Metal oxide/hydroxide and their composite materials for supercapacitor application

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Metal oxide/hydroxide and their composite materials for supercapacitor application

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

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Symbols with the same meaning in all chapters

C_{sp}	specific capacitance	F g ⁻¹
I	current density	A g ⁻¹
Δt	galvanostatic discharge time after IR drop	s
m	mass of active material in one electrode	mg
M	mass of the active materials in two electrodes	mg
ΔV	electrochemical potential window of a working electrode	V
V	electrochemical potential window of a supercapacitor device	V
E	energy density	Wh kg ⁻¹
P	power density	W kg ⁻¹
A	area	cm ⁻²

ABSTRACT

Supercapacitors are a kind of electrochemical energy storage devices, which can provide high power transient energy supply. They have moderate energy density $\sim 10 \text{ Wh kg}^{-1}$ and high power density up to 10 kW kg^{-1} . The enhancement of energy density of supercapacitor will be benefit for various applications, such as consumer device, energy backup, industrial heavy duty machine and so on.

This thesis focuses on the strategies to enhance the electrochemical energy storage performance of pseudocapacitive metal oxide/hydroxide materials. The corresponding strategies are: 1) constructing one dimensional electrode nanostructure of active material ($\text{Ni}_x\text{Co}_{4-x}\text{O}_4$ polycrystalline nanowire, Ni-Co layered double hydroxide- Zn_2SnO_4 hybrid material); 2) hybridization of active material with conducting additives ($\text{Ni}_x\text{Co}_{4-x}\text{O}_4$ reduced graphene oxide composite material); 3) enhancing the electric conductivity of pristine active material (Ni-Co-Al layered hydroxides); 4) creating facile mass transfer by novel device configuration (fabrication of interdigitated finger electrode based micro supercapacitor using MnO_x -polyaniline). Based on these strategies, several physical/electrochemical factors are found to be crucial in achieving high electrochemical performance, such as high aspect ratio nanowire structure, the effective electrochemical active area, fast surface faradic reaction, and high aspect ratio design of interdigitated electrodes. The rational design of electrochemically

active materials, as well as the micro electrode device, lead to enhanced supercapacitor properties with higher energy densities and higher power densities. Overall, this thesis contributes to the rational design, synthesis, and insightful understanding to the electrochemical behavior of metal oxides/hydroxides and their composite materials.

Chapter 1 Introduction

1.1 Background

The rapid development of human society requires gigantic supply of energy. Coal, petroleum and natural gas, such fossil fuels are the major components for global energy consumption. However, these primary energy sources have limited reserves on earth and the distributions of resources are extremely imbalance. For example, as shown in Figure 1.1, Middle East has the largest reserve on earth with 56 % of total oil volume, while Europe has only 1 % of the reserve. It makes the reliance on the oil transport and security become especially important. Besides, the combustion of fossil fuels causes critical impacts on the global environment, such as greenhouse effect^[1] and air pollution.^[2] Thus, it is urgent to develop alternatives for traditional primary fuel sources.

World Oil Reserves by Region

Figure 1.1 World oil reserves by region. Data source: US energy information administration from Oil and Gas Journal.

Water energy, wind energy, solar energy and so on are a group of renewable clean energy sources, which can be transformed into the electricity for civilian use. The storage of generated electricity with high efficiency is a crucial process during the off-peak hour of electricity generation. Pumped water, compressed air, flow batteries, flywheel, hydrogen storage and supercapacitors are several mainstream technologies for grid level electricity storage.^[3] Among them, supercapacitors are of great interest for their high power densities, high energy storage efficiency and high cycling stability. Moreover, the supercapacitor technology can be transplanted to portable devices, hybrid electric vehicles and energy backups.^[4] The versatility of supercapacitor is of great interest for various applications.

Supercapacitors are a kind of electrochemical energy storage devices, which can provide high power transient energy supply. They have moderate energy density $\sim 10 \text{ Wh kg}^{-1}$ and high power density up to 10 kW kg^{-1} . This energy storage characteristic bridges the gap between batteries and conventional dielectric capacitors. Though supercapacitors currently have lower energy densities than batteries ($\sim 100 \text{ Wh kg}^{-1}$), the high power densities of supercapacitors satisfy a lot of high power delivery applications. According to the US Department of Energy, the development of supercapacitors has been placed the equal importance as batteries for future energy storage systems.^[5] Supercapacitors have an important role as complementary part or replacing batteries in energy storage fields, such as

back-up power supplies and load leveling.

The development of high energy density supercapacitors is of great significance for future applications. There are two types of supercapacitors, electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store energy through the reversible adsorption/desorption of electrolyte ions on porous carbon electrode surface, while pseudocapacitors utilize reversible faradic reaction of redox active materials to store electrochemical energy. Due to the difference in the energy storage mechanism, EDLCs usually have good reversibility as well as high power density. On the other hand, pseudocapacitors have higher energy density. Thus, the research in pseudocapacitor is critical in the development of high energy density supercapacitors.

