impedes its practical applications.^[91] Graphene sheets can also be generated by unrolling carbon nanotubes (CNTs) via simultaneous intercalation of NH_3 -solvaged Li^+ into interlayer space of MWCNTs.^[93] Another variation of the unrolling techniques uses strong oxidizing agents KMnO_4 to cut along the longitudinal direction of MWCNTs.^[94]

Microwave-assisted heating technique was also adopted for synthesis of water-soluble graphene due to the strong microwave absorption ability of graphitic materials.^[95] Recently, electrochemical exfoliation of graphite and HOPG has been reported to be an effective way to prepare graphene and attracted increasing attentions.^[96-98] Although intensive research efforts have taken, the synthesis of graphene/graphene oxide in both high-quality and large-quantity *via* an economic and environmentally-friendly way is still a challenge.

1.3.2 Graphene for Soft Energy Storage Devices

Graphene is extremely attractive for energy conversion and storage applications because of its unique properties mentioned above. The electrochemistry of graphene has been investigated intensively with respect to surface chemistry and structure, heterogeneous charge transfer rate constants on redox species, electrochemical operating window, and electrocatalysis of molecules recently.^[99, 100]

Recently, the sharp proliferation of portable, ultrathin/lightweight and wearable electronics, such as roll-up displays, touch screens, implantable

medical devices, conformable health-monitoring electronic skin, wearable sensors and active radio-frequency identification tags (RFID), have promoted increasing demand for new power sources with high energy/power density, low cost, environmentally-friendly, as well as ultrathin, lightweight and flexible features.^[101-104]

One key challenge for soft energy storage devices lies in the development of deformable and high energy density electrodes with multiple merits via selecting and designing both current collector and electrode active materials.^[102, 104] Soft electrodes are generally made from various functional organic and/or inorganic materials building on flexible conductive substrates without binders and conductive additives. Various soft electrodes have been prepared from paper-like carbonaceous electrode support, such as carbon nanotubes network (CNTs),^[105, 106] graphene paper,^[101, 103] carbon cloth^[107, 108] and other conductive paper (cellulose, textile, etc.).^[104, 109] Among them, electrodes based on CNTs network and/or graphene paper supports have attracted more attentions because of lightweight, good electric conductivity,^[75] large surface area^[80] and good physical/chemical stability.^[81] Particularly, graphene foam (GF), a 3-D interconnected network of chemical vapour deposition-grown graphene, has proven to be effective scaffold for soft energy storage devices.^[103] Various soft electrodes based on GF, including GF/Fe₃O₄,^[110] GF/LFP^[103, 111] and GF/MnO₂,^[112] have been prepared and exhibit enhanced electrochemical performance.

Although significant process has been made until now, the synthesis of high-quality graphene via an economic and environmental-friendly way remains extremely challengeable. In addition, the exploring of graphene-based

composites for their practical applications in flexible energy storage devices including supercapacitors and rechargeable batteries is high-desirable and meaningful. These issues and challenges are the focus of this thesis. Briefly, chapter 2 focus on the developing of a novel electrochemical exfoliation method for the synthesis of high-quality graphene flakes, includes the revelation of underlying mechanism, the optimization of synthesis conditions, and the evaluation of electrochemical performance in oxygen reduction reaction. Chapter 3 is focused on the synthesis of flexible graphene foam (GF)/ Fe_3O_4 hybrid electrode *via* atomic layer deposition approach, and investigating their applications in flexible lithium-ion battery. Chapter 4 is focused on developing a novel method for the synthesis of flexible GF/ carbon nanotubes (CNTs) hybrid films, and exploring their applications in flexible supercapacitor. Chapter 5 is focused on developing a new kind of flexible Nickel/Iron battery based on GF/CNTs hybrid films and investigating their electrochemical performance.

Chapter 2

Electrochemical Exfoliation Synthesis of Graphene

The synthesis of graphene in both high quality and quantity via economic ways is highly desirable and meaningful for practical applications. Here a facile, environmental-friendly and cost-effective multiple electrochemical exfoliation approach has been developed for the synthesis of high quality graphene flakes with high yield (nearly 50%) by using graphite rod from spent zinc-carbon/pencil core as carbon source. Various protonic acid (i.e H_2SO_4 , H_3PO_4 or $\text{H}_2\text{C}_2\text{O}_4$) aqueous solution were chosen as electrolyte. The unique cell configuration enables multiple exfoliation process to improve both the quality and yield of graphene sheets. After nitrogen doping, the exfoliated graphene flakes processes good electrocatalytic activity, stability and toxicity tolerance for alkaline solution-based oxygen reduction reaction.

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2.1 Introduction

Since the first fabrication of single-sheet graphene through micromechanical cleavage of bulk graphite was reported,^[84] a number of methods have been developed for generating graphene with high quality and low cost. Micromechanical cleavage,^[84] chemical vapor deposition (CVD)^[77, 87] and epitaxial growth^[86] produce graphene with high crystal quality but they are impractical for commercial applications due to low production rate and relatively high cost. Chemical exfoliation of graphene based on Brodie, Staudenmaier and Hummers methods, which involves the oxidation of graphite with oxidants and strong acids, and the subsequent chemical or thermal reduction, has been investigated extensively due to scalability and low cost.^[88] Unfortunately, the use of oxidants and strong acids severely damages the sp^2 -bonded of graphene and deteriorates its performance in various applications even though these damages could be recovered partly by subsequent reduction process.^[115] Recently, electrochemical exfoliation of various carbon precursors, including graphite rods, carbon papers or HOPG, has been demonstrated to be an effective approach for the generating graphene. Using graphite rods as electrodes and ionic-liquid/water solution as electrolyte, Ionic liquid functionalized graphene sheets have been prepared *via* a one-step electrochemical approach.^[116] Lu et al^[96] performed a detailed study and proposed a mechanism for the electrochemical exfoliation of graphite in ionic liquid solution, which involves (i) anodic oxidation of water, (ii) hydroxylation or oxidation of graphite edge planes, (iii) intercalation by ionic liquid anions between graphite layers, forming the graphite-intercalation-compounds (GICs), and (iv) Oxidative cleavage and precipitation of the GICs. Simulating to the

electrochemical reactions between graphite anode and organic carbonates in lithium ion batteries, Wang et al^[98] successfully prepared graphene flakes with few-layer *via* electrochemical exfoliation of graphite in propylene carbonate (electrolyte). The employment of bulky organic ions or molecules as intercalants may facilitate the intercalation process and the expansion of graphene layers. However, the use of organic compounds that are sensitive to moisture and oxygen and a long reaction time impede their practical applications. In the past few decades metal chlorides, strong protonic acids and other inorganic reagents have been the most promising.^[117] The expansion of graphite sheets in these intercalated compounds was realized by violent releasing of gases via fast heating. Very recently electric power has been used to drive the expansion and exfoliation of sulfate-intercalated graphite. In an electrochemical cell using protonic acid aqueous solution as electrolyte Su et al^[97] applied a relatively high (10 V) voltage to graphite anode for the synthesis of graphene sheets. Among many different electrolytes examined, including HBr, HCl, HNO₃, and H₂SO₄, only H₂SO₄ exhibited ideal exfoliation efficiency from natural graphite flake or highly oriented pyrolytic graphite. In Su's paper the anode (graphite) and cathode (Pt) were placed parallel with a separation of a few cm away. Similarly almost all the electrochemical cells for graphite exfoliation reported are in the parallel configuration.

Herein we report an improved synthesis of high-quality graphene in a vertical cell configuration *via* multiple electrochemical exfoliation of graphite rod. Unlike previous reports, the unique cell configuration enables multiple exfoliation processes to improve both the quality and yield of graphene sheets. The mechanism of multiple electrochemical exfoliation of spent graphite rod

was discussed in detail. The experiment conditions are optimized. The structure and electrocatalytic activity of multiple electrochemical exfoliated graphene flakes was investigated.^[113]

2.2 Experiment and Characterization

2.2.1 Material synthesis

Synthesis of Graphene Flakes. Graphene flakes were prepared via multiple electrochemical exfoliation (MEE) approach. Briefly, Graphite rod from spent Zinc-Carbon dry cells was utilized as positive electrode and the carbon source for graphene in the multiple electrochemical exfoliation process. The anode (graphite rod) and cathode (platinum wire) were placed at the bottom and top of the electrochemical cell, respectively, with protonic acid (e.g. H_2SO_4 , H_3PO_4 or $\text{H}_2\text{C}_2\text{O}_4$) aqueous solution as electrolyte. Upon the application of a constant current, 0.1 A, the electrolyte solution was found to change from colorless to black with the increase of reaction time. The water soluble MEE-Graphene was transferred into container, followed by ultra-sonication for few minutes. And then, the sonicated graphene was washed, dried and collected. Domestic microwave oven (Panasonic, inverter) was used to aid the expansion of the MEE-graphene. For comparison control experiment was conducted via conventional (parallel) electrochemical configuration.

Synthesis of Nitrogen-doped Graphene Flakes. To prepare the N-doped graphene, a certain amount of the as-prepared graphene flakes was annealed at 800 °C for 1h in the flow of 400 sccm Ar/NH_3 (95/5, v/v).

2.2.2 Material Characterization

Structural and Morphology Characterization. The morphology was investigated via Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM, JEM-2010, 200 kV), Optical Microscopy and Atomic Force Microscopy (AFM, Nanoscope V, diDimension). Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer 2000 FTIR spectrometer), Thermogravimetric Analysis (TGA) and X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 250 spectrometer (Thermo Electron, Altrincham, U.K.), using an Al $K\alpha$ X-ray source (1486 eV)) were conducted to shed more light on the chemical composition of the ORR catalysts.

Electrochemical Performance Evaluation. Cyclic voltammetry (CV) measurements were performed in a standard three-electrode system (platinum foil-counter electrode, Ag/AgCl electrode-the reference electrode, MEE-Graphene-working electrode) using an Autolab PGSTAT302 electrochemical test system (Eco Chemie, Netherland). The working electrode was prepared as follows ^[118]: i) 10 mg of N-doped GO was ultrasonically dispersed into 1 ml of 2-propanol containing Nafion solution (5 wt%, dupont); ii) 10 μ l of the above catalyst ink was coated on the glassy carbon disk (5 mm in diameter) and dried at 80 for 15 min. As-prepared GO and Pt-loaded carbon catalyst (Pt/C 20% on Vulcan XC-72R, E-TEK division, PeMEAS Fuel Cell Technology) with the same amount were also studied for comparison by using the same electrode configuration. Oxygen reduction reaction (ORR) measurement was conducted in a 0.1 M KOH aqueous electrolyte saturated with oxygen at a scan rate of 10 mV/s on the rotating-disk electrode system (Eco Chemie, Netherland). For the control experiment, the bare glassy carbon electrode was tested. Methanol

toxicity test was conducted at a constant potential -0.5 V (vs Ag/AgCl). The voltammetric stability test of both N-doping GO and 20% Pt/C were performed in O₂-saturated 0.1 M KOH within the potential window of -1.0 ~ 0.2 V (vs. Ag/AgCl) for 20,000 cycles. The scan rate is 100 mV/s. All measurements were carried out at room temperature. All potentials presented in the graphs and in the discussion were converted with reference to the reversible hydrogen electrode (RHE), which is independent of pH value. The number of electron transferred (*n*) was calculated based on Koutecky-Levich equation.

2.3 Results and Discussions

2.3.1 The Synthesis of Graphene Flakes

Unlike conventional parallel two-electrode electrochemical cell, in our experiments graphite rod obtained from spent Zn-C primary battery (anode) and platinum wire (cathode) were placed vertically at bottom and top of the electrochemical cell, respectively. As shown in Figure 2.1a, the graphite rod was surrounded with a plastic tube as an insulator container and only the top surface of it was exposed to the electrolyte solution. Constant current of 0.1A was applied across the two electrodes. The Potential of 6 ~ 8 V could drive the anions into the intercalation space and make the exfoliation to proceed. Comparative experiment was also conducted via conventional method (by rotating 90° the vertical cell becomes a parallel-electrode setup) (Figure 2.1b). An apparent colour change from transparent to dark for the aqueous electrolyte solution was observed in vertical cell after only few minutes, which is much shorter than that of conventional method, indicating our improved exfoliation

process is more efficient and exhibits higher exfoliation rate than that of conventional parallel configuration.

Figure 2.1. Multiple electrochemical exfoliation method vs. Conventional (parallel) electrochemical exfoliation method both in configuration (a, b) and in Production (c).

Significantly larger quantity of graphene sheets was collected in the same reaction time period, in comparison with conventional method (Figure 2.1c), which is attributed to the multiple electrochemical exfoliations of graphite particles in our unique cell. In conventional (parallel) cells, exfoliated graphite sheets/particles leave from the graphite rod and precipitate at the bottom of the

reaction container whereas in our vertical-configuration cell the exfoliated graphite sheets/particles leaving from the graphite rod may undergo more than one rounds of electrochemical exfoliation.

TEM, AFM and Optical microscopy were employed to analyze the graphene sheets obtained from the multiple electrochemical exfoliation (MEE) in our vertical configuration cell. Optical and TEM images reveal that the as-prepared products consists of a large amount of exfoliated graphene with lateral size ranging from 1 to few μm (Figures 2.2a, 2.2c and 2.2d). AFM images provide more details in distribution of thickness. A representative AFM images of exfoliated graphene flake with thickness about 4.84 nm is shown in Figure 2b. It was estimated that approximately 32% of the graphene flakes have thicknesses in the range 4-6 nm while nearly 80% of them are located in the thickness range of 4-8 nm based on the statistical sampling of exfoliated graphene flakes (Figure 2.2b). The total yield of graphene flakes dispersed in DI water excluding the large graphite pieces is nearly ~50% (Figure 2.1c). In a control experiment, parallel configuration cell under the same condition produced substantially less graphene sheets (less than ~20%, Figure 2.1c) in a much slower rate. The average thickness of graphene sheets obtained from the conventional cell was greater than 15 nm, not mentioning those big graphite particles fallen on the bottom of the cell, i.e. electrolyte container.

Figure 2.2. (a) TEM image and corresponding selected area electron diffraction pattern for multiple electrochemical exfoliation (MEE) graphene flakes. (b) AFM image of exfoliated graphene flakes spin-coated onto a SiO₂ (285 nm)/Si substrate. The thickness is ~ 4.84 nm, corresponding to 10 to 15 layers. (c) The low-magnification Optical microscopy image of MEE graphene flakes on SiO₂/Si substrate. (d) Thickness and lateral size distribution histograms for MEE graphene sheets, as estimated from corresponding AFM images. The graphene flakes are mainly distributed in the range of 2-8 nm thickness ($\sim 80\%$) with lateral size about 1-5 μm . (e) XPS C1s spectra, (f) TGA plots for raw materials, parallel configuration graphene flakes and MEE graphene flakes. (g) FTIR of MEE graphene flakes.

In addition, FT-IR, XPS, and Thermogravimetric analysis (TGA) were employed to characterize the multiple exfoliated graphene samples (obtained from vertical cell) and single exfoliated graphene (obtained from conventional

cell), respectively. The characteristic FTIR peaks reveal the presence of various functional groups including C-O (at 1060 cm^{-1}), C-O-C (1250 cm^{-1}), C=O/COO (at $1690\sim 1710\text{ cm}^{-1}$), and COO-H/CO-H (1365 cm^{-1})^[119] on the multiple exfoliated graphene samples (Figure 2.2g). These functional groups can be eliminated by heating. A weight loss at $\sim 100\text{ }^{\circ}\text{C}$ is observed from TGA (Figure 2.2f), probably due to the vaporization of adsorbed moisture or water. It should be noted that there is major weight loss that starts at $\sim 150\text{ }^{\circ}\text{C}$ and continues up to $800\text{ }^{\circ}\text{C}$, which certainly results from the decomposition of functional groups. More significant loss for “MEE” sample than “SEE” one (30 %wt. vs. 20% wt.) indicates less functional groups on the “SEE” sample.^[120] The XPS C1s spectra further verifies the presence of oxygen functional groups (Figure 2.2e). The appearance of shoulder peaks at 286, 287 and 289 eV in XPS C1s spectra (blue area), which are assigned to C-O, C=O and carboxyl groups, respectively, indicates the significant oxidization of MEE graphene.^[94]

We suspect that increase of the electrolysis time is favorable for multiple exfoliations in terms of increasing production of exfoliated graphene and promoting more uniform thickness distribution. It is true that the average size of graphene reduced while the portion of big graphite particles falls when the reaction time increases from 0.5 h to 2 h,. The properties of MEE graphene with different reaction time were investigated using TGA, XPS and FTIR (Figure 2.3) in order to learn more about multiple electrochemical exfoliation process. It is interesting to find that the FTIR intensity of functional groups, such as C-O (at 1060 cm^{-1}) and C-O-C (1250 cm^{-1}), C=O stretch in carboxylic acid ($1690\sim 1710\text{ cm}^{-1}$), and COO-H/CO-H (1365 cm^{-1}) remarkably decrease with exfoliation time (Figure 2.3a).^[121] This phenomenon is attributed to the remove

of function groups resulted from heating with the extension of reaction time. The reduction of these functional groups is further confirmed from TGA results, where slightly decrease in the total weight loss are observed (Figure 2.3c), i.e. 31.2%, 29.4% and 27.7% for MEE 0.5h, MEE 1h and MEE 2h, respectively. Particularly, a remarkable decrease in hydroxyl content (C-O, 286.6-286.8 eV) was observed from MEE 0.5 to MEE 2h (Figure 2.3b).

Figure 2.3. FT-IR spectrum (a), XPS spectra (b) and TGA curve (c) of MEE GO prepared via reaction time at 0.5 h, 1 h and 2 h, respectively.

Previously reports indicated that the successful electrochemical exfoliation of graphite was strongly dependent on the graphite structure, and hence exfoliation was observable only on high quality crystalline graphite such as HOPG, natural graphite flakes or paper.^[122, 123] Controversially, there is no

special requirement for our design on the quality and morphology of graphite source. Recycled graphite rod obtained from spent Zn-C primary batteries and pencil core could be equally well exfoliated in design without the need of special pre-treatment or cleaning. Our design here would no doubt open up a wide opportunity for recycling of anode material in spent Li-ion batteries.

Electrolyte plays an important in electrochemical exfoliation of graphene. Various aqueous protonic acids including phosphoric acid, oxalic acid, sulfuric acid, acetic acid and formic acid were tested as the electrolyte in our work. Those acids with bulky anions, such as phosphoric acid, sulfuric acid, and oxalic acid were all proven to be effective in the exfoliation of spent graphite rod. The diverse choices of aqueous electrolyte provide us with more freedom to adjust the oxidization states of exfoliated graphene and reduce the production cost even further. Among them, oxalic acid solution is the best electrolyte. Since the corresponding exfoliation is fast and the graphene sheet product obtained from oxalic acid has the large solubility in DI water. Moreover it is easier to clean the product by just heating the exfoliated graphene in air, thus eliminating the need of washing the sample. Formic acid and acetic acid are not suitable electrolyte, as no obvious exfoliation was observed. This phenomenon may be due to the smaller size of anions (HCOO^- , H_3CCOO^-), resulting in weak anion salvation and weak expansion of graphite sheets by the anion intercalation.^[124]

2.3.2 The Mechanism for Electrochemical Exfoliation

In our vertical design, only the top surface of the graphite rod is exposed to the electrolyte. When a high enough potential ($\sim 6\text{-}8\text{ V}$) is applied across the two electrodes, the electrolyte anions such as OH^- , HSO_4^- and SO_4^{2-} and their

solvated complexes (in the case of dilute H_2SO_4 being used as the electrolyte) are driven to anode, i.e. the graphite electrode of positive potential (Figure 2.4).

Figure 2.4. Schematics of multiple electrochemical exfoliation (MEE) process. The digital photograph of the dispersed exfoliated graphene sheets in DMF solution, and the corresponding typical TEM images are shown. The mechanism of electrochemical exfoliation that consisting of anodic oxidation of graphite (eqs1-3) and water (eq4, and the intercalation of anions into graphite rod (C_s -surface of graphite rod, C_b -bulk of graphite rod) (eq5), is illustrated. Schematic of graphite intercalation compound (GIC) with both hydroxyl and carboxyl groups formed is shown.

Involved mechanism was proposed and described in details. Electrochemical oxidation reactions triggered by the current flow which removes the electrons from anode may take place, including the anodic oxidation, hydroxylation and carboxylation of graphite (as well as water oxidation), as described in Equations 1-4 (Scheme in Figure 2.4). These processes take place initially at surface, grain boundary or structural defect sites,

generating $\bullet\text{OH}$, $\bullet\text{COC}$, $\text{CO}\bullet$, and $\text{COO}\bullet$ functional groups on the graphite surface. During these processes, CO_2 and O_2 can be produced as the electrolysis products (Equations 1 & 4).^[125, 126] The release of gaseous bubbles was obviously observed during the electrochemical process, which became vigorous with increasing exfoliation time, as if water boiled. The anodic corrosion/etching as well as the violent gas release open up the edge sheets on the graphite rod surface and facilitates the intercalation of bulky anions (as well as their solvated moieties) into the graphite layers, forming graphite-intercalation-compounds (GIC) ($\text{C} + \text{A}^- \rightarrow \text{CA} + \text{e}^-$) (Equation 5). The intercalation and the hydrolysis of the intercalated complex ($\text{CA} + \text{H}_2\text{O} \rightarrow \text{COH} + \text{H}^+ + \text{e}^-$)^[124, 127] lead to the expansion of graphene sheets and the cleavage/exfoliation of functional graphene sheets. Here, a mixture of GIC and graphite oxide is obtained. The exfoliated particles can be pushed up by the gas bubbles if they are small in size or light in weight. Or they would sink if the exfoliated particles are large and heavy. Nevertheless the precipitating big GIC particles can continue the electrochemical exfoliation when they have electric contact with anode. Multiple exfoliation process would proceed until smaller graphene sheets form and become suspension in the solution. Therefore, the exfoliated graphene sheets produced in our cells have higher quality than those generated in conventional parallel configuration cells, thinner and better distributed in layer numbers.^[113]

2.3.3 Electrochemical Performance of Resulted Graphene Flakes

Graphene can find wide applications in catalysis and energy storage devices. We have used the as-prepared graphene sheets, i.e. MEE-Graphene which were obtained from the electrochemical exfoliation of graphite rod in our

vertical cell, as the carbon material for Li-ion battery anode. It was found that MEE-graphene was superior over commercial graphite. The first-cycle discharge capacity of commercial graphite is 564 mAh/g (current density is 200 mA/g), which is then reduced and stable at 236 mAh/g after 200 cycles (Figure 2.5a). On the other hand, a very high capacity 1046 mAh/g is recorded on as-prepared MEE-graphene for the first cycle while the reversible specific capacity remain as high as 312 mAh/g even after 200 cycles, which is 32% higher than that of raw materials (Figures 2.5a, b and c). The larger initial discharge capacity results from the oxygen functional groups that contributing to excess lithium ion storage sites. Although the specific capacity decreases with increasing current, the our as-prepared MEE-Graphene is still capable of delivering an impressive 234 mAh/g at 500 mA/g and 173 mAh/g at 1000 mA/g (Figure 2.5d). These results corroborate the great potential of the as-prepared MEE-graphene as high-performance electrode for lithium-ion batteries.

The electrocatalytic performance of the exfoliated graphene oxygen reduction reaction (ORR) was also evaluated. To optimize its electrocatalytic performance, nitrogen-doping was performed *via* annealing as-prepared MEE-Graphene at 800 °C for 1 h in the flow of 40 sccm Ar/NH₃ (95/5, v/v). The appearance of N1s and a sharp decrease in the intensity of O1s in XPS spectra clearly suggest the incorporation of N in the exfoliated graphene oxide, and the reduction/remove of functional groups. The calculated N/C atomic ratio is 5.4 atomic %, similar to that of N-doped graphene reported by previous work.^[128, 129] The high resolution XPS N1s spectrum reveals the presence of pyridinic N (398.2 eV), pyrrolic N (400.5 eV), quantum N (401.1 eV) and N-oxides of

pyridine N (402.1 eV), which have been claimed to improve ORR performance of carbon effectively in our previous reports.^[128, 129]

Figure 2.5. Galvanostatic charge-discharge profiles of (a) commercial graphite and (b) As-prepared MEE-graphene, at a current density of 200 mA/g and with various cycle numbers. (c) The comparison of discharge capacity for the two kinds of carbon materials at 200 mA/h/g with increasing cycle number. (d) Rate performance of As-prepared MEE-graphene with increasing discharge/charge rate from 100 to 1000 mA/g.

The ORR catalytic activities of the MEE graphite oxide before and after N-doped were studied using rotating disk electrode (RDE) measurements in O_2 -saturated 0.1M KOH electrolyte (Figure 2.6). A clear two-step process with onset potentials at 0.82 V and 0.40 V, respectively, has been detected for the as-prepared MEE GO, consisting well with previous reports on pure CNT^[130] and graphene^[131] (Figure 2.6a). On the other hand the N-doped graphene electrode exhibits a well-defined, one-step process, suggesting a four-electron pathway

for ORR on N-doped graphene (Figure 2.6b). Furthermore, a much more positive ORR onset potential (0.92 V, vs. RHE) and higher cathodic currents are noticed, indicating the enhanced ORR catalytic performance.^[132] The reduction and enhancement in electrocatalytic sites during N-doping process are responsible for the enhanced ORR activities. Moreover, the corresponding Koutecky-Levich plots at different potential exhibit good linearity and their slopes were nearly the same over the potential range of 0.65 ~ 0.80 V, corroborating the first-order reaction kinetics with almost constant electron-transfer numbers for ORR over a wide electrode potential (inset in Figure 2.6b).^[133] The electron-transfer number n was calculated to be 3.9 according to the slopes of Koutecky-Levich plots, suggesting that nearly four-electron transfer process taken place in this potential range.

Figure 2.6. ORR curves for as-prepared GO (a) and N-doped GO (b) in O_2 -saturated 0.1 M KOH solution (scan rate is 100 mV/s) at room temperature. The Inset in (b) shows corresponding Koutecky-Levich plots derived from the ORR measurement. Polarization curves for the ORR on N-doped GO (c) and 20% Pt/C catalysts (d) on a rotating disk electrode, before and after 20,000 potential cycles. (Sweep rate, 100 mV/s; rotating rate, 2500 rpm). (e) Voltammerty

curves for both N-doped GO and 20% Pt/C catalysts before and after 20,000 cycles with a sweep rate of 100 mV/s. (f) Current (i)-time (t) chronoamperometric responses obtained for both N-doped GO (black line) and 20% Pt/C catalysts (red line) at 0.5V in O₂-saturated 0.1 M KOH solution to methanol. The arrow indicates the addition of 2% (weight ratio) methanol.

The stability tests were conducted in order to confirm the feasibility of MEE N-doped graphene for ORR application. ORR curves for N-doped graphene after 20,000 CV cycles is plotted in Figure 2.6c. It is interesting to note that there is only slightly decrease in limiting current, and the onset potential remains the same (Figure 2.6c). The good catalytic stability was further confirmed by the overlap of CV curves before and after 20,000 cycling (Figure 2.6e). Unlike N-doped graphene electrode, negative shifts in onset potential, reduction in limiting current as well as loss of surface area of CV curves were observed for 20% Pt/C electrode (Figure 2.6d & Figure 2.6e).

The N-doped graphene was further subjected to test the poisoning effect in the presence of methanol. As illustrated in Figure 2.6f, the current response decreases sharply upon the addition of 2 wt% methanol for 20% Pt/C electrode. In contrast, the N-doped graphene electrode displays a strong and stable amperometric response, suggesting a high selectivity due to the much lower ORR potential than that required for oxidization of methanol molecules.^[131]

2.4 Conclusion

In conclusion, a simple, green and cost effective multiple electrochemical exfoliation approach has been designed for synthesising graphene in high quality and quantity, due to multiple electrochemical exfoliation. The mechanism of multiple electrochemical exfoliation of graphite

was discussed in detail. The experiment conditions are optimized. The as-prepared graphene exhibit good electrochemical performance for anode materials in lithium ion batteries. Moreover, after N-doping, the exfoliated graphene sheets have been demonstrated to possess good electrocatalytic activity, stability and toxicity tolerance for alkaline electrolyte-based oxygen reduction reaction. Our present findings pave the way for scaled-up preparation, and further commercialization of graphene in a low cost and environmental friendly way.

Chapter 3

High-Performance Graphene Foam/Fe₃O₄ hybrid films for Lithium Ion Battery

The development of deformable electrodes with high electrochemical performance in addition to ultrathin, lightweight and flexible, is one key challenge in flexible electrochemical energy storage devices. Graphene foam (GF), is a three-dimensional (3D) interconnected network of high-quality chemical vapour deposition-grown graphene. It possesses high porosity, good electric conductivity and mechanical integrity, is a good scaffold for flexible electrodes. In chapter 3, thin, lightweight, and flexible Fe₃O₄/GF electrode has been designed based on the 3D interconnected current collector *via* a bottom up approach assisted by atomic layer deposition. The 3D interconnect feature of GF provides a highly conductive pathway for ions and electrons. Benefiting from the unique design, the electrode delivers high reversible capacity and fast charge/discharge capability.