The pseudocapacitive electrode materials include transition metal oxides/hydroxides (MnO_x , Co_3O_4 , NiO , V_2O_5 , $\text{Co}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ and more), transition metal nitride (VN) and redox active conducting polymers (polyaniline, polypyrrole and more).^[6] Nanostructuring electrode materials is the most prevalent approach to achieve better electrochemical performance.^[7] Nanosized materials, which are termed as nanomaterials, indicate that the materials have at least one dimension which is below 100 nm. According to the dimensions, nanomaterials can be categorized into 3 groups, namely 0D nanoparticles, 1D nanostructures (nanowires, nanotubes or heterostructures) and 2D nanosheets. The resulting

nanomaterials have a lot of intriguing properties, which is distinct from their bulk materials. For example, nanomaterials usually possess high surface areas, short ion diffusion length and greater tolerance towards pulverizing volumetric changes.^[7] These characteristics help to increase the contact between electrolyte and electrode material, increase the material utilization and increase the long term cycling stability.

1.2 Research objectives and scope

Numerous efforts have been devoted to improve the electrochemical performance of pseudocapacitive electrode materials. Significant advances have been made in the synthesis, characterization and understanding of electrochemical behavior of pseudocapacitive materials. However, there are still many challenges to explore new materials; elevate the electrochemical performances of materials towards high energy density, high power density and high stability. The main objectives of this research work are to explore following aspects:

- To investigate metal oxides/hydroxides and their composite/hybrid materials for improved supercapacitor performance.
- To understand the correlation between the physical properties of materials and their electrochemistry behaviours.
- To explore new supercapacitor device design to enhance supercapacitor performance.

Currently, the pseudocapacitive transition metal oxides/hydroxides are the main research hot zone for high performance supercapacitor. In order to achieve superior electrochemical performance, the electric conductivity, electrolyte-electrode contact and surface faradic reaction are especially important. Five approaches are proposed to achieve the above objectives.

First of all, nickel cobalt oxide ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$) is a pseudocapacitive electrode material with better intrinsic electron conductivity ($\sim 0.1 \sim 10^2 \text{ S cm}^{-1}$). One dimensional nanostructured $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is proposed to create facile electron conduction channels as well as provide high surface area for electrolyte-electrolyte contact. Under this approach, high aspect ratio $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire structure grown on current collector were synthesized and carefully characterized.

Second, composite material of metal oxide and carbon is proposed to further enhance the electron conduction within the material matrix and reduce the resistance of the electrode. $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and reduced graphene oxide (rGO) was synthesized and detailed electrochemical analysis was carried out. The surface fast charge storage and diffusion controlled charge storage were distinguished.

Ni and Co based layered hydroxides are another important family of pseudocapacitive electrode material. However, the intrinsic insulating nature of hydroxides restricts the power performance. In the third approach, conducting Zn_2SnO_4 nanowires are proposed to act as nano current collectors to provide facile

electron conduction. Additionally, in the case of Ni-Co LDH on Zn_2SnO_4 , the relationship between electrochemical active surface area of nanomaterial and geometry of current collector was comprehensively studied.

Fourth, the enhancement of electric conductivity of Ni-Co-Al layered hydroxides by chemical treatment is proposed for achieving better rate performance. Ni-Co-Al layered hydroxide was prepared and the Al was selectively etched by NaOH. Meanwhile, the Co^{2+} was oxidized into more conducting Co^{3+} . The influence of conductivity in electrochemical performance was investigated in detail.

Last but not the least, the in-plane configuration of interdigitated electrode is proposed for achieving high rate performance by utilizing fast mass transfer between adjacent electrodes. Interdigitated finger electrodes were fabricated using lithography and metallization process. MnO_2 -polyaniline was selected as the example to study the influence of electrode design on the electrochemical performance.

1.3 Organization of the thesis

This thesis presents the synthesis and characterization of Ni-Co based spinel oxide and layered hydroxide and their hybrid/composite material for enhanced pseudocapacitive supercapacitor application. Meanwhile, the fabrication of interdigitated electrode based supercapacitor is demonstrated using MnO_2 -polyaniline as prototype electrode material.

Chapter 1 presents the background of global energy consumption and the importance of developing versatile energy storage technology. The objectives and relevant research approaches for achieving enhanced supercapacitor performance are presented.

Chapter 2 first provides a related literature review of basic principles of supercapacitor and current electrode materials of choice for supercapacitor. The emphasis is put on the discussion of current status of Ni-Co based spinel and layered hydroxide materials for supercapacitor. Finally, the possible approaches for achieving high performance pseudocapacitive are reviewed.

Chapter 3 introduces the experimental approaches applied in the thesis, including the material synthesis/characterization methods, interdigitated finger electrode fabrication and micro supercapacitor fabrication/characterization methods.

Chapter 4 introduces the synthesis and characterization of porous polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire grown on nickel foam for enhanced supercapacitor application. Apart from the previous reported methods, we prepared a high aspect ratio nanowire material by a crystallization-dissolution-recrystallization mechanism. The one dimensional porous structure enables good electrode-electrolyte contact and facile electron conduction.