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3.1 Introduction

The prosperity of hybrid electric vehicles (HEV), portable electronics and micro-electro-mechanical systems (MEMS) has promoted increasing demand for high-performance lithium ion batteries (LIB).^[134, 135] This is strongly dependent on scrupulous selection of active materials and unique nanostructures design that ensuring fast pathway for electron/ions diffusion. Fe₃O₄ has been demonstrated to be an attractive anode material due to high theoretical energy capacity, low cost, low toxicity, and ease of fabrication.^[136, 137] However, Fe₃O₄ always suffers from poor cyclability caused by drastic volume expansion during Li⁺ ion intercalation/deintercalation process.^[137] Particularly, the loss of electrical connection of Fe₃O₄ from current collectors resulting from high volume changes during continuous charge–discharge process has been reported, which significantly limits its practical application.^[138] Many approaches have been proposed to improve energy and rate performance, such as fabricating Fe₃O₄ nanomaterials into optimized nanostructure and shapes^[136, 139-141] or embed the active materials in a cushioning medium including conductive medium^[137, 142-146] or other stable metal oxides.^[147, 148]

Building nanostructures is considered as an effective strategy to improve the electrochemical performance of the LIB electrode due to several advantages over their bulk counterparts.^[136, 146, 149-151] i) The nanostructure processes a short transport path for Li⁺ diffusion. ii) The well electric/mechanical contact at electrode/electrolyte interface ensures facile charge transport. iii) The nanostructure could accommodate the large volume expansion during charge/discharge process, and maintain the structural integrity of the electrode. Indeed various nanostructures including solid/hollow nanoparticle,^[152, 153]

nanotube,^[139] nanowire,^[154] porous nanosheet,^[155] and nanowall,^[156] have been built to improve the performance of iron oxide-based electrodes. In addition, via combining with other conductive additives, such as metal nanostructures,^[137] polymers,^[157] carbon materials^[143, 144, 146] and other stable materials,^[148] the electric conductivity of iron oxide-based electrode could be further optimized *via* reducing the diffusion length. Particularly, the hybridization of Fe₃O₄ with carbon allotropes including porous carbon, carbon nanotubes and graphene, provides great opportunity in improving the performance of Fe₃O₄ as the LIB electrodes.^[142, 155, 158]

Although intense efforts have been made, the improvement in electrochemical performance of Fe₃O₄ LIB electrode is still marginal. The fabrication of Fe₃O₄ based electrodes good rate performance and long cycle life is still challengeable but highly desirable. In this work, GF/Fe₃O₄ hybrid electrode was prepared via a novel and facile bottom up approach. The unique hybrid electrode delivers several characteristics: i) good electric contact and facile electron/ions transportation.^[103, 159] ii) good mechanical contact and integrity ensures long cycle time. iii) adjustable and large active material loading. iv) iii) lightweight, flexible features ensures that the GF/Fe₃O₄ hybrid electrode used directly without the employing of binder or other conducting additive, which is highly desirable for application in flexible power source. Benefiting from this unique design, the GF/Fe₃O₄ hybrid electrode demonstrates good cycling performance (up to 500 cycles) and fast charge/discharge feature (10 C).^[110]

3.2 Experiment and Characterization

3.2.1 Materials Synthesis

Synthesis of graphene foams. The 3D graphene foams were prepared via chemical vapour deposition.^[159, 160]

Synthesis of ZnO. Prior to ALD deposition, GF was treated with oxygen plasma (March PX-250 plasma etching system). The diethyl zinc (DEZ, 99.99%, Sigma Aldrich) and H₂O were adopted as the Zn and O precursors for the deposition of ZnO (Beneq TFS 200 system) at 200 °C. The thickness was controlled by the deposition cycles. In this work, samples with thickness 10, 30, and 50 nm, were prepared via controlling the deposition cycles at 60, 180, and 300 cycles, respectively.

Formation of Fe₃O₄ nanostructure. The GF/Fe₃O₄ electrode is achieved via i) bathing ZnO-coated GF into a mixture of FeCl₃ (30 mM) and glucose solution (30 mM) for 24 h, and followed with ii) annealing in Ar atmosphere at 400 °C for 2 h.

3.2.2 Material Characterization

Structure and Morphology Characterization. The morphology of the samples were characterized with JEOL JSM 6700F field emission scanning electron microscopy (SEM) and JEOL JEM-2010 transmission electron microscopy (TEM). The element chemical information is collected *via* X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 220i-XL system, monochromatic Al Ka1 source (1486.6 eV)) and Thermogravimetric analysis (TGA) (TGA Q500, Thermal Analysis Instruments, Burlington, MA)

Electrochemical Performance Evaluation. Electrochemical performance was evaluated on CR2032-coin-type cells using the free-standing GF/Fe₃O₄ as working electrode and lithium foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixed organic solvent consisting of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v). The assembled cells were assembled and aged in the glove box prior to the electrochemical measurements. Galvanostatical discharge/charge testing were performed over the voltage range of 0.01 ~ 3.0 V (vs. Li⁺/Li) using a NEWARE cell tester. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using a CHI 660D workstation (CHI instrument Co. Shanghai).

3.3 Results and Discussions

3.3.1 The Synthesis of GF/Fe₃O₄ Hybrid Films

The bicontinuous mesoporous Fe₃O₄ nanostructure was prepared *via* the ZnO sacrificial layer assisted hydrolysis process.^[161] Three steps are involved for the synthesis of the GF/Fe₃O₄ nanostructure electrodes (Figure 3.1). Firstly, self-supported graphene foam was achieved via i) catalytic decomposition of CH₄ on Ni foam, and ii) the etching away of Ni backbone (Figure 3.1a).^[159] Secondly, ALD-deposited ZnO coated onto the graphene foam, forming a thin layer (Figure 3.1b). ALD is a thin film deposition technique that lead to uniform and conformal films with precise thickness control *via* self-limiting surface reactions.^[162, 163] GF was treated by oxygen plasma prior to ALD to introduce hydroxyl bonds on the surface, and ensure the conformal coating of ZnO.^[164, 165] Thirdly, ZnO was converted into FeOOH *via* bathing GF/ZnO into the mixed solution of FeCl₃ solution with glucose. After annealing in an Ar

atmosphere, the bicontinuous mesoporous GF/Fe₃O₄ was then obtained (Figure 3.1c). The glucose here is converted into amorphous carbon surrounding around the Fe₃O₄ nanoparticles accompanying with pyrolysis process.^[146] The indirect ALD approach for the synthesis of GF/Fe₃O₄ in this work is superior over the direct ALD coating method in terms of high growth rate, large active materials loading, and flexible/low requirement for temperature and ozone atmosphere.^[166, 167] More importantly, different from the compact thin film formed in tradition direct ALD method, unique bicontinuous/mesoporous-nanostructure could be generated, which is particularly desirable for the fast charge/discharge electrode.

Figure 3.1. Schematic illustration of the samples. (a) graphene foam, (b) GF/ZnO, and (c) GF/Fe₃O₄.

The morphology of the GF/Fe₃O₄ bi-continuous structure is characterized via SEM and TEM. GF inherits the 3D structure of the Ni foam backbone well, with porous feature (Figures 3.2a and d). Note that GF is ultrathin and lightweight. Particularly, its thickness or the areal density (0.1 mg cm⁻¹ ~ 0.8 mg cm⁻¹) could be tuned *via* controlling the carbon source amount and growth time. There is no obvious change in the morphology of graphene foam after

ZnO coating, corroborating the conformal coating of ZnO (Figure 3.2b). More details about the tiny particle of ZnO could be found in Figures 3.2c and 3.3b. The excellent coating of ZnO is the key prerequisite for the good coverage of Fe_3O_4 on GF. By adjusting the deposition amount of ZnO, the mass loading of the Fe_3O_4 can be easily controlled. The graphene foam surface becomes rough, covered by small particles, after the replacement reaction of ZnO into Fe_3O_4 (see in Figures 3.2c, 3.2f, 3.3c and 3.3d). The HRTEM image (Figure 3.3e) and corresponding SAED image (Figure 3.3f) reveal that the nanoparticle is single crystalline with an average diameter of 30 nm. The lattice fringe distance of 0.25 nm is detected. It is attributed to the (311) plane of Fe_3O_4 . A closer inspection reveals the formation of bicontinuous/mesoporous nanostructure with Fe_3O_4 nanocrystallites interconnected with each other. The characteristics of both graphene and Fe_3O_4 were also revealed via selected area electron diffraction (SAED) pattern (Figure 3.3f).

Figure 3.2. SEM images of GF (a, d), GF/ZnO (b, e) and GF/ Fe_3O_4 (c, f).

Figure 3.3. TEM images of GF (a), GF/ZnO (b), and GF/Fe₃O₄ (c). HRTEM image of GF/Fe₃O₄ (d), an individual Fe₃O₄ nanoparticle (e) and SAED patterns of GF/Fe₃O₄ (f).

To learn more about the structure and composition of the GF/Fe₃O₄ electrodes, X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were conducted (Figure 3.4). Note that GF exhibits two typical diffraction peaks at 26.5 and 54.6 degree, correspond to the (002) and (004) reflection planes of graphitic carbon (JCPDS card 75-1621), respectively.^[168] More diffraction peaks appear for GF/ZnO composites, result from the hexagonal structure of ZnO (JCPDS card 36-1451). The high deposition temperature ensures that ALD ZnO is crystalline. After the replacement of ZnO with Fe₃O₄, the characteristic peaks of ZnO disappear accompanying with the appearance of the typical peaks of magnetite Fe₃O₄ (JCPDS, card 19-0629) (Figure 3.4a). Three typical peaks of graphene, centering at 1580 cm⁻¹ (G), 2550 cm⁻¹ (G'), and 2720 cm⁻¹ (2D) are identified by

Raman spectra (Figure 3.4b).^[159, 160, 168] The absence of the defect-related D band at 1350 cm^{-1} corroborates the high quality of the GF. It should be also noted that the Raman intensity of the 2D band is much smaller than the 2D band, indicating that the GF is multilayer.^[160, 168] These features ensure it suitable for serving as the scaffold for electrodes. Three more peaks appear at 438, 496, and 569 cm^{-1} after the ZnO deposition, corresponding to ZnO E_2 and A_1 phonons, respectively.^[169] Note that, the D band appears after the ZnO deposition, indicating that defects were introduced during these process. The typical Raman modes of Fe_3O_4 can be clearly identified at 667 cm^{-1} for GF/ Fe_3O_4 composite, corresponds to the A_{1g} mode.^[142] In addition, an enhanced D band and a broadened but decreased 2D band are observed. The former is attributed to the introduction of more defects, while the latter may originates from the amorphous carbon layer that surrounding around Fe_3O_4 surface.^[170] Corresponding XPS results were shown in Figures 3.4c and d. Two typical characteristics of Fe_3O_4 located at 710.9 and 724.2 eV that are corresponding to the Fe $2p_{3/2}$ and $2p_{1/2}$ states, respectively, are found.^[171] There is no satellite peak detected, corroborating the final product is Fe_3O_4 rather than Fe_2O_3 .^[171]

Figure 3.4. (a) X-ray diffraction patterns and (b) Raman spectra of the GF, GF/ZnO and GF/Fe₃O₄ nanostructures. XPS of the Fe 2p states (c) and the O 1s state (d) of Fe₃O₄.

3.3.2 Electrochemical Performance of GF/Fe₃O₄

Cyclic voltammetry (CV) and charge/discharge curves were collected to evaluate the electrochemical property of the GF/Fe₃O₄ electrodes systematically. There are two well defined reduction peaks located at 0.67 V and 0.27 V in the 1st discharge process (Figure 3.5a), corresponding to the structure transition (Fe₃O₄ + xLi⁺ + xe⁻ → Li_xFe₃O₄) and the further reduction of Li_xFe₃O₄ to Fe(0) by conversion reaction [Li_xFe₃O₄ + (8-x) Li⁺ + (8-x) e⁻ → 4Li₂O + 3Fe].^[140, 172, 173] Note that these two cathodic peaks positively shifted to 1.1 V and 0.75 V, with the anodic peaks located at 1.6 V and 2.3 V, respectively, for the subsequent cycles. These two redox pairs were attributed to the reversible

reduction/oxidation ($\text{Fe}_3\text{O}_4 \leftrightarrow \text{Fe}$) reactions during lithiation/delithiation process.^[172, 173]

Figure 3.5. (a) cyclic voltammetry (CV) curves of, and (b) discharge/charge profiles of the GF/Fe₃O₄ electrode at 1C rate. (c) Cycling profiles of the GF and GF/Fe₃O₄ electrodes at 1C rate.

Apart from the reaction peaks for Fe₃O₄, one more redox pair is found at 0.1 V (cathodic) and 0.27 V (anodic), indicating that GF taken part in electrochemical reactions.^[103, 174] Note that this redox pair exhibits lower peaks' intensity that those of Fe₃O₄. This is probably because of the high loading of Fe₃O₄ (80% of weight percentage) as also confirmed by the TGA result. The 2nd and 3rd CV curves almost overlap with each other, suggesting the good reversibility of GF/Fe₃O₄ electrode. There are two voltage plateaus located at 0.4 V and 0.65 V in the 1st cycle (Figure 3.5b), corresponding to irreversible reactions induced by the formation of SEI. They disappear since the 2nd cycle,

consisting well with the CV curves. The GF/Fe₃O₄ hybrid electrode has demonstrated a high initial capacity of 1192 mAhg⁻¹ in the 1st cycle and a lower capacity of 785 mAhg⁻¹ in the 2nd cycle, giving rise to a columbic efficiency of 66%. The irreversible reactions involved in the formation of the SEI layer account for the 34% capacity loss.^[144, 146, 158] The discharge/charge measurements were carried out up to 500 cycles to evaluate the cycle performance. After deep cycling to 300 and 500 cycles, the plateaus of the discharge–charge profiles are not so evident as in the initial stage (Figure 3.5b), which are in agreement with the previous reports.^[173, 175] The good cyclic performance is revealed in Figure 3.5c. It is noted that the capacity decreases slightly for the initial 100 cycles, and then increases gradually. The hybrid electrode could deliver a capacity of 870 mAh/g up to 500 charge/discharge cycles, which is better than that of previous reports.^[142, 143, 173] In summary, the electrode displays relatively stable performance and high capacity retention (Figure 3.5c). On the other hand, pure Fe₃O₄ electrode always displays much shorter cycle life (<100 cycles) even at a much smaller charge/discharge rate (i.e. 0.5 C).

Figure 3.6. Rate capability of the GF/Fe₃O₄ LIB electrode. (a) Specific capacity of the GF/Fe₃O₄ electrode under different discharge/charge rates. (b) Discharge-charge profiles of the GF/Fe₃O₄ electrode at different current rates. (c) Cycling profiles of the GF/Fe₃O₄ electrodes at 6C and 10C rates.

Galvanostatic discharge/charge measurements were conducted at various C rates to evaluate the rate performance of GF/Fe₃O₄. The specific capacity decreases with increasing C rates (Figures 3.6a and b). A specific capacity of 190 mAh g⁻¹ was achieved at 60 C, suggesting that the full charge could complete in one minutes. The GF/Fe₃O₄ hybrid electrode still delivers a high capacity of 800 mAh g⁻¹ even when the C rate reduces back to 1 C, corroborating the high stability and good reversibility. The retained capacities of ~400 and 300 mAh g⁻¹ could be identified at 6 C and 10 C charge/discharge rates, respectively, till 500 cycles (Figure 3.6c).

Figure 3.7. SEM images under low magnification (a), high magnification (b) and TEM image (c) of GF/ Fe_3O_4 after 500 cycles at 1 C. (d) Electrochemical impedance spectroscopy results for GF/ Fe_3O_4 before and after 500 cycles at 1 C.