Chapter 5 presents the synthesis and characterization of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -reduced graphene oxide (rGO) composite material. The decomposition of intercalated

anions in Ni-Co LH precursors lead to an enhanced electrochemical activity of the composite material. The interfacial and bulk charge storage behaviors were quantitatively studied.

Chapter 6 introduces the synthesis and characterization of Ni-Co layered hydroxide (LH)-Zn₂SnO₄ (ZTO) nanowire hybrid material. One dimensional conducting ZTO nanowires act as the current collectors for thin nanosheet coating of Ni-Co LHs. The enhanced conductive of nanowire current collector enables higher rate performance of hybrid material. At the same time, the relationship between the preparation parameters and electrochemical behavior was quantitatively studied.

Chapter 7 presents a simple strategy for enhancing the electric conductivity of Ni-Co-Al layered hydroxide. The chemical etching using NaOH not only generated surface defects, but also converted less conducting Co²⁺ to more conducting Co³⁺. The conductivity of layered hydroxide was enhanced, which led to a much better rate performance.

Chapter 8 introduces the design and fabrication of micro supercapacitor based on interdigitated finger electrode. The relationship between electrode design and the electrochemical behavior of the micro supercapacitor device was quantitatively studied.

Chapter 9 summarizes the findings of the above chapters, gives the conclusions and makes recommendations for future work.

Chapter 2 Literature Review

2.1 Supercapacitors: energy storage mechanisms and materials overview

The energy storage characteristic of supercapacitor device can be illustrated from the Ragone plot in Figure 2.1. Supercapacitor devices generally have a low energy density less than 10 Wh kg^{-1} but high power density up to 10 kW kg^{-1} . The energy and power characteristics of supercapacitors currently sit between that of conventional dielectric capacitors and batteries.

Figure 2.1 Ragone plot of energy and power density of different devices. [Nature Materials]^[6], copyright (2008).

An illustration of a typical supercapacitor device is shown in Figure 2.2a. A functional supercapacitor device contains 4 parts: cathode, anode, separator and electrolyte. Electrochemically active materials are coated onto metallic current

collectors to act as cathode and anode respectively. A separator is sandwiched in between to ensure electrical insulation inside the device and provide ion transport between cathode and anode. Electrolyte fills the internal space of the device to act as charge carriers between cathode and anode. Meanwhile, it also provides ions for electrochemical energy storage.

Figure 2.2 (a) schematic representation of a supercapacitor device;^[8] (b) illustration of the supercapacitor device voltage during charge and discharge process.^[9]

The electrochemical reactions as well as the device voltage change of supercapacitor can be illustrated in Figure 2.2b.^[9] During the charging process, the anions from electrolyte will react with cathode, while the cations from the electrolyte will react with anode. The reactions will cause the potential difference between cathode and anode of the supercapacitor device. Specifically, the cathode reaction will increase the potential of cathode against open circuit voltage. And the

anode reaction will lower the potential of anode against open circuit voltage. For the discharge process, it is the other way round. Thus, in principle, it is required that both cathode and anode materials of supercapacitor should have electrochemical reactions in their respective electrochemical potential range.

Generally speaking, there are two categories of supercapacitor electrodes according to the different energy storage principles, electrochemical double layer capacitors (EDLCs) and pseudocapacitors.^[10] EDLCs utilize reversible electrostatic adsorption/desorption of electrolyte ions on the surface of electrodes. Charge separation occurs on the polarization at the electrode-electrolyte interface, producing what Helmholtz described as the double layer capacitance C :

$$C = \frac{\epsilon_r \epsilon_0 A}{d}$$

Where ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant in the vacuum, d is the effective thickness of the double layer and A is the electrode surface area.^[6] Carbon materials with high surface area are the most common material used in EDLCs, such as active carbon, ordered mesoporous carbon, CNT, and graphene.^[11] A summarization of carbon based EDLC materials and their electrochemical performances is shown in Table 2.1.^[11] The advantages of carbon based EDLCs are high power density, high stability and adaptable to both aqueous and organic electrolytes. On the other hand, the specific capacitance of carbon material is usually below 200 F g^{-1} . As a result, the energy density of carbon based

EDLCs are not high.

Table 2.1 Summarization of electrochemical performance of carbon based EDLCs ^[11]

		Aqueous electrolyte		Organic electrolyte	
Materials		/F g ⁻¹	/F cm ⁻³	/F g ⁻¹	/F cm ⁻³
commercial carbon(ACs)	activated	< 200	< 80	< 100	< 50
Particulate carbon from SiC/TiC		170-220	< 120	100-120	< 70
Functionalized porous carbon		150-300	< 180	100-150	< 90
Carbon nanotube (CNT)		50-100	< 60	< 60	< 30
Templated porous carbons (TC)		120-350	< 200	60-140	< 100
Activated carbon fibers (ACF)		120-370	< 150	80-200	< 120
Carbon cloth		100-200	40-80	60-100	24-40
Carbon aerogels		100-125	< 80	< 80	< 40

The other kind of supercapacitor electrode is called pseudocapacitive electrode.