3.3.3 Underlying mechanism for the enhanced electrochemical performance

In order to reveal the underlying mechanism for the enhanced electrochemical performance, the composite electrodes were characterized after 500 charge/discharge cycles at 1 C (Figure 3.7). Despite somewhat pulverization, the Fe_3O_4 layer still keeps good electric and mechanical contact with GF, and the individual Fe_3O_4 nanocrystallites can still be well maintained (Figures 3.7a, b and c). Corresponding electrochemical impedance spectroscopy (EIS) result (Figure 3.7d) reveals an evidently decrease in the resistance of GF/ Fe_3O_4 after cycling, which is attributed to the reduction of Fe_3O_4 into Fe during the irreversible reactions.

Note that the specific capacity increases with prolonged cycling gradually. Similar trend has been observed for many other metal oxide-based electrodes previously,^[176-179] but there is no consensus on the reason until now. There are three possibilities that may take responsible for it: (i) More active sites would be released for lithium storage resulting from the pulverization of the electrode, and thus result in the increase in capacity. (ii) Fe nanoparticles would be generated resulting from the irreversible reactions (SEI formation), which will improve the overall conductivity of the electrode, agreeing well with the EIS results (Figure 3.7d).^[168] Therefore, the specific capacity would increase benefiting from the enhanced charge-transfer kinetics. (iii) The organic/gel-like SEI layer would form on the electrode surface.^[143, 176, 179] It could improve the mechanical cohesion of the active materials without hindering the ion transfer and provide excess lithium ion storage sites by a so-called “pseudo-capacitive-type” behavior, especially in the low potential region.

Figure 3.8. TEM images for graphene oxide (a-c) and carbon nanotubes (d-e): (a) GO, (b) GO/ZnO and (c) GO/Fe₃O₄, (d) CNTs, (e) CNTs/ZnO and (f) CNTs/Fe₃O₄.

The good performance of the GF/ Fe₃O₄ electrodes is attributed to the unique design of the mesoscale structure that takes advantages of both high electrical conductivity and good structural stability. More importantly, this ALD approach for Fe₃O₄ is general and is suitable for other carbon substrates (Figure 3.8). As mentioned above, the deposition of ZnO is determinant via affecting the homogeneity and mass loading of the resulting active materials. It is foreseeable that, the method we reported here is possible to scale up and push the iron oxide-based LIB electrodes into real applications, given the compatibility with reduced graphene oxide and industry-scale ALD. Note that the total loading amount of the active materials is not high in our work, which also retards the practical application. This issue could be addressed by stacking the as fabricated GF supported active material electrodes together to form a multilayer film.^[110]

3.4 Conclusion

In conclusion, a novel approach to prepare bicontinuous-mesoporous Fe₃O₄ nanostructures on 3D GF has been demonstrated. Benefiting from the rational design and the unique mesoscale structure, a high capacity of 785 mAh g⁻¹ (1 C) could be collected and maintained up to 500 cycles. Even at the high rate of 60 C, the electrode could deliver a capacity of 190 mAh g⁻¹. The good electrochemical performance is attributed to the tightly grafting of Fe₃O₄ onto GF that benefits from the uniform ALD coating of ZnO. Particularly, this fabrication method is general and suitable for many other conductive substrates.

Chapter 4

Graphene Foam (GF)/Carbon Nanotubes (CNTs) Hybrid Film-based High-Performance Flexible Asymmetric Supercapacitors

In chapter 3, graphene foam (GF) has been described to be an attractive scaffold for flexible electrodes. However, bearing in mind that high active material loading with good electric/mechanical contact in electrodes is highly desirable for high-performance flexible devices, the relatively low active material loading results from insufficient surface area of GF limits the practical applications of GF as efficient electrode support for flexible and lightweight energy storage devices. In order to further increase active material loading, a facile approach was developed for fabricating a novel 3D electrode support consisting of graphene foam (GF) with covalently bonded carbon nanotubes (CNTs) in chapter 4. The hybrid films exhibit high flexibility and robustness, and are an ideal support for flexible electrodes. The lightweight and flexible asymmetric supercapacitors (ASCs) have been fabricated based on the unique GF/CNTs hybrid film. These aqueous electrolyte-based ASCs deliver high energy/power density and good cycling stability in addition to good mechanical flexibility. They are particularly suitable for flexible power sources.

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4.1 Introduction

Carbon is a fascinating material that exists in various structural forms by different hybridization ways of atomic orbitals (sp^2 and sp^3). In addition to bulk phases of carbon (graphite, diamond), other nanoscale low-dimensional carbon allotropes, such as zero-dimensional fullerenes, one-dimensional carbon nanotubes and two-dimensional graphene have been discovered and investigated intensively.^[181, 182] The diversity of microstructures and bonding types ensures versatility in properties and applications for various carbon allotropes.^[83, 183] The hybrid structures of different carbon materials would no doubt further extend the diversity of carbon-based micro-/macrostructures, with integrated properties inheriting from the each constituent structure. Indeed hybrid structures such as CNTs/fullerenes,^[184] CNTs/carbon film,^[185] graphene/CNTs,^[186-189] and graphene/fullerenes,^[190] have displayed improved physical/chemical performance over their single component, because of the synergistic effects. These hybrid structures were used in various areas, such as sensors, drug delivery, nanoelectronics, and energy storage and conversion.^[100, 191-196] Theoretical calculation^[197, 198] predicated that covalently bonded carbon nanotubes and graphene could lead to superior properties in three dimensions without sacrificing inherited properties in the planer and axial directions. Such hybrid structures would be of particular interest for many applications, especially for implementation in microelectronics and microelectrochemical devices because of good electrical conductivity,^[199] large specific surface area,^[80] unique heterogeneous electron transfer and charge carrier rates, and good electrochemical stability.^[81]

Many approaches, including solution-based processes,^[188, 191, 200]

microwave irradiation,^[201] and chemical vapor deposition^[183, 186, 202-204], have been attempted to prepare high-quality graphene/CNTs hybrid electrodes. Graphene/CNTs hybrid films prepared by You et al.^[200] and Yu et al.^[205] via simple liquid phase mechanical mixing display improved performance as supercapacitor electrodes. However, this kind of hybrid films exhibit poor electric/mechanic connection between CNTs and graphene, which limits its application in fast charge/discharge power devices. The synthesis of high-quality graphene/CNTs hybrid materials with strong bonding connection among them is therefore highly desirable. In-situ growth by chemical vapor deposition has been proved to be an effective approach to achieve this. For example, graphene/CNTs hybrid films with good flexibility and electrical conductivity have been synthesized via vertically growing CNTs arrays on catalyst-patterned graphene films.^[187] Recently, Zhu and coworkers^[202] have demonstrated the covalently-bonded graphene/CNTs hybrid films. Similar results were also reported via the CVD growth of CNTs on nickel-supported graphene.^[206] Noted that CNTs are grown only on the graphene surfaces where the catalyst particles are deposited by e-beam evaporation or dip-coating in the above-mentioned studies. The insufficient surface area of these graphene/CNTs hybrid films makes it challenging to achieve high loading of electroactive materials per unit area, which is critically important for flexible devices with high energy density. This also impedes the practical applications of graphene/CNTs hybrid films in flexible/lightweight supercapacitors. Therefore, it is highly desirable to design graphene/CNTs hybrid films with strongly connected and large quantity of CNTs that could substantially extend the porous architecture and enlarge the surface area.

To increase the amount of CNTs and the subsequent mass loading of electroactive materials while maintaining the good electric/mechanic contact between CNTs and graphene, a unique 3D architecture that consists of carbon nanotubes (CNTs) and graphene foam (GF) has been developed. The catalytic chemical vapor deposition is chosen for the growth of CNTs onto GF. A hydrothermal method is adopted to deposit catalysts onto GF to improve the subsequent loading of CNTs substantially. Electrodes including GF/CNTs/MnO₂ (positive electrode) and GF/CNTs/Ppy (negative electrode) have been prepared based on the 3D GF/CNTs hybrid films (current collectors). Flexible and lightweight asymmetric supercapacitors (ASCs) have been fabricated and demonstrated good electrochemical performance. An ASC (1 × 4 cm²) could be charged to 1.6 V within 30 seconds, and drive a 0.45 W motor or power three 5-mm-diameter red light-emitting diodes (LED, 1.8 V, 20 mA) simultaneously.

4.2 Experiment

4.2.1 Material Synthesis and Device Fabrication

Synthesis of Graphene Foam (GF). Chemical vapor deposition was chosen for the growth of GF on nickel foam.^[207]

Synthesis of Graphene Foam (GF)/Carbon nanotubes (CNTs) Hybrid Films. GF serves as template for the subsequent growth of CNTs. A hydrothermal method is adopted for the deposition of the NiCo catalyst. The CNT growth is carried out at 750 °C. The gas flow of C₂H₄, H₂ and Ar is 20, 40 and 100 sccm, respectively.

Synthesis of GF/CNTs/MnO₂ Hybrid Films. A hydrothermal method is

adopted for the synthesis of MnO₂ nanosheets.^[180] The samples are denoted as GF/CNTs/MnO₂-n, where n is the loading amount of MnO₂ (mg/cm²).

Synthesis of GF/CNTs/Polypyrrole (Ppy) Hybrid Films. A chemical polymerization method is adopted for the synthesis of the GF/CNTs/Ppy hybrid films.^[208] The samples are referred as GF/CNTs/Ppy-m, where m is the amount of pyrrole monomer (μl) used during the synthesis.

Assemble of GF/CNTs/MnO₂ // GF/CNTs/Polypyrrole (Ppy) Asymmetric Supercapacitors (ASCs). ASCs were assembled using an electrolyte-soaked (0.5 M Na₂SO₄) separator sandwiched between a piece of GF/CNTs/MnO₂ (1 × 4 cm²) and a piece of GF/CNTs/Ppy (1 × 4 cm²). The ASC devices are denoted as ASC-n, where n is the loading amount of MnO₂ (mg/cm²).

4.2.2 Material Characterization

Structure and Morphology Characterization. Field-emission scanning electron microscopy (FESEM, JEM-6700F, 10.0 kV), Transmission electron microscopy (TEM, JEM-2010, 200 kV), Raman spectroscopy (Renishaw, 532 nm excitation laser).

Electrochemical Performance Evaluation. Cyclic voltammetry (CV) curves, Galvanostatic charge/discharge curves, and electrochemical impedance spectroscopy (EIS, 100 KHz-0.01 Hz) were collected using CHI 760D workstation. Three-electrode system (working electrode: GF/CNTs/MnO₂ or GF/CNTs/Ppy; reference electrode: saturated Ag/AgCl; Counter electrode: Pt plate) was chosen for individual electrodes' testing. The EIS results are fitted via the software Z-View. Two-electrode system is adopted for the ASCs' testing.

The areal capacitance of the individual electrode was calculated from the corresponding CV curves:

$$C = \frac{1}{s \nu \Delta V} \int_{V_0}^{V_0 + \Delta V} I dV$$

where I (A) is the response current, ν is the scan rate (V/s), s is the apparent surface area (cm²), V_0 is the lower potential limit, and ΔV is potential window (V).

The areal capacitance (C_s , F/cm²) and specific capacitance (C_m , F/g) of ASCs were calculated from corresponding charge/discharge curves:

$$C_s = 4 \frac{I}{s} \frac{dt}{dV} \quad \text{or} \quad C_m = 4 \frac{I}{m} \frac{dt}{dV}$$

The equation: $C_- V_- = C_+ V_+$, is used for the charge match between two electrodes. The energy density (E) and power density (P) are calculated according to the equations:^[196]

$$E = C V_{max}^2 / 8$$

$$P = V_{max}^2 / (4 m R_{ESR})$$

$$R_{ESR} = V_{drop} / (2 I)$$

where V_{max} is the maximum voltage of the ASC, R_{ESR} is the equivalent series resistances.

4.3 Results and Discussions

4.3.1 Fabrication of GF/CNTs Hybrid Films

Figure 4.1 schematically illustrates the synthesis procedure of the

GF/CNTs hybrid film: i) GF is deposited on nickel foam *via* catalytic decomposing of CH_4 at $1000\text{ }^\circ\text{C}$ (Figures 4.1a and b).^[207] Self-supported GF with intact 3D microstructure is collected *via* etching nickel substrate (Figure 4.1c). The areal density of GF could be controlled easily via adjusting growth conditions. ii) The uniform coating of NiCo-catalyst precursor on GF is achieved via a facile hydrothermal process (Figure 4.1d). The high loading of NiCo catalysts increase the mass loading of CNTs subsequently, and hence the surface-to-volume ratio of the GF/CNTs hybrid film. Note that little defects are introduced, suggesting that the high quality of GF could be maintained well during hydrothermal method process. iii) GF/NiCo-precursor is converted to GF/ NiCo_2O_4 by heating in air at $350\text{ }^\circ\text{C}$ prior to the growth of CNTs (Figure 4.1e). This could effectively prevent NiCo catalyst particles from agglomeration at high temperatures. The NiCo_2O_4 nanoneedles are then reduced to form well dispersed catalyst islands in the presence of H_2 , and further catalyze the decomposition of C_2H_4 to form 3D GF/CNTs framework (Figure 4.1f). During the synthesis process, apparent color change could be detected, while the macroscopic 3D framework is well preserved.

Figure 4.1. Illustration of the growth procedure of GF/CNTs hybrid films. (a) Ni foam substrate; (b) direct growth of graphene films on nickel foam via CH_4 decomposition; (c) removal of Ni network to form free-standing graphene foam (GF); (d) deposition of NiCo-precursor on the GF via a hydrothermal method; (e) conversion of GF/NiCo-precursor to $\text{GF/NiCo}_2\text{O}_4$; (f) growth of carbon nanotubes onto GF at 750°C in the presence of H_2 and C_2H_4 using the Ni-Co-O catalyst, forming 3D GF/CNTs hybrid structure.

Large sized GF/CNTs hybrid film with good flexibility can be prepared easily (Figures 4.2 a1-a2). The well-defined interconnected network structure of GF/CNTs hybrid film, with a layer of entangled CNTs that are in intimate contact with graphene is detected in Figures 4.2b and c. The multi-walled CNTs, with about 15 – 20 walls, 20 – 25 nm in diameter and a few hundred nanometers to several micrometers in length (Figure 4.2d, Figures 4.2e and f). A bamboo-like structure with complete knots (indicated by the white arrow) is clearly observed from the inset in Figure 4.2e, because of the growth of a complete inner graphene layer prior to contraction of the catalyst particle.^[209, 210] Note that most of catalyst particles locate at the top of CNTs (Figures 4.2d and

f), corroborating a tip-growth mechanism.^[211] It also further verifies the excellent interconnection between GF and CNTs. In addition, the cross sectional images (Figure 4.2g) reveal that there are CNTs on the outer and inner surfaces of GF backbones. To evaluate the crystalline quality of the resulting GF/CNTs hybrid film (Figure 4.2h), Raman spectra are collected. The presence of the characteristic G peak at 1580 cm^{-1} , 2D peak at 2710 cm^{-1} , the 2D/G intensity ratio as well as the absence of the D peak at 1350 cm^{-1} in the spectrum of GF corroborate the high quality of GF.^[113] Note that a sharp D peak appears after CNTs growth, resulting from the generation of defects during growth process. This is further verified via the corresponding SAED patterns.^[212] Nevertheless, GF/CNTs hybrid film exhibits a sheet resistance of $191\text{ }\Omega/\text{sq}$ (178 S/m), which is much smaller than that of pure GF ($352\text{ }\Omega/\text{sq}$, 101 S/m), corroborating the good electrical conductivity of GF/CNTs hybrid film. The 3D architecture of GF is well extended by the densely grown CNTs, and exhibits significant increase in surface area (Figure 4.2i) ($98\text{ m}^2/\text{g}$ vs. $30\text{ m}^2/\text{g}$).^[113] It should be stressed that, the GF/CNTs hybrid films with different CNTs loading could be easily prepared, offering the possibility to further optimize the hybrid film.