Pseudocapacitive behavior arises in several circumstances: monolayer adsorption of ions at an electrode surface, as in the underpotential deposition of metals; surface redox reactions of materials; or ion intercalation without phase change.^[12]

These reactions are faradic in nature, which shows capacitive response. Among them, the fast surface redox reactions are widely investigated in transition metal oxides/hydroxides, metal nitrides and some conducting polymers.^[6] The

pseudocapacitance C could be acquired from constant current charge-discharge experiment:

$$C = \frac{Q}{\Delta E}$$

Where Q is the charge passed, ΔE is the potential change. Comparing with EDLC, the faradic reaction is able to achieve much higher energy density. ^[6]

The summary of popular pseudocapacitive electrode materials is listed in Table 2.2. Due to the benefit of redox reactions, the theoretical specific capacitances of pseudocapacitive materials are much larger than those of carbon based EDLC materials. Therefore, much higher energy densities of supercapacitor electrodes could be achieved using pseudocapacitive materials.

Table 2.2 Summarization of pseudocapacitive electrode materials			
Materials	Theoretical value F g ⁻¹	Experimental value F g ⁻¹	Remarks
Co ₃ O ₄	3560	85~2200 ^[13]	Moderate conductivity, high stability ~ 10 ⁻³ ~10 ⁻² S cm ⁻¹
Co(OH) ₂	>3000	562~993 ^[14, 15]	Low capacitance
MnO ₂	1370	386~600 ^[16]	Poor conductivity ~10 ⁻⁶ ~10 ⁻⁵ S cm ⁻¹ , low alkali and proton ions diffusion
NiO	2573	124~1100 ^[17]	Moderate

			conductivity, high stability $\sim 10^{-3} \sim 10^{-2} \text{ S cm}^{-1}$
Ni(OH) ₂	2069	398~1560 ^[18, 19]	Insulating, poor rate performance
V ₂ O ₅	-	440~1550 ^[20, 21]	Mixed behavior of pseudocapacitive and battery
RuO ₂	2000	700~1340 ^[22]	Metallic conductivity, high stability
Polyaniline	750	400-500 ^[23, 24]	0.1-5 S cm^{-1} , poor stability
Polypyrrole	620	500~557 ^[25]	10-50 S cm^{-1} , poor stability
Poly(3,4-ethylenedioxythiophene)			300-500 S cm^{-1} , low capacitance

RuO₂ has been studied extensively since the early development of supercapacitor. The high experimental capacitance, high rate property as well as stable performance have attracted a lot of attentions.^[22, 26, 27] However, the high cost and toxicity restrict the real application of such materials. Apart from RuO₂, early transition metal oxides/hydroxide and redox active conducting polymers have been investigated as the replacement for RuO₂. MnO₂ is one of the promising candidates with low cost, environmental friendly and satisfactory operation window in both aqueous and organic electrolytes, and high theoretical capacitance.^[16] However, the

intrinsic nature of MnO_2 is not satisfactory for the high rate performance supercapacitor. The poor electric conductivity and low electrolyte ion (H^+ and alkali ion) diffusion constant hinder the electrochemical reaction kinetics and the utilization of bulk materials. As a result, the experiment values are still not competitive, especially for thick electrodes. V_2O_5 has similar electrochemical behavior with MnO_2 . The energy storage behavior of V_2O_5 often consists of pseudocapacitive as well as battery type Li/Na ion intercalation,^[28] where the battery type capacity is usually the major contribution of energy storage. Similarly, the electrochemical reaction kinetics is limited by the slow electrolyte ion diffusion rate in the material. Though high experimental capacitance has been reported for V_2O_5 , the low active material mass is also a concern for achieving satisfactory energy density.^[21] It is also noteworthy to mention that the application of MnO_2 or V_2O_5 in organic solvent based electrolytes suffers from several drawbacks. For example, the Li^+ ion has a slow diffusion rate in the crystal lattice $\sim 10^{-15} \text{ cm}^2 \text{ s}^{-1}$.^[29] The slow diffusion kinetics will inevitably lead to low power density. Meanwhile, the electrical conductivity of Li^+ ion organic electrolyte (several S cm^{-1}) is comparably lower than aqueous electrolyte. Additionally, the limited abundance of lithium in earth (0.006 w.t %), uniformly distribution in nature (e.g sea salt, rock salt) and difficulty in recycling make the development of Li^+ ion organic electrolyte based supercapacitors more costly.

Apart from MnO_2 , V_2O_5 , cobalt and nickel based metal oxides and hydroxides have also been attracting continuous interests. These group VIII B metal elements have similar electrochemical redox reactions as well as high specific capacitances. Meanwhile, Co_3O_4 and NiO have 2~3 orders of magnitude higher electrical conductivity than MnO_2 and V_2O_5 , which would be beneficial for achieving superior rate performance. However, nickel and cobalt based materials could only be used in alkaline electrolyte, due to the following electrochemical reaction:

Non-alkaline aqueous electrolyte and organic electrolyte could not provide necessarily high OH^- concentration for the electrochemical reactions.

Conducting polymer is another alternative choice for developing high performance supercapacitor. The pseudocapacitance comes from the doping and de-doping process during the electrochemical reactions. Benefited from the conducting nature, these materials usually have low resistance, high power and good electrochemical performance at high current level. However, the poor cycling stability has been haunting these materials, especially when materials are in their bulk or thick film forms.

In summary, pseudocapacitive electrodes materials are of great value for scientific

research to develop next generation high performance supercapacitors. However, several major issues, such as poor electrical conductivity, low bulk material utilization and short cycling life, need to be tackled in order to elevate the supercapacitor performance to next level.

2.2 Nickel cobalt oxide/hydroxide based materials for pseudocapacitive supercapacitor electrode

2.2.1 Nickel cobalt spinel oxide for pseudocapacitive supercapacitor electrode

Based on above discussions, nickel and cobalt based metal oxides and hydroxides have extraordinary high theoretical specific capacitances above all the other pseudocapacitive materials. In recent years, nickel cobalt oxide ($\text{Ni}_x\text{Co}_{2-x}\text{O}_4$) and nickel cobalt based layered hydroxides (LDHs) have attracted a lot of attentions due to the interesting nature of materials as well as the superior electrochemical performance. In this section, material properties and relevant studies of these two materials will be discussed and reviewed.

$\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is a kind of spinel structured ternary metal oxide, where $0 < x \leq 1.1$ is required to maintain the pristine phase.^[30, 31] The crystal structure of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is shown in Figure 2.3. Oxygen anions are arranged in the closed packed cubic structure. Cobalt (III) cations occupy the octahedral sites of the lattice and Co (II) cations occupy the tetrahedral sites of the lattice. The cell parameter of NiCo_2O_4 is $a=8.11 \text{ \AA}$, while the cell parameter will be larger if the Ni content is further increased.^[28] Experiment data shows that Ni is dissolved in the lattice of Co_3O_4 ,

replacing the octahedral sites of Co (III). High content of Ni > 60 % will lead to the phase separation of NiO and NiCo₂O₄. For Ni_xCo_{3-x}O₄, the electrical conductivity of is estimated to be two orders higher than Co₃O₄ and NiO.^[32] The conductivity of Ni_xCo_{3-x}O₄ material has been studied by a few groups. Hu et al reported that the conductivity of Ni_xCo_{3-x}O₄ single crystalline nanoplate to be 62 S cm⁻¹,^[33] and Fujishiro et al. reported 0.6 S⁻¹ for polycrystalline thin film Ni_xCo_{3-x}O₄ at 300 °C.^[34] The intrinsic superior conductivity of Ni_xCo_{3-x}O₄ makes it highly intriguing for the development of supercapacitor electrode.

Figure 2.3 Spinel structure of NiCo₂O₄. The green atom represents cobalt atom, the red atom represents oxygen atom, and the grey atom represents nickel atom.

The surface nature and electrochemical activity of Ni_xCo_{3-x}O₄ was investigated by L. De Faric et al..^[31] Ni_xCo_{3-x}O₄ has Ni enriched surface when the Ni content is higher than 20 %. As a result, the electrochemical surface behavior is dominated by

Ni sites. Until now, $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ has been extensively studied as electrochemical catalyst for oxygen evolution reaction.^[35-37] However, the investigation for supercapacitor electrodes is still scarce. Previous reports have shown the promising performance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and related materials, meanwhile it is still not satisfactory. For example, an epoxide derived sol-gel method was demonstrated by Wei et al. to synthesize $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals. An impressive capacitance of 1400 F g^{-1} was achieved.^[38] However, the loading mass of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ was only 0.4 mg cm^{-2} , which was quite low. Hu et al proposed a Pechini type sol-gel synthesis of NiCo_2O_4 with a high specific capacitance of 1532 F g^{-1} .^[39] However, such material suffered from 50 % capacitance loss after just 500 cycles, showing a very poor stability.

Apart from the nanocrystals of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$, morphology control strategy has also been adapted to explore the electrochemical performance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$. Urchin like assembly of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires was synthesized by Xiao et al. with high rate performance.^[40] The specific capacitance could reach $634 \text{ F g}^{-1} @ 1 \text{ A g}^{-1}$, meanwhile it maintains $530 \text{ F g}^{-1} @ 10 \text{ A g}^{-1}$. Yuan et al. showed a growth of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanosheets on nickel foam to achieve a high specific capacitance of $1450 \text{ F g}^{-1} @ 20 \text{ A g}^{-1}$.^[41] The thin coating of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and high conductivity of nickel substrate ensure the high rate performance. However, such strategy only has a low loading mass of 0.8 mg . Furthermore, hierarchical porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ has

also been studied as the supercapacitor electrode by Chang et al..^[42] The structure was assembled by $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ porous nanosheets, which shows a high specific capacitance of 1500 F g^{-1} . Despite the high value of specific capacitance, the performance under high current densities was not investigated.

Based on above discussion, at current stage, the electrochemical performance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is promising to achieve a high level of specific capacitance. Meanwhile, problems, such as low loading mass, poor long term stability and unsatisfactory rate performance, still haunt this material. Future research is of great interest to fully explore the merit of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$.