Figure 4.2. (a1-a2) Representative photograph of the film. (b-d) Typical FESEM images. (e,f) TEM images of CNTs in the GF/CNTs hybrid film. (g) Cross-sectional images of GF/CNTs branch. (h) Raman spectra of GF/CNTs hybrid film. (i) Comparative specific surface area (SSA) of GF/CNTs and GF. Inset of (d) suggests the tip-growth mechanism for CNTs. Arrows in the inset of (e) indicate the bamboo-like structure. The inset in (g) reveals the uniform growth of CNTs on both outer and inner surfaces of GF branches.

4.3.2 Fabrication of GF/CNTs/MnO₂ and GF/CNTs/Ppy Hybrid Films

Figures 4.3a and c reveal the nanostructure of the GF/CNTs/MnO₂ hybrid film, where CNTs are uniformly surrounded by flower-like MnO₂ nanosheets, forming unique CNTs (core)-MnO₂ (shell) nanostructure. A highly porous network was assembled by the flower-like MnO₂ nanosheets with thickness of a few nanometers (Figures 4.3a and c). The successful deposition of MnO₂ is further verified by the appearance of typical MnO₂ Raman peaks at 568 cm⁻¹, 640 cm⁻¹ as well as the decrease in intensity of G peak (Figure

4.3e).^[213] This hybrid electrode design provides better current collector/active materials contact, and ensures large accessible surface area and fast mass transfer for electrolyte. It is also found that the introduction of CNTs in the GF is crucial to achieve high loading of active materials. For example, the areal density of MnO₂ of GF/CNTs/MnO₂ film is 6.2 mg/cm² (at 0.6 mM manganese source), which is 6 times of that of GF/MnO₂ film. The relatively high and adjustable loading mass of electroactive MnO₂ on GF/CNTs hybrid film offers the opportunity to optimize the electrochemical performance of the assembled ASC devices further.

Conducting polymers/graphene composites have been investigated intensively as promising electrode materials for supercapacitors.^[214, 215] GF/CNTs/Polypyrrole (Ppy) hybrid film was prepared in this work, and used as the negative electrode to match with the GF/CNTs/MnO₂ hybrid film positive electrode for an ASC. The in-situ chemical polymerization is chosen for achieving the conformal coating of Ppy on GF/CNTs film (Figures 4.3b, d).^[208] Corresponding Raman spectra corroborate the synthesis of Ppy with characteristic peaks at 971 cm⁻¹, 1060 cm⁻¹ and 1330 cm⁻¹ (Figure 4.3f). A series of samples with different polypyrrole loading amounts were prepared to optimize the electrochemical performance of GF/CNTs/Ppy hybrid film.

Figure 4.3. Representative FESEM images for GF/CNTs/MnO₂ (a, c) and GF/CNTs/Ppy (b, d) and corresponding Raman spectra (e) for GF/CNTs/MnO₂ and (f) GF/CNTs/Ppy.

4.3.3 Electrochemical Performance of GF/CNTs/MnO₂ and GF/CNTs/Ppy

Hybrid Films

The electrochemical performance of individual electrode is investigated via a three-electrode system. The electrolyte is 0.5 M Na₂SO₄ aqueous solution. The self-supported hybrid film is used as the working electrode directly because of good electric conductivity and mechanical integrated structure. To investigate the contribution of MnO₂ to the capacitance of the hybrid film and optimize the loading mass of MnO₂, a series of CV curves are collected at different scan

rates for different films (Figures 4.4a &b). The current response increases with the increase in MnO₂ mass loading density from 0.6 to 6.2 mg/cm², indicating an increase in the total capacitance.^[216] However, the total capacitance decreases when the mass loading density of MnO₂ further increases to 8.4 mg/cm². Figure 4.4e further supports the presence of optimal mass loading density, where the GF/CNTs/MnO₂-8.4 sample displays a lower areal capacitance compared to the sample GF/CNTs/MnO₂-6.2, especially at low scan rates. Electrochemical impedance spectroscopy (EIS) study of GF/CNTs/MnO₂ hybrid films with different mass loading density of MnO₂ is conducted to understand the inferior performance of GF/CNTs/MnO₂-8.4 mg/cm² (Figure 4.4f). The impedance data is fitted with an equivalent electrical circuit consisting of the electrolyte resistance (R_s), charge transfer resistance (or polarization resistance, R_{ct}), Warburg element (W) and constant phase element (CPE) (inset in Figure 4.4f).^[217, 218] Note that the charge transfer resistance (R_{ct}) increases with the increase of mass loading density. There are two factors accounting for this trend: (i) the poor intrinsic electrical conductivity of MnO₂, and (ii) the increase in the thickness of MnO₂ layer that impedes the ion diffusion and migration process. Interestingly, R_{ct} increases slightly with the MnO₂ loading amount ranging from 0.6 to 6.2 mg/cm², but jumps sharply from 31.6 Ω (for GF/CNTs/MnO₂-6.2) to 56.2 Ω (for GF/CNTs/MnO₂-8.4). This phenomenon excludes the effect of factor (i) to some extent. The factor (ii) might take the main responsibility for the sharp increase in R_{ct} when the thickness of MnO₂ layer is close to the diffusion length of Na⁺ at these scan rates.^[219] Typically, the ion diffusion length in GF/CNTs/MnO₂ hybrid films decreases as the scan rate increases, thus giving rise to the decrease in the

optimal mass loading density. For example, the optimal mass loading density at 75 mV/s is 3.9 mg/cm² whereas it is 2.1 mg/cm² at 200 mV/s.

Figure 4.4. CV curves of GF/CNTs/MnO₂ hybrid films with different loading of MnO₂ (from 0.6 to 8.4 mg/cm²) at the sweep rate of 5 mV/s (a) and 50 mV/s (b). (c) Rate-dependent CV curves of GF/CNTs/MnO₂-2.1 hybrid film. (d) Specific capacitance vs. sweep rate for GF/CNTs/MnO₂ hybrid films with different loading of MnO₂. (e) Areal capacitance vs. mass loading for GF/CNTs/MnO₂ hybrid films at different sweep rates. (f) Corresponding Nyquist plots of GF/CNTs/MnO₂ hybrid films. An equivalent electrical circuit consisting of the electrolyte resistance (R_s), interface charge transfer resistance (R_{ct}), Warburg element (W) and constant phase element (CPE , is illustrated in the inset of (f).

A series of rate-dependent CV curves of GF/CNTs/MnO₂-2.1 hybrid film are plotted to investigate the effect of scan rates on electrochemical performance (Figure 4.4c). Note that the CV curves deviate from a rectangular shape of ideal double-layer capacitors, resulting from the relatively large resistance and overpotential.^[216] The specific and areal capacitance of the GF/CNTs/MnO₂ hybrid films is calculated and plotted in Figure 4.4d,e respectively. Particularly, the high specific capacitance of 215 F/g (Figure 4.4d), which corresponds to 130 mF/cm² (Figure 4.4e), is obtained for sample

GF/CNTs/MnO₂-0.6 at a scan rate of 10 mV/s. The value is much higher than those of MnO₂-based electrodes in previous reports, such as 62 mF/cm² at 5 mA/cm² for PEDOT/MnO₂,^[220] 70 mF/cm² at 2 mA/cm² for TiO₂/MnO₂,^[221] 64 mF/cm² at 0.08 mA/cm² for SnO₂/MnO₂,^[222] 41 mF/cm² at 0.12 mA/cm² for TiN/MnO₂ coaxial arrays,^[223] 105 mF/cm² at 0.06 mA/cm² for WO_{3-x}/Au/MnO₂ nanowire^[224] and comparable to that of hydrogenated ZnO/MnO₂/Carbon cloth (138.7 mF/cm² at 1 mA/cm²).^[225] A high capacitance of 106 F/g (63 mF/cm²) could be retained, even at a high scan rate of 100 mV/s. Moreover, the GF/CNTs/MnO₂ hybrid film displays good cycling performance with nearly overlapped CV curves after 5000 cycles.

Similar to GF/CNTs/MnO₂ hybrid films, the current responses in the CV curves of GF/CNTs/Ppy hybrid films increase with more Ppy deposition, resulting from the increased amount of active materials that contribute to the total capacitance (Figures 4.5a & b). Typical CV curves deviate from an ideal rectangular shape, especially with high Ppy loading and at high scan rates (Figures 4.5c & d). Note that the difference in the areal capacitance for GF/CNTs/Ppy hybrid films is smaller particularly at high sweep rates (Figure 4.5e), which is attributed to the reduced ion diffusion length and increased R_{ct} , as discussed for the case of GF/CNTs/MnO₂ hybrid films. The EIS results of GF/CNTs/Ppy hybrid films (Figure 4.5f) shows slight decrease initially, and followed with the increase in R_{ct} when Ppy loading increase gradually. The theoretic calculation indicates that the resistance of CNTs network usually comes from CNT/CNT junctions.^[226] The slight decrease in R_{ct} is probably resulting from the uniform coating of Ppy onto the GF/CNTs film that improves the electric conductivity between CNT/CNT junctions.^[106] However, further

increasing the Ppy loading blocks the ion diffusion and migration process eventually, giving rise to the increase of R_{ct} from 10.7 Ω for GF/CNTs/Ppy-1000 to 28.6 Ω for GF/CNTs/Ppy-2000.

Figure 4.5. Comparative CV curves of GF/CNTs/Ppy hybrid films at scan rates of (a) 5 mV/s and (b) 50 mV/s. CV curves for (c) GF/CNTs/Ppy-250 and (d) GF/CNTs/Ppy-1500 measured at different sweep rates. (e) The plot of Areal capacitance vs. scan rate and Nyquist plot (f) of GF/CNTs/Ppy hybrid films.

4.3.4 Electrochemical Performance of GF/CNTs/MnO₂ // GF/CNTs/Ppy

ASCs

The charge balance of positive and negative electrodes is crucial to

maximize the energy density of ASCs.^[227] Based on the results above, two couples of electrodes exhibiting close total amount of charge in a wide range of sweep rates, are chosen for the fabrication of ASC-0.6 and ASC-2.1, respectively. The weight ratio of positive electrode (MnO_2) and negative electrode (Ppy) is 1.2:1 for ASC-0.6 and 1.3:1 for ASC-2.1.

The ASC device, consisting of an electrolyte-soaked separator sandwiched by positive and negative electrodes, is illustrated schematically in Figure 4.6a. Two pieces of poly(ethylene terephthalate) (PET) sheets are used as the flexible substrate. Considering the working window for GF/CNTs/ MnO_2 and GF/CNTs/Ppy hybrid films are 0 ~ 1.0 V and -0.6 ~ 0.2 V, respectively (Figure 4.6b), the ASC device is expected to work stably over a voltage window of 0 ~ 1.6 V in 0.5 M Na_2SO_4 . Figure 4.6c illustrates the CV curves with different working windows. Note that the maximal voltage window of 1.6 V exceeds the theoretical decomposition voltage of water (1.23 V), resulting from the high overpotential of hydrogen evolution on the GF/CNTs/Ppy hybrid electrode. CV curves of ASC-2.1 and ASC-0.6 are plotted in Figure 4.6d and Figure 4.6e, respectively. The assembled full cells exhibit quasi-rectangular CV curves at low scan rates, agreeing with a good capacitive behavior.^[228] The CV curves remain symmetrical even at a high scan rate of 500 mV/s, corroborating the good reversibility of electrochemical processes.

Figure 4.6. (a) Schematic illustration of an ASC that consists of GF/CNTs/MnO₂ positive electrode, electrolyte-soaked separator and GF/CNTs/Ppy negative electrode. (b) CV curves of GF/CNTs/MnO₂ and GF/CNTs/Ppy half cells in 0.5 M Na₂SO₄ solution at a scan rate of 20 mV/s. (c) CV curves of ASC-2.1 measured with different potential windows (at 50 mV/s). CV curves of ASC-2.1 (d) and ASC-0.6 (e) measured between 0 and 1.6 V with different scan rates from 10 to 500 mV/s.

Figure 4.7a illustrates the typical galvanostatic charge/discharge curves of the fabricated full cell. The charge-discharge curves deviate from the linear voltage-time relation, suggesting pseudo-capacitive behavior involved in the hybrid electrodes.^[229] The ASC-2.1 exhibits a Coulombic efficiency of 74 - 85%, while the value for ASC-0.6 is above 95% at current density of 1 ~ 3 mA/cm². There are two possibilities that may contribute to the relatively low Coulombic efficiency: i) ASC-2.1 exhibits large resistance with high mass loading; and ii) some unavoidable electrolysis of water takes place because of the high working voltage. Figure 4.7b provides Ragone plot of the ASCs. Importantly, ASC-2.1 exhibits a maximum energy density of 22.8 Wh/kg at 860 W/kg and a high power density of 2.7 kW/kg at 6.2 Wh/kg. ASC-0.6 delivers

better rate performance, with a maximum energy density of 22.2 Wh/kg at a power density of 3.2 kW/kg. Even at a high power density of 10.3 kW/kg, ASC-0.6 still displays an energy density of 10.9 Wh/kg. This is superior to that of many other MnO₂-based symmetric or asymmetric supercapacitors,^[219, 228, 230-236] as given in the same plot for comparison. The fast charge transport and lower resistance of ASC-0.6 may account for its superior rate performance over ASC-2.1, as revealed by the EIS in Figure 4.7c. A typical diffusion-controlled Warburg capacitive behavior with a diagonal line in the low frequency region and small depressed semicircle in the high frequency region,^[217, 218] have been observed. The series resistance of the devices is estimated to be 17.7 Ω (R_s , 1.6 Ω ; R_{ct} , 16.1 Ω) for ASC-0.6 and 26.4 Ω for ASC-2.1 (R_s , 6.4 Ω ; R_{ct} , 20.0 Ω). Note that the serial resistances of ASCs are small, corroborating the compact fabrication that ensures fast charge transfer in the cell. The overall volumetric and gravimetric energy and power densities were calculated based on the packaged cell configuration (Table 4.1).^[237] The ASC-2.1 and ASC-0.6 deliver a maximum volumetric energy density of 8.7 Wh/L and 2.7 Wh/L, respectively, based on the fully packaged cell. The value is quite satisfactory, and higher than reported MnO₂-based ASCs^[236] and Ni(OH)₂-based ASCs.^[238] In addition, decent volumetric power densities of 1.2 kW/L for ASC-0.6 and 1.0 kW/L for ASC-2.1 have been delivered. The ASCs also display good cycling stability. Specially, High capacitance retentions of 90.2% for ASC-0.6 and 83.5% for ASC-2.1 (Figure 4.7d) were reported, even after 10,000 charge/discharge cycles, which are comparable with or better than those of previously reported ASCs.^[239-241]

Figure 4.7. (a) Galvanostatic charge/discharge curves of ASC-2.1 at different current densities. (b) Ragone plot of the ASCs and some other reported devices. (c) Nyquist plots for ASC-2.1 and ASC-0.6. (d) Cycling performance of ASC-2.1 at a current density of 1.5 mA/cm^2 for 10000 cycles. Inset of (d) shows the charge/discharge curves for the 1st and 10000th cycles. (e) CV curves of ASC-2.1 at different bending angles. Optical images show two ASCs connected in series powering (f) LEDs and (g) a small rotation motor.