2.2.2 Nickel cobalt layered double hydroxides for pseudocapacitive supercapacitor electrode

Layered double hydroxides (LDHs) are a class of two dimensional (2D) layered materials. The general formula of LDHs obeys $\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2\text{A}^{n-}_{x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and trivalent metal cations, respectively; x is defined as the molar ratio of $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$ and generally has a value ranging from 0.2 to 0.33; A^{n-} are the interlayer anions. The structure of LDHs is shown in Figure 2.4, which consists of metal-hydroxyl host slabs and charge-balancing anions in the interlayer galleries. Most metals, such as Mg, Al, Fe, Ni, Co, Cu, Zn and so on, can form the positive charged layers in LDHs. Meanwhile, various kinds of anions could be intercalated into the interlayers.^[43]

Figure 2.4 Schematic illustration of the crystal structure of layered double hydroxides.

Layered double hydroxides (LDHs) have drawn considerable attention in various applications, such as anion exchangers,^[44] UV absorbents,^[45] catalysts^[46] and drug delivery systems.^[47] Especially for electrochemical applications, the large interlayer spacing gives a better accessibility of electrolyte into reaction sites. Meanwhile, the electrochemically redox active transition metal containing hydroxides (Co and Ni) usually possess high specific capacitances, which are favorable for high energy density storage.^[48-50] This enables a large variety of functionality and hybrid possibility for potential applications. As a result, nickel and cobalt based layered double hydroxides (LDHs) are the other promising candidate for high performance supercapacitor electrode.

There are three types of LDHs that are most widely studied as supercapacitor electrode materials, Co-Al LDHs, Ni-Al LDHs and Ni-Co LDHs. However, as Al is an electrochemically inactive element in the LDHs, the specific capacitances of

Co-Al LDHs and Ni-Al LDHs are much lower than Ni-Co LDHs. Thus, focus will be put on Ni-Co LDHs in the following discussion. Various methods have been applied for the preparation of Ni-Co based LDHs. Gupta et al. applied electrochemical deposition of $\text{Co}_x\text{Ni}_{1-x}$ LDHs onto stainless steel substrate to get micron sized sheet like structures with 20~30 nm in thickness.^[51] The specific capacitance could reach 2104 F g^{-1} with a Co/Ni ratio of 0.72:0.28. However, the capacitance dramatically faded as the test current density went up to 10 A g^{-1} . Meanwhile, the stability of material was not investigated as well. Yan et al. reported a preparation of hollow Ni-Co LDH microsphere from silica template for supercapacitor application.^[48] The specific capacitance can achieve as high as 2275.5 F g^{-1} at 1 A g^{-1} , whereas the capacitance only maintain 44 % at 25 A g^{-1} , indicating a inferior rate performance. Another example is that Hu et al. synthesized $\text{Ni}_{0.59}\text{Co}_{0.41}$ LDHs nanosheets from co-precipitation method.^[50] The sample showed a high capacitance of 1809 F g^{-1} at 1 A g^{-1} . Similarly, Xie et al. produced $\text{Ni}_{0.43}\text{Co}_{0.57}$ LDHs nano particles from polyvinyl pyrrolidone assisted chemical co-precipitation method. It showed a high specific capacitance of 2614 F g^{-1} . However, the electrochemical stability of co-precipitated sample was disappointing.

Despite the high specific capacitance demonstrated in the literatures, the synergic behavior of Ni and Co in LDHs has been observed as well in above literatures.

Vialat et al. and studied the electrochemical behavior of NiAl LDH, CoAl LDH and NiCoAl LDH in detail.^[52] It is found that Co based LDH shows a high rate performance pseudocapacitive behavior, while the electrochemical process of Ni based LDH is mainly governed by ion diffusion, showing a slower electrochemical kinetics. The charge transfer resistance of NiAl LDH is much larger than that of CoAl LDH. Moreover, when the Co/Ni > 0.66, the strong synergic effect of Co and Ni shows both high capacitive behavior of Ni based LDH as well as a high rate performance of Co based LDH. It is noteworthy to mention that even if the rate performance of Ni-Co LDH is improved from NiAl LDH, the testing current density of Ni-Co LDHs is still below 20 A g⁻¹ in previous reports. The intrinsic insulating nature of LDHs always leads to a poor rate performance at high current densities.

In summary, the Ni-Co based LDHs show a promising value of specific capacitance, while problems such as poor rate performance, poor cycling stability still need to overcome.

2.3 Approaches for high performance supercapacitor

Pursuing better electrochemical performance is always a main target for supercapacitor development. In this section, several possible approaches focusing on the improvement of energy density at high power densities will be discussed.

2.3.1 Physical model of pseudocapacitive electrode

Electrochemical reactions always involve the following steps: the mass transfer of electrolyte, the charge transfer at the electrode surface, the chemical reactions before and after charge transfer and other surface reaction at the electrode surface.^[53] Generally, the physical model of a pseudocapacitive electrode can be explicated as the modified Randles circuit as shown in Figure 2.5a.^[54]

Figure 2.5 (a) equivalent circuit of a typical pseudocapacitive electrode; (b) a typical Nyquist plot from electrochemical impedance test.

where R_s is the combination of intrinsic resistance of substrate, contact of material with substrate, electrolyte resistance (also known as equivalent series resistance, ESR); R_f is the resistance of faradic reaction; C_{dl} is the electric double layer capacitance; W is the Warburg impedance (diffusion controlled element) and C_f is the limit capacitance. The information of above factors could be extracted from electrochemical impedance spectrum (EIS) test.^{[55],[56]} A typical Nyquist plot is shown in Figure 2.5b. At high frequency region, the first intercept at real axis

represents the ESR, while the diameter of the semicircle indicates the faradic resistance R_f . The 45° slope after the semicircle is called Warburg impedance. When the slope is more parallel to the $-Z''$ axis, it suggests better the electrolyte diffusion within the system and a better capacitive behavior. On the contrary, the electrochemical reaction is affected by the supply of electrolyte ions.

Normally, the capacitance of pseudocapacitive electrode should consist of two to three parts, such as electrochemical double layer capacitance (very small) of electrode, instant pseudocapacitive charge storage, and/or diffusion controlled capacitance.^[57] As mentioned above, the key processes in electrochemical reaction involves electrolyte diffusion, charge transfer and the chemical reaction. These factors correspond to the Warburg impedance, ESR and faradic reaction resistance in the supercapacitor electrode physical model. Thus, theoretically, any enhancement in mass transfer, electric conductivity and ion diffusion in the bulk material will be helpful to elevate the electrochemical performance. Experimentally, the strategy should be aimed at reducing the resistance of material for good electron conduction, increasing the surface area for better electrolyte contact, and reduce the dimension of material for shorter ion diffusion distance.

2.3.2 One dimensional nanostructure of nickel and cobalt oxide/hydroxide for high performance supercapacitor

As discussed in chapter 2.2, problems nickel cobalt oxide as well as nickel cobalt layered double hydroxides are to be tackled for high performance supercapacitor

applicatoin. Based on the theoretical considerations in chapter 2.3.1, it is of great value to investigate into solutions to achieve highly conductive electrodes with good mass transfer and electrolyte contact. Constructing 1D nanostructured electrode materials is one of the promising strategies, which have received considerable attentions. One dimensional nanostructured electrode stands for electrode materials organized in a 1D manner, in which the active material could act as the 1 D backbone, or is supported on the 1D core. In the following sections, promising solutions for such target will be reviewed and discussed.

Template assisted synthesis of 1D nanostructures is a reliable and controllable method for synthesizing various kinds of nano materials. According to the template used during synthesis, it can be divided into 2 categories, soft template approach and hard template approach. For soft template method, the synthesis process involves the usage of surfactants, which can self-assemble into various micelles in the solution. They will act as capping reagents, structure directing reagents and/or micro reaction containers.^[58] However, reports regarding the surfactant assisted synthesis of metal oxide/hydroxides for supercapacitor application are quite limited. On the other hand, hard template assisted synthesis method has been widely adapted for the preparation of supercapacitor electrode materials. The principle can be illustrated by Figure 2.6a as shown below. Active materials could be deposited in contact with the substrate inside the AAO tunnels. Depending on

the diameters of hard templates, nanowires or nanotubes could be successfully achieved. Various methods could be utilized to deposit materials inside hard templates, such as electrochemical deposition, sol-gel method, chemical vapor deposition (CVD) and so on.^[59]

Figure 2.6 (a) Schematic illustration of deposition of electrode materials into AAO template; (b) and (c) typical SEM images of NiO nanotube structure prepared using AAO template.^[60]

For example, Dar et al. prepared Ni nanotubes using AAO template by electrochemical deposition and NiO nanotubes were obtained by heat treatment.^[60]

Typical SEM images of the NiO nanotube structure are shown in Figure 2.6b and c.

The nanostructured electrode material was vertically aligned on the current

collector with open access to electrolyte. High specific capacitance of 2076 F g^{-1} was achieved at 12 A g^{-1} and 1786 F g^{-1} at 70 A g^{-1} , with a 86 % retention. The supreme performance originated from 1D electron conduction path, facile electrolyte diffusion inside the tubular structure and high surface area of solid-liquid contact. Similarly, Xu et al. deposited Co(OH)_2 in AAO template and obtained Co_3O_4 nanotubes after removal of template and sintering at 500°C .^[61] However, the electrochemical performance is just moderate. The specific capacitance is only 574 F g^{-1} at 0.1 A g^{-1} , while it maintained 478 F g^{-1} at 1.0 A g^{-1} . No further high current density test was carried out. Wang et al. synthesized $\alpha\text{-Ni(OH)}_2$ by infiltration of reagents into AAO template.^[62] A maximum specific capacitance of 833 F g^{-1} could be obtained at a current of 5 mA cm^{-2} , while it could maintain 736 F g^{-1} at 10 mA cm^{-2} . More importantly, unlike other Ni(OH)_2 electrode materials, such nanowire structure showed very low ESR and faradic charge transfer resistance.