The development of multifunctional flexible electronics promotes increasing demands for power sources that are Lightweight and flexible in addition to good electrochemical performance. To explore the practical application of our ASCs as flexible power source, the assembled cell was mechanically bending during the measurement of CV curves (Figure 4.7e). At different bending angles, perfectly overlapped CV curves and similar specific capacitance are reported, suggesting that the device could be bent to a large extent without degrading the performance, benefiting from the flexible feature

and good integrity of the hybrid electrodes.^[242] By connecting two pieces of packaged cells in series, output voltage window of 3.2 V was achieved. Benefiting from the high performance, the ASC could power three red LEDs (1.8 V, 20 mA, 5 mm diameter) after charging for only 30 s (Figure 4.7f) or even drive a small rotation motor (3V, 0.45 W) with charging for only a few seconds (Figure 4.7g).

Table 4.1. Parameters for the asymmetric supercapacitors (ASCs) and the calculated volumetric and gravimetric energy/power densities based on the fully packaged cell.

		Thickness (μm)	Density (g/cm^3)	Weight percentage	Volume percentage
ASC-0.6	Positive Electrode (GF/CNTs/MnO ₂ -0.6)	33	0.41	28.5	35.9
	Negative Electrode (GF/CNTs/Ppy-250)	30	0.42	26.4	32.6
	Separator	29	0.39	23.9	31.5
	Electrolyte (0.5 M Na ₂ SO ₄)	-	1.06	21.2	-
ASC-2.1	Positive Electrode (GF/CNTs/MnO ₂ -2.1)	36	0.79	38.9	37.1
	Negative Electrode (GF/CNTs/Ppy-1000)	32	0.75	32.1	33
	Separator	29	0.39	15.4	29.9
	Electrolyte (0.5 M Na ₂ SO ₄)	-	1.06	13.6	-
		E _{max} (Wh/kg)	P _{max} (kW/kg)	E _{max} (Wh/L)	P _{max} (kW/L)
ASC-0.6	Active materials (MnO ₂ +Ppy)	22.2	10.3	-	-
	Electrodes (including GF/CNTs films)	9.4	4.4	3.9	1.8
	Full Cell	5.2	2.4	2.7	1.2
ASC-2.1	Active materials (MnO ₂ +Ppy)	22.8	2.7	-	-
	Electrodes (including GF/CNTs films)	16.2	1.9	12.5	1.5
	Full Cell	11.5	1.3	8.7	1.0

Remarks: The electrolyte is absorbed by the electrodes and thus does not take up any volume in the packaged cell.

For ASC-0.6: total cell mass is 18.8 mg; total volume is 36.8 μL ; density of packaged cell is 0.51 g/cm^3 .

For ASC-2.1: total cell mass is 29.3 mg; total volume is 38.4 μL ; density of packaged cell is 0.76 g/cm^3 .

4.3.5 Underlying Mechanism for Enhanced Electrochemical Performance

The performance of our ASCs is quite satisfactory, especially considering the relatively high and tunable loading density of electroactive materials. The unique design of the 3D interconnected nanostructure of the flexible electrodes may account for the enhanced performance. Specifically, the densely grown CNTs extend the 3D architecture of GF to offer a large surface-to-volume ratio that allows high active materials loading, and also provides good electric/mechanical contact within the hybrid films. Serving as current collector and mechanical supports, the GF/CNTs hybrid films ensures short diffusion length for ions, facile transfer pathways for electrons, and good integrity for active materials. Moreover, relative large mass fraction of electroactive materials is achieved, benefiting from the lightweight and highly porous feature of the GF/CNTs film and the additive-free design of the electrodes. Such electrodes would surely lead to a high energy density of real ASCs in practice, and show apparent advantages over those conventionally prepared with additives (e.g., carbon black and binder) and planar or 3D metallic current collectors.

Additionally, the proper selection of positive/negative electrode materials as well as the well charge balance between the two electrodes also contribute to the good performance of ASCs.^[180]

4.4 Conclusions

In conclusion, novel GF/CNTs hybrid films with unique architecture were prepared via chemical vapor deposition. The resulting GF/CNTs hybrid films deliver good flexibility, high conductivity, and large surface-to-volume

ratio. Using the hybrid films as electrode substrate for the deposition of pseudo-capacitive materials, lightweight and flexible asymmetric supercapacitors (ASCs) have been fabricated. The good performance in terms of energy/power densities, cycling stability and flexibility have been demonstrated by the ASCs. This is attributed to the unique 3D nanostructure of the integrated electrodes, which allows high loading of electroactive materials and ensures facile charge transport. Such ASCs would be promising high-performance power source for flexible electronics.

Chapter 5

A Flexible Alkaline Rechargeable Ni/Fe Battery Based on Graphene Foam/Carbon Nanotubes Hybrid Film

The proliferation of wearable and portable electronics requires high-performance power sources that are lightweight, ultrathin, flexible and low cost in addition to high performance features. Here, a new type of flexible Ni/Fe cell is designed and fabricated by employing Ni(OH)₂ nanosheets and porous Fe₂O₃ nanorods grown on lightweight and flexible graphene foam (GF)/carbon nanotubes (CNTs) hybrid films as electrodes. The assembled f-Ni/Fe cells are able to deliver high energy/power densities (100.7 Wh/kg at 287 W/kg and 70.9 Wh/kg at 1.4 kW/kg) and outstanding cycling stabilities (retention 89.1% after 1,000 charge/discharge cycles). Benefiting from the use of ultra-light and thin GF/CNTs hybrid films as current collectors, our f-Ni/Fe cell can exhibit a volumetric energy density of 16.6 Wh/l (based on the total volume of full cell). This value is comparable to that of thin film battery and better than that of typical commercial supercapacitors. Moreover, the f-Ni/Fe cells can retain the electrochemical performance with repeated bendings. These features endow our f-Ni/Fe cells a highly promising candidate for next generation flexible energy storage systems.

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5.1 Introduction

The sharp proliferation of portable electronics and electrical vehicles requires high-performance power sources that process high energy density and power density and with lightweight, ultrathin, flexible, cost-effective and environmental friendly characteristics.^[104, 195, 244] Among various energy storage devices, aqueous rechargeable batteries have attracted much because of high ionic conductivity, environmental issues, good safety and low cost.^[245-248] Many types of aqueous rechargeable batteries have been explored, including aqueous alkali-ion (Li^+ , Na^+ , K^+) batteries,^[249, 250] aqueous metal-ion batteries (Al^{3+} , Zn^{2+})^[251, 252] and aqueous nickel/metal (zinc, cadmium, cobalt and iron) batteries.^[246, 247, 253, 254] In contrast to reversible intercalation/deintercalation chemistry for aqueous alkali-ion batteries and metal-ion batteries, the nickel/metal battery are mainly based on faradaic reactions that involve one or multi-electron reactions on electrode materials.^[246] Numerous electrochemical redox couples have been explored for alkaline rechargeable nickel/metal batteries, such as nickel/cadmium,^[247, 248] nickel/zinc,^[255] nickel/cobalt^[246] and nickel/iron^[253, 254]. Among these, aqueous Ni/Fe batteries are particularly favorable because (i) both Ni and Fe active materials are insoluble in alkaline solution, and has no requirement for the separator (in contrast with Ni/Zn and Ag/Zn batteries);^[256, 257] (ii) both Ni and Fe are earth-abundant elements and exhibit low toxic or corrosive effect.^[254, 256, 257] Indeed, the nickel-iron battery, which was invented in 1899-1902, has been well developed.^[256, 257] More recently, the century-old nickel-iron battery was revisited and re-discovered to explore its potential application for modern energy supply systems. Different from traditional Ni/Fe batteries, hybrid materials based on novel inorganic

nanoparticles (or rods) and carbon allotropes (carbon fibers,^[253] carbon nanotubes and graphene^[254]) are now chosen as electrode materials, which indeed have improved the rate performance and energy density of Ni/Fe cells. Nevertheless, in the recent demonstrated high-performance Ni/Fe batteries,^[254] the active materials are in powder form, so that carbon black and binders are still required. These additives, together with the heavy Ni foam current collector, will lower the weight specific capacity of the full cells. To push the performance particularly in flexible electronic devices, it is highly desirable to design novel electrode architecture that is binder-free, bendable and durable in long-term cycling.

Recently, we have developed a class of graphene foam/carbon nanotubes (GF/CNTs) hybrid films as an excellent current collector for electrodes (chapter 4).^[258] These hybrid films are lightweight, ultrathin, highly conductive, and have large surface-to-volume ratios. They are ideal for depositing nanometer sized active materials without binders or carbon additives towards flexible and high-performance power sources. In this work, rechargeable Ni/Fe batteries are constructed by direct growth of Ni(OH)₂ nanosheets (cathode material) and mesoporous Fe₂O₃ nanorods (anode material) on the GF/CNTs hybrid films. These novel flexible Ni/Fe cells demonstrate superior energy and power densities stemming from the nanosized feature of active materials and the hierarchical structure of the electrodes. Stable capacities on repeated bending and long-term (up to 1,000) cycling are demonstrated.

5.2 Experiment

5.2.1 Materials Synthesis

Synthesis of Graphene Foam (GF)/Carbon nanotubes (CNTs) hybrid film.

The GF/CNTs hybrid films were synthesized *via* a modified recipe.^[180]

Synthesis of GF/CNTs/Ni(OH)₂ hybrid film. Ni(OH)₂ nanosheets were electrochemical deposited on GF/CNTs hybrid film directly in 0.1 M Ni(NO₃)₂ aqueous solution at a scan rate of 100 mV/s with working windows at -1.2 - 0 V (vs.SCE). The mass of Ni(OH)₂ loading was controlled via adjusting the number of cyclic voltammetry from 50 to 200. The samples are denoted as GF/CNTs/Ni(OH)₂-n, where n is the areal mass density of Ni(OH)₂ (unit of mg/cm²).

Synthesis of GF/CNTs/Fe₂O₃ hybrid film. A simple hydrothermal method is used for then synthesis of GF/CNTs/Fe₂O₃ hybrid film. Briefly, a piece of GF/CNTs film was immersed into a mixture solution of Fe(NO₃)₃•9H₂O (Merck AR, >99.0%) (with monomer amount at 1.5, 3 and 6 mM), DI water (50 mL) and 15 mmol urea (AR, >99.0%), followed by the addition of 5 mL of 30 % HCl. The mixture was then transferred into a Teflon-lined autoclave and heated at 150 °C for 15 h. The as-prepared precursor was then washed with DI water and annealed at 550 °C for 1.5 h in Ar to obtain GF/CNTs/Fe₂O₃ hybrid films. The samples are denoted as GF/CNTs/Fe₂O₃-n, where n is mass loading amount of Fe₂O₃ (mg/cm²).

Assemble of GF/CNTs/Ni(OH)₂-GF/CNTs/Fe₂O₃ rechargeable batteries (F-Ni/Fe batteries). Flexible Ni/Fe batteries with high performance were assembled using a piece of GF/CNTs/Ni(OH)₂ (1×4 cm²) and a piece of GF/CNTs/Fe₂O₃ (1×4 cm²), with an electrolyte-soaked (6 M KOH) separator in between.

5.2.2 Materials Characterization

Structural and Morphology Characterization. Field-emission Scanning Electron Microscopy (FESEM, JEM-6700F, 10.0 kV), Transmission Electron Microscopy (TEM, JEM-2010, 200 kV), X-ray diffraction (XRD, Bruker D-8 Avance), X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 250 spectrometer (Thermo Electron, Altrincham, U.K) (Al K α X-ray source (1486 eV)) and the N₂ adsorption/desorption (ASAP2020 volumetric adsorption analyzer (Micromeritics, USA)) were used to characterize the samples.

Electrochemical Performance Evaluation. Cyclic voltammetry (CV) curves, Galvanostatic charge/discharge curves and electrochemical impedance spectroscopy (EIS, 100 KHz-0.01 Hz) were conducted on using CHI 760D workstation. The three-electrode system is chosen for individual electrode testing.

Calculations. The specific capacity (C*, mAh/g) of positive or negative electrode in **three-electrode** configuration were calculated according to the equation:

$$C^* = \frac{I}{m} \Delta t$$

where I is the discharging current, m is the mass of the individual electrodes, Δt is the discharge time.

The specific capacity (C*, mAh/g) of f-Ni/Fe cells in **two-electrode** configuration were calculated according to the equation:

$$C^* = \frac{I}{M} \Delta t$$

where I is the discharging current, M is the total mass of the two electrodes, Δt is the discharge time.

The equation: $C_- V_- = C_+ V_+$, is used for the charge match between two electrodes. The energy density (E) and power density (P) are calculated according to the equations below:

$$E = \int IVdt/dm$$

$$P = E/\Delta t$$

5.3 Results and Discussions

5.3.1 The Synthesis of GF/CNTs/Ni(OH)₂ and GF/CNTs/Fe₂O₃

The in-situ electrochemical deposition method was employed to prepare Ni(OH)₂ on GF/CNTs hybrid films because it not only produces thin nanosheet structure of Ni(OH)₂ active material but also allows a fine tuning of mass loading of Ni(OH)₂ via modulating the concentrations of electrolyte and deposition time (Figure 5.1).^[259, 260] The flower-like Ni(OH)₂ nano-sheets surrounding the CNTs uniformly with outer diameters ranging from 150 to 300 nm (depending on the mass loading amount) were revealed in Figure 5.2a. The loading density of Ni(OH)₂ is adjustable. TEM images (Figures 5.2b and 5.2c) collected from Ni(OH)₂ nanostructure also verify its nano-sheet morphology, and the SAED pattern (inset in Figure 5.2c) corroborates that the Ni(OH)₂ nano-sheets are polycrystalline. Well-resolved lattice fringes of 0.26 nm was observed (Figure 5.2d), corresponding to the (101) plane of α -Ni(OH)₂ (JCPDS #38-0715). X-ray diffraction (XRD) results further confirms the formation of rhombohedral α -Ni(OH)₂. Note that all the peaks could be indexed to

rhombohedral α -Ni(OH)₂ except the crystalline peaks at 26.4 ° and 44.3 ° that result from GF/CNTs substrate (Figure 5.2e). X-ray photoelectron spectroscopy (XPS) analysis was conducted to shed more light on composition and oxidization stage of Ni(OH)₂. Two typical peaks centered at 855.6 eV and 873.0 eV were observed (Figure 5.2e), corresponding to Ni 2p_{3/2} and Ni 2p_{1/2} of Ni(OH)₂, respectively.^[261] Meanwhile, two satellite lines associated with Ni 2p also appeared.

Figure 5.1. Schematic illustration of the synthesis of GF/CNTs-based electrodes.

Figure 5.2. *Characterization of the GF/CNTs/Ni(OH)₂ hybrid film. (a) Typical FESEM image (inset is magnified SEM image) and (b) Low-magnification TEM image of the hybrid film and corresponding element mappings of Ni and O. (c) TEM image (inset is selected area electron diffraction (SAED) pattern) and correspond HRTEM image (d). (e) XRD pattern and (f) XPS spectra.*

GF/CNTs/Fe₂O₃ hybrid films were prepared *via* a facile hydrothermal reaction of FeOOH nanorods followed by thermal annealing (Figure 5.1). Representative SEM images in Figure 5.3 reveal the well-defined interconnected network structure of GF/CNTs/Fe₂O₃, where the columnar Fe₂O₃ nanorods coated around CNTs uniformly with outer diameter ranging from 200 nm to 300 nm. TEM images (Figures 5.3b and 5.3c) clearly identifies the

mesoporous nanorod structure of Fe_2O_3 with a diameter of 50–150 nm and a length ranging from 50 to 500 nm. This was further confirmed by magnified TEM image in Figure 5.3d, where the pore size is around 5–10 nm. Corresponding specific surface area of the GF/CNTs/ Fe_2O_3 hybrid film is around $68 \text{ m}^2/\text{g}$, which is even comparable with rGO/ Fe_2O_3 composites^[138] reported previously and higher than that of mesoporous Fe_2O_3 .^[262] The SAED (inset of Figure 5.3d) pattern indicates that Fe_2O_3 nanorods are polycrystalline. The well-defined lattice fringes with distances of 0.19 and 0.27 nm (Figure 5.3e) correspond to the d-spacing of (024) and (104) planes, respectively. In additions, the homogeneous distribution of both Fe and O corroborates the uniform coating of Fe_2O_3 (Figures 5.3f1-f2). The XRD pattern of the as-prepared GF/CNTs/ Fe_2O_3 is shown in Figure 5.3g. The characteristic peaks in XRD can be well indexed as tetragonal $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 33-0664).^[157] XPS result (Figure 5.3h) exhibits typical Fe 2p spectrum of Fe_2O_3 with two peaks centered at 711.0 and 724.6 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively^[171]. The presence of satellite line of the main Fe 2p_{3/2} located at 719.0 eV further verifies the Fe_2O_3 phase rather than Fe_3O_4 .^[171]

Figure 5.3. Characterization of the GF/CNTs/Fe₂O₃ hybrid film. (a) Typical FESEM image (inset is magnified SEM image) and (b) Low-magnification bright-field TEM image and (c) dark field TEM image of the hybrid film. (d) TEM image (inset is selected area electron diffraction (SAED) pattern), correspond HRTEM image (e), and (f1-f2) corresponding element mappings of Fe and O. (g) XRD pattern and (h) XPS spectra.

5.3.2 Electrochemical Performance of GF/CNTs/Ni(OH)₂ and GF/CNTs/Fe₂O₃

The electrochemical properties of both GF/CNTs/Ni(OH)₂ cathode and GF/CNTs/Fe₂O₃ anode were investigated in a three-electrode configuration containing 6 M KOH solution. Hereby, we start our discussion based on the charge-matching electrodes, viz., GF/CNTs/Ni(OH)₂-0.9 positive electrode and GF/CNTs/Fe₂O₃-0.6 negative electrode (0.9 and 0.6 denote the areal mass densities of the corresponding active materials in unit of mg/cm²). Figures 5.4a and 5.4b exhibit typical cyclic voltammetry (CV) curves of GF/CNTs/Ni(OH)₂-0.9 and GF/CNTs/Fe₂O₃-0.6 in aqueous electrolyte. The oxidization and reduction potential peaks of Ni(OH)₂ are observed at 0.36 and 0.21 V (vs. SCE), respectively. This corresponds to the reversible reaction as follows: ^[248, 253, 263]

The GF/CNTs/Fe₂O₃ electrode displays two oxidization peaks around -0.89 and -0.71 V in the anodic scan, corresponding to the formation of Fe(OH)₂ (with the oxidization from Fe⁰ to Fe²⁺) and FeOOH (with the oxidization from Fe²⁺ to Fe³⁺), respectively. One well-defined reduction peak at around 1.05 V was found in the cathodic curve, which is assigned to the reduction from Fe³⁺ to Fe²⁺. The missing of another cathodic peak (corresponding to the reduction of Fe²⁺ to Fe⁰) may be due to distortion by the H₂ evolution.

The current intensity and the shifts of both the anodic peak (to a more positive potential) and cathodic peak (to a more negative potential) positions, $\Delta E_{a,c}$, increase with increasing scan rate. ^[264, 265] These are attributed to an increase in the charge diffusion polarization within the pseudoactive material when the scan rate increases. ^[238] The peak currents (I_{pa}) is plotted as a function

of sweep rate (ν) and $\nu^{1/2}$, respectively, in Figure 5.4c for the GF/CNTs/Ni(OH)₂-0.9 electrode and in Figure 5.4d for the GF/CNTs/Fe₂O₃-0.6 electrode. It can be seen that the I_{pa} vs. $\nu^{1/2}$ plots exhibit a linear relationship, whereas the I_{pa} vs. ν plots display a non-linear behavior. Generally, I_{pa} vs. $\nu^{1/2}$ plot shows linear relationship regardless of the scan rate for a kinetically uncomplicated redox reaction in semi-infinite diffusion controlled CV, and the I_{pa} vs. ν plots is expected to be linear for an adsorption process.^[20, 46, 49, 51, 266, 267] Therefore, it is reasonable to deduce that the oxidization processes are diffusion limited based on the linear relationship between I_{pa} and $\nu^{1/2}$ for both GF/CNTs/Ni(OH)₂-0.9 positive electrode and GF/CNTs/Fe₂O₃-0.6 negative electrode, consisting well with previous reported results about LiFePO₄.^[49]

The typical discharge curves were plotted for Ni(OH)₂ electrode (Figure 5.4e) and Fe₂O₃ (Figure 5.4f) with various discharge current densities. A well-defined plateau at around 0.25 V was observed for Ni(OH)₂ electrode, consisting well with eq (5.1). The oxidization reactions of iron anode in alkaline electrolytes could be described as:^[248, 256, 268-271]

or/and

The well-defined plateau around -0.77 V (vs. SCE) can be assigned to the reaction (5.4). The plateau corresponding to reaction (5.2) is not evident in either CV or discharge curves, which suggests that the anodic process is dominated by reaction (5.4). Possibly reaction (5.2) takes place synchronously

with the hydrogen evolution during the cathodic scan when the H₂ evolution occurs at a more positive potential.

The gravimetric capacitance of GF/CNTs/Ni(OH)₂ electrode and GF/CNTs/Fe₂O₃ electrode (in Figures. 4e and 4f) were calculated from the corresponding galvanostatic discharge curves following the equation $C^* = I\Delta t/m$, where I is the discharging current, Δt is discharging time, and m is the mass of individual electrode. The gravimetric capacity of GF/CNTs/Ni(OH)₂-0.9 and GF/CNTs/Fe₂O₃-0.6 are 195 and 278 mAh/g, respectively, at 1 A/g. Even at a high sweep rate of 4 A/g, the gravimetric capacitances retain at 93 and 109 mAh/g, respectively. This implies good rate capabilities for both hybrid electrodes. Additionally, these hybrid electrodes show good cycle stability with capacity retention at 97.2 % for GF/CNTs/Ni(OH)₂-0.9 (Figure 5.4g) and 96% for GF/CNTs/Fe₂O₃-0.6 (Figure 5.4h) after 1,000 cycles at a sweep rate of 10 mV/s.

The electrochemical performance of hybrid electrodes is strongly affected by mass loading of active materials. Note that the gravimetric capacitance and rate performance degrade with the increase in active materials loading, although the corresponding current response increases. This is attributed to the decrease in electric conductivity related to the increase in the thickness. It is noted that the equivalent series resistance (ESR) increases from 2.9 Ω for GF/CNTs/Ni(OH)₂-0.5 to 4.6 Ω for GF/CNTs/Ni(OH)₂-1.2. Similar trend was noted for GF/CNTs/Fe₂O₃ electrodes with different mass loading. This dependence of electrochemical property on mass loading of active materials demonstrates the importance of electrode design to achieve optimized performance of full cells.

Figure 5.4. Electrochemical characterizations of the hybrid film electrodes. Left column: GF/CNTs/Ni(OH)₂-0.9 cathode. Right column: GF/CNTs/Fe₂O₃-0.6 anode. (a, b) Cyclic voltammetry curves at a sweep rates of 5 mV/s. (c, d) Variation of anodic peak current (I_{pa}) with scan rate. (e, f) Galvanostatic discharge curves at various current densities. (g, h) Cycling performance. Insets are the corresponding CV curves after 1,000 cycles.

5.3.3 Electrochemical Performance of f-Ni/Fe Battery

Based on the results above, Ni/Fe full cells were fabricated by using GF/CNTs/Ni(OH)₂-0.9 hybrid film as cathode and GF/CNTs/Fe₂O₃-0.6 as anode. These two electrodes were chosen because the mass loading ratio of Ni(OH)₂ to Fe₂O₃ (0.9 mg : 0.6 mg) corresponds to a reasonably good charge balance between them. The total active materials weight is 6 mg with cell size at 4 cm². Figure 5.5a shows the CV curves of the f-Ni/Fe cell at various scan rates. Well-defined redox couples were observed, corresponding to the overall reaction in the Ni/Fe cell,^[253]

Note that the difference in the anodic peak and cathodic peak positions, $\Delta E_{a,c}$, increase with increasing scan rate for f-Ni/Fe cell. The I_{pa} vs. $\nu^{1/2}$ plot of f-Ni/Fe cell exhibits the same trend as that of single electrodes and indicates that a diffusion limited oxidization reaction takes place during the charging process.^[46, 49, 266, 267] The f-Ni/Fe cell delivers high specific capacity of 119 mAh/g at a sweep rate of 5 mV/s and 78 mAh/g at a sweep rate of 40 mV/s (Figure 5.5b), implying its good rate capability. Typical galvanostatic discharge curves at different current densities are given in Figure 5.5c. Consistent to the CV curves, the discharge profiles exhibit good reversibility with distinct discharge voltage plateau from 0.9 to 1.1 V, depending on current density, suggesting its application feasibility for energy storage.^[253, 254, 270] The specific capacity calculated based on discharge curves ranges from 118 to 50 mAh/g when the current density changes from 0.3 to 8 A/g. It is noteworthy that the discharge (Figure 5.5c) completes in short times ranging from 20 min to 30 sec,

depending on the current density. These discharge time is much faster than conventional Ni/Fe batteries that usually require hours. These values also outperform a recently reported Ni/Fe cell based on carbon fibers^[253] with a specific capacity of 80 mAh/g and charge/discharge time of hours. The series resistance of the devices can be estimated to be 5.9 Ω ($R_s = 3.8 \Omega$; $R_{ct} = 2.1 \Omega$) from the EIS data. The relatively small serial resistances of our f-Ni/Fe cell imply a fast charge transfer between the electrolyte and electrodes.

Ragone plots are important to evaluate the performance of a battery. The energy and power densities (E and P) were calculated using $E = \int_0^{\Delta t} IV(t) dt$ and $P = E/\Delta t$, where I is the discharging current, V is discharging voltage, dt is time differential, and Δt is the discharge time. We constructed the plot in two ways, viz., one based on the active material mass only (open symbols); and the other based on the whole device mass (solid symbols) (Figure 5.5d) Detailed calculation and comparisons are presented in Tables 5.1 – 5.3). Considering only the total mass of active materials, our f-Ni/Fe cell delivers an energy density of 100.7 Wh/kg at 287 W/kg and 70.9 Wh/kg at 1.4 kW/kg, respectively. Even at a high power density of 6.0 kW/kg, an energy density of 37.4 Wh/kg can still be achieved. When the total mass of the cell is considered, the use of lightweight GF/CNTs hybrid films current collector in our f-Ni/Fe cell results in a gravimetric energy density of 30.3 Wh/kg. This value is three folds that of typical commercial supercapacitors and much higher than that of Ni/Fe cells using nickel foams as the current collector (Table 5.3).^[254] The maximum power density is 1.8 kW/kg, which is comparable to that of commercial supercapacitor and four-folds higher than that of lithium thin film battery.

Figure 5.5 | Performance of the flexible Ni/Fe full cells. Cyclic Voltammetry curves (a) and corresponding gravimetric capacitance (b) at different sweep rates. (c) Galvanostatic discharge curves at various current densities and (d) The Ragone plot. Comparisons are made in two ways: based on the active material mass only (upper half), and based on the whole device mass (bottom shaded half). (e) Cycling performance of the f-Ni/Fe cell at a current density of 1.3 A/g for 1,000 cycles. Inset shows the charge/discharge curves for the 1st and 1,000th cycles. (f) Cycling performance of f-Ni/Fe cell at different bending angles. Inset shows the charge/discharge curves at different bending angles.

In order to explore real applications of the f-Ni/Fe cell, the volumetric energy/power densities based on the whole cell configuration were also

calculated (Table 5.1). A maximum volumetric energy density of 16.6 Wh/l has been achieved, which is two-folds higher than the reported MnO_2 -based^[272] and $\text{Ni}(\text{OH})_2$ -based asymmetric supercapacitors^[238] (Table 5.3), both are two typical high-capacity supercapacitive materials. The maximum volumetric power density is 1.0 kW/l. Moreover, the f-Ni/Fe cell exhibits good cycling stability with capacity retention of 89.1% after 1,000 charge/discharge cycles (Figure 5.5e). This result is better than the recently reported Ni/Fe cells which showed 80% capacity retention after 800 cycles.^[254] Moreover, the capacity could retain at 78% when the stability test extended further to 2,000 cycles. And the CNTs-supported structures were well maintained although the surfaces of electrodes show some degree of aggregations during long the charge/discharge process.

The development of multifunctional flexible electronics requires power sources that are flexible and lightweight in addition to high performance. For practical application consideration, the f-Ni/Fe cells were mechanically bent during the measurement of charge/discharge curves (Figure 5.5f). It was noted that there was little changes in the charge/discharge curves under different bending angles (up to 60°). Therefore our f-Ni/Fe cell can be bent to a large extent without sacrificing its performance.^[242] The practical application of our f-Ni/Fe cell was further demonstrated by driving a fan or light-emitting diodes (LEDs) using two f-Ni/Fe cells connected in series. Benefitting from the high power/energy density, the f-Ni/Fe cell could power one red LED (1.8 V, 20 mA, 5 mm diameter) and one yellow LED (1.8 V, 30 mA, 5 mm diameter) simultaneously after charging for only 30 sec, or drive a small rotation motor (3V, 0.45 W) after charging for only a few sec.

Table 5.1. Parameters for the flexible Ni/Fe cell (f-Ni/Fe Cell) and the calculated gravimetric and volumetric energy/power densities based on the fully packaged cell.

		Thickness (μm)	Density (g/cm^3)	Weight percentage (%)	Volume Percentage (%)
Ni/Fe Cell	Positive Electrode (GF/CNTs/ $\text{Ni}(\text{OH})_2$ -0.9)	31	0.50	31.1	34.5
	Negative Electrode (GF/CNTs/ Fe_2O_3 -0.6)	30	0.42	25.1	33.3
	Separator	29	0.39	22.6	32.2
	Electrolyte (6 M KOH)	-	1.23	21.2	-
		E_{max} (Wh/kg)	P_{max} (kW/kg)	E_{max} (Wh/L)	P_{max} (kW/L)
Ni/Fe Cell	Active materials ($\text{Ni}(\text{OH})_2$ + Fe_2O_3)	100.7	6.0	-	-
	Electrodes (including GF/CNTs films)	53.9	3.2	24.7	1.5
	Full Cell	30.3	1.8	16.6	1.0

Remarks: The electrolyte is absorbed by the electrodes and thus does not take up any volume in the packaged cell. For f-Ni/Fe Cell: total cell mass is 20.0 mg; total volume is 36.4 μL ; density of packaged cell is 0.55 g/cm^3 .

Table 5.2. Comparison of electrochemical performance of commercial supercapacitors.

Company	Active Materials	Electrolyte	Operation Voltage (V)	C (F)	Weight (g)	Volume (mL)	E _{max} (Wh/kg)	P _{max} (kW/kg)	E _{max} (Wh/L)	P _{max} (kW/L)
Nesscap (0300C0)	Pseudo-capacitor	Organic (Propylene carbonate and acetonitrile)	2.3	300	25.2	19	8.7	2.9	11.5	3.8
Nesscap (0120C0)	Pseudo-capacitor	Organic (Propylene carbonate and acetonitrile)	2.3	120	15.0	10.2	5.9	3.3	8.6	4.9
Nesscap (0025C0)	Carbon Materials	Organic (acetonitrile)	2.7	25	6.5	5.0	3.9	5.4	5.1	7.0
Maxwell (BCAP3000)	Carbon material	Organic	2.7	3000	510	395.2	6.0	12.0	7.7	15.5
Maxwell (BCAP2000)	Carbon material	Organic	2.7	2000	360	292.1	5.6	14.0	6.9	17.3
ESMA (EC404)	Hybrid	Aqueous	1.5	12000	900	552.4	4.2	1.6	6.8	2.6
ESMA (EC401)	Hybrid	Aqueous	1.5	10000	1100	552.4	2.8	2.6	5.6	5.2
ESMA (EC503)	Hybrid	Aqueous	1.5	7200	600	389.3	3.7	2.3	5.7	3.5
ESMA (EC502)	Hybrid	Aqueous	1.5	6000	700	389.3	2.7	3.2	4.9	5.8
ESMA (EC501)	Hybrid	Aqueous	1.5	6000	700	389.3	6.5	1.9	11.7	3.4

Remarks: Data are collected from internet web home pages of corresponding companies.

Table 5.3. Comparison of electrochemical performance of asymmetric supercapacitors.

Ref.	Active Materials	Electrolyte	Operation Voltage (V)	Current Collector	Weight (mg)	Volume (μ L)	E _{max} (Wh/kg)	P _{max} (kW/kg)	E _{max} (Wh/L)	P _{max} (kW/L)
254 ¹	Ni(OH) ₂ /MWNT // FeO _x /graphene	1M KOH	1.6	Nickel Foam	71.19	-	3.6	0.91	-	-
238 ²	Ni(OH) ₂ // EGO	6 M KOH	1.8	Ultrathin Graphene foam	5.2	7.4	6.9	44.0	4.8	30.8
272 ²	MnO ₂ //AG	1 M Na ₂ SO ₄	2.0	Nickel Foam	39	9.6	1.2	7.5	5.0	31.5
Our work	Ni(OH) ₂ /Fe ₂ O ₃	6 M KOH	1.6	GF/CNTs hybrid films	20	36.4	30.3	1.8	16.6	1.0

Remarks: ¹The calculation for Ref 254 based on data providing in Ref 254. The weight of electrolyte and separator are not included during calculation process. ²The data came from Ref. 238 and Ref. 272 directly.

5.3.4 Underlying Mechanism for Enhanced Electrochemical Performance

Due to its high performance, the Ni/Fe cells demonstrated here could bridge the gap between conventional thin film Li-ion batteries and supercapacitors for flexible electronics. The nanostructured active materials are grown directly surrounding the highly-conductive CNTs. This feature may have contributed the following advantages: (1) It assures a favorable electric contact and facilitates the electron transportation. (2) It promotes good mechanical integrity, accounting for the high cycling stability and flexibility. (3) The lightweight and highly porous features of the GF/CNTs substrate significantly increases the mass loading of active materials as compared to direct growth onto the GF or a planar metallic current collectors. This also eliminates the additives (e.g., carbon black and binder). Benefiting from the unique hierarchical design, the gravimetric energy density and volumetric energy density of our f-Ni/Fe cells are comparable to thin film lithium ion battery and better than typical commercial supercapacitors.^[243]

5.4 Conclusions

In conclusion, flexible Ni/Fe cells are designed and fabricated successfully based on lightweight and flexible GF/CNTs current collectors without using binders or carbon additives. The high volumetric energy/power densities, good cycling stability and flexibility of the f-Ni/Fe cell are clearly demonstrated. Such high-performance alkaline batteries could bridge the energy density gap between supercapacitor and thin film lithium ion battery, and be promising candidate for next generation flexible energy storage systems. The design we proposed is scalable for mass production and could be extended to the fabrication of other binder-free and flexible Ni/Metal alkaline batteries.

Chapter 6

Conclusions, Comments and Future Work

6.1 Conclusions

The synthesis and characterization of low-dimensional carbon materials, including graphene oxide/graphene, graphene foam (GF), GF/carbon nanotubes (CNTs) hybrids, and their composites with nanostructured metal oxides are conducted in this thesis. Their applications in energy storage devices, including lithium-ion battery, aqueous asymmetric supercapacitors and aqueous Ni/Fe battery, are explored.

(1) Electrochemical Exfoliation of Graphite. High-quality graphene flakes is synthesized via a facile electrochemical exfoliation method. The corresponding mechanism is investigated and proposed. Specifically, electrochemical oxidation reactions triggered by the current flow which removes the electrons from anode may take place, including the anodic oxidation (eq 2-1), hydroxylation (eq 2-2) and carboxylation (eq 2-3) of graphite (as well as water oxidation, eq 2-4), as described in Equations 1-4.

These processes occur initially at surface, grain boundary or structural defect sites, generating •OH, •COC, CO•, and COO• functional groups on the graphite

surface. CO_2 and O_2 can be produced as the electrolysis products (Equations 1 & 4). Simultaneously, the release of gaseous bubbles was obviously observed during the electrochemical process, and became vigorous with increasing exfoliation time, as if water boiled. The anodic corrosion/etching as well as the violent gas release open up the edge sheets on the graphite rod surface and facilitates the intercalation of bulky anions (as well as their solvated moieties) into the graphite layers, forming graphite-intercalation-compounds (GIC) ($\text{C} + \text{A}^- \rightarrow \text{CA} + \text{e}^-$) (Equations 5). The intercalation and the hydrolysis of the intercalated complex ($\text{CA} + \text{H}_2\text{O} \rightarrow \text{COH} + \text{H}^+ + \text{e}^-$) lead to the expansion of graphene sheets and the cleavage/exfoliation of functional graphene sheets.

Various aqueous protonic acids with bulky anions including phosphoric acid, sulfuric acid, oxalic acid, were all proven to be effective during exfoliation process. The diverse choices of aqueous electrolyte provide us with more freedom to adjust the oxidization states of exfoliated graphene and reduce the production cost even further.

Our present findings provide deep understanding of the underlying mechanism for electrochemical exfoliation of graphite, effective guides for optimized/controlled synthesis of graphene, and promising approaches for graphene commercialization in future.

(2) Design High-Performance GF/ Fe_3O_4 composite Anode for Lithium-ion Battery. GF/ Fe_3O_4 hybrid electrodes have been prepared via atomic layer deposition approach. The formed GF/ Fe_3O_4 composite exhibits several characteristics: (i) the good electric conductivity and mechanical properties of GF provide efficient ion/electron transportation and mechanical integrity; (ii)

the bi-continuous nanostructure Fe_3O_4 formed by interconnected nanocrystallites are homogeneously distributed on the graphene foam surface with a intact physical contact. The direct contact and interconnection ensure an efficient lithium ion and electron transport between Fe_3O_4 and graphene, as well as ion transport between the electrolyte and the active material. (iii) the binder and conducting agent-free design, as well as atomic layer deposition approach allow a high active material (Fe_3O_4) loading without sacrificing the flexibility of GF/ Fe_3O_4 electrodes. Benefiting from the rational design and the unique mesoscale structure, the GF/ Fe_3O_4 electrodes display remarkable rate and cycle performance. Our results provide efficient guides for optimized design of flexible electrodes.

(3) Design High-Performance Asymmetric Supercapacitors based on GF/CNTs Hybrid Films. A novel electrode support (GF/CNTs) consisting of carbon nanotubes supported on graphene foam (GF) with covalent bonding has been prepared. The densely grown CNTs extend the 3D architecture of GF without sacrificing the good ohmic and mechanical contact between them, and provide a high surface-to-volume ratio that allows high active materials loading. The GF/CNTs hybrid films show several critical merits, including: (i) good electric conductivity; (ii) large specific surface area; (iii) high active materials mass loading, which could be 4-5 folds higher than pure GF (3-8 mg/cm²); (iv) Ultrathin and Lightweight with thickness range from 30 to 100 μm ; (v) large size, good flexibility and mechanical integrity; and (vi) excellent electrochemical stability. These features successfully overcome limitation of the insufficient surface area of these graphene/CNTs hybrid films prepared from traditional dip-coating or beam evaporation, and provide GF/CNTs hybrid

film with great potential for applications in next-generation flexible energy storage devices. The assembled asymmetric supercapacitors (ASCs) (GF/CNTs/MnO₂ // GF/CNTs/Ppy) based on GF/CNTs electrode scaffolds display high energy/power density and are capable of repeated bending without structure failure and degradation in performance. These results presented in this work would no doubt provide a promising approach for flexible electrode design in future.

(4) Design High-Performance Ni/Fe Battery based on GF/CNTs Hybrid Films. In addition to the development of novel electrode scaffold (chapter 4), to explore the promising applications of traditional energy storage devices in modern energy supply systems would be no doubt another promising approach to meet the increasing demand of high-performance, flexible energy power sources. Along this line, the century-old Ni/Fe battery was revisited and re-discovered in this work. By employing Ni(OH)₂ nanosheets and porous Fe₂O₃ nanorods grown on lightweight and flexible graphene foam (GF)/carbon nanotubes (CNTs) hybrid films as electrodes, we designed and fabricated a new type of flexible Ni/Fe cell. Remarkably, the assembled f-Ni/Fe cells are able to deliver high energy/power densities (100.7 Wh/kg at 287 W/kg and 70.9 Wh/kg at 1.4 kW/kg, based on the total mass of active materials) and outstanding cycling stabilities (retention 89.1% after 1,000 charge/discharge cycles). Benefiting from the use of ultra-light and thin GF/CNTs hybrid films as current collectors, our f-Ni/Fe cell can exhibit a volumetric energy density of 16.6 Wh/l (based on the total volume of full cell), which is comparable to that of thin film battery and better than that of typical commercial supercapacitors. Moreover, the f-Ni/Fe cells can retain the electrochemical performance with repeated

bendings. These features endow our f-Ni/Fe cells a highly promising candidate for next generation flexible energy storage systems. Our present results would no doubt provide a novel direction for the development of flexible energy storage devices.

6.2 Comments and Future Work

6.2.1 Electrochemical Exfoliation of Graphite

Although electrochemical exfoliation of graphite has proved to be an effective method to prepare high-quality graphene flakes in an economical and environmentally-friendly way, there are several challenges remaining that need to be addressed before pushing its commercial application: (i) the quality of graphene (size, thickness, defects, etc.) is subjected to the raw materials to some extent; (ii) the production is limited to lab-scale at the moment. Therefore, several further justifications are needed: (i) investigate the effect of raw graphite materials on the quality of resulting graphene in a qualitative way via employing XPS, XRD, Raman spectroscopy and electrochemical characterization methods; (ii) design and built equipments that are suitable for large-scaled production, optimize the synthesis conditions further, and evaluate the quality of resulting graphene in terms of size, thickness, defects and electrochemical performance.

6.2.2 GF and GF/CNTs Hybrid Film based Flexible Energy Storage

Devices

The key challenges for flexible power sources lie in (i) the development of deformable electrodes with high energy density, and (ii) the understanding of underlying mechanism. In our work, we have developed a kind of novel

GF/CNTs hybrid film for flexible electrode scaffolds, and demonstrated its applications in several traditional energy storage systems. Although our designs and results are quite attractive, more research work are required to illustrate the underlying mechanism in a qualitative and quantitative way, and optimize electrochemical performance further.

6.2.2 .1 Design Novel GF/CNTs/CNTs Hybrid Films for Flexible Electrode Scaffolds

Our results in Chapter 3, 4 and 5 indicates that the densely grown CNTs could extend the 3D architecture of GF without sacrificing the good ohmic and mechanical contact between them, which provides a high surface-to-volume ratio that allows high mass loading of active materials. Along this line, we try to design a new kind of GF/CNTs/CNTs hybrid films assisted by ALD method in order to increase the active materials loading further. ALD is a powerful tool to deposit nano-sized catalyst on the surface of GF/CNTs hybrid films, forming GF/CNTs/catalysts composites. The GF/CNTs/CNTs hybrid films is then achieved after the second-growth of CNTs on GF/CNTs/catalysts composites.

6.2.2.2 Explore the Underlying mechanism of flexible energy systems

The electrochemical properties of active materials (e.g., specific capacity, reversibility, rate capability, cycling behavior, etc.) are strongly dependent on the structure and element changes during electrochemical reaction processes.^[273-276] Therefore, the establishment of clear relationships between electrochemical and structural/element data is no doubt one key issue for better understanding and further improving the electrochemical performance of electrode materials for high-performance flexible energy storage devices.

In-situ Raman spectroscopy is a convenient and non-destructive tool for studying electrochemical reaction processes within numerous electrodes in aqueous and non-aqueous energy storage devices.^[277, 278] Raman spectroscopy has been found to be very sensitive to the state of metal oxide, with the Raman frequencies being dependent on the metallic oxidization state. Therefore, it is particularly suitable for the investigation of underlying mechanism for redox couples involved in many aqueous electrochemical capacitors, or metal-ion rechargeable batteries. In additions, our group has strong background in Raman spectroscopy, which would help me a lot for further work in this area.

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