Apart from template assisted 1 D structure fabrication method, direct growth of 1 D material by template free method is an alternative choice. It provides a more facile approach to synthesize material without preparation and removal of template material. Li et al. first introduced a chemical bath preparation of Co_3O_4 micro-wires, whose diameter is over 500 nm with tens of micron in length.^[63] The micro-wires were formed by the ammonia evaporation induced low supersaturation,

where screw dislocation driven growth of 1 D structure was realized.^[64] This approach has been adapted by Gao et al. and directly grew Co_3O_4 arrays on nickel foam current collector.

Figure 2.7 (a) Schematic illustration of 1D nanostructure directly grown on current collector; (b) and (c) SEM images of Co_3O_4 nanowires.^[63] Reprinted (adapted) with permission from Mesoporous Co_3O_4 Nanowire Arrays for Lithium Ion Batteries with High Capacity and Rate Capability. Copyright (2008) American Chemical Society.

The schematic illustration is shown in Figure 2.7a. This strategy eliminates the use of insulating binder and poor electrochemically active carbon additive in conventional electrode preparation. The nanowire structure is beneficial to enhance the electron conduction between materials and current collector. Meanwhile, facile electrolyte diffusion can also be ensured. As shown in Figure 2.7b and c, there is a plenty of space between Co_3O_4 nanowires, which offers good electrolyte contact. As a result, this Co_3O_4 arrays on nickel foam showed a high specific capacitance of

568 F g⁻¹ at a current density of 30 mA cm⁻² with high loading mass. Similar approach is utilized by Xia et al. to fabricate hollow Co₃O₄ arrays on nickel foil,^[65] high specific capacitances with 599 F g⁻¹ at 2 A g⁻¹ and 439 F g⁻¹ at 40 A g⁻¹ were achieved. Furthermore, the electrochemical performance of this type of Co₃O₄ was further improved by Cheng et al..^[66] Additional Ag nanoparticles were coated outside the Co₃O₄ arrays by a simple silver mirror reaction. The specific capacitance was improved to 1006 F g⁻¹ at 2 A g⁻¹ and 900 F g⁻¹ at 10 A g⁻¹. The capacitance retention was 35.8 % higher than pristine Co₃O₄ arrays. Meanwhile, the long term cycling stability is also greatly enhanced. There was only 5 % capacitance degradation after 5000 cycles.

The other widely used synthesis method for cobalt oxide/hydroxide based 1 D nanostructure is provided by Xiao et al. and Jiang et al..^[40, 67] The usage of urea as hydrolysis reagent could produce nanowires of Co(OH)₂ or Ni-Co bimetallic hydroxides, which can be transformed into Co₃O₄ and Ni_xCo_{3-x}O₄ respectively. For Jiang et al., the Co(OH)₂ nanowire arrays grown on graphite paper could reach 642.5 F g⁻¹ at 1 A g⁻¹ and 330.75 F g⁻¹ at 20 A g⁻¹, showing a good rate performance. For the Ni_xCo_{3-x}O₄, it shows a moderate specific capacitance of 658 F g⁻¹ at 1 A g⁻¹ and 530 F g⁻¹ at 10 A g⁻¹, showing an excellent rate performance.

So far, these are the only two template free methods for the preparation of cobalt oxide/hydroxide based materials. However, the reports on high electrochemical

performance are still scarce. The material prepared by ammonia evaporation method has large diameter over 500 nm, which leads to poor utilization of material. While, the material prepared by urea induced hydrolysis has low aspect ratio, in which the specific capacitance value is low.

Nickel hydroxide/oxide based materials have also been studied during the past few years. One dimensional form structures, such as nanowire,^[68] nanorod^[69, 70] and nanobelt^[71] have been prepared. Similar to the direct material-current collector design, Salunkhe et al. reported a growth of Ni-Co hydroxide nanorod arrays on stainless steel substrate.^[70] Despite the low conductivity of nickel-cobalt hydroxide, the binder free electrode showed a low ESR of 0.2 ohm with high rate performance. The specific capacitance was able to maintain 70 % when the scan rate increased from 20 mV s⁻¹ (456 F g⁻¹) to 200 mV s⁻¹. Meanwhile, the stability of Ni-Co hydroxide nanorod arrays was also good. Only 9 % degradation of capacitance was experienced after 1000 cycles. However, the loading mass of the active material is only 0.3 mg. Lu et al. reported a high specific capacitance of NiO nanorod arrays on nickel foam. It was claimed to achieve as high as 2018 F g⁻¹ at 2.27 A g⁻¹ and maintain 1536 F g⁻¹ and 22.7 A g⁻¹. The high rate performance could be explained by the theory mentioned above. The direct material-current collector contact and facile electron and electrolyte conduction are beneficial for high rate performance. Nevertheless, the loading mass of NiO on nickel was still very low,

which makes the high electrochemical performance disputable.

Based on above discussions, it is obvious that one dimensional nanostructures of nickel and cobalt based metal oxide/hydroxide material are of great value to enhance the electrochemical performance. The 1D electron conduction route, short ion diffusion distance and vast open structure are the intrinsic advantages of 1D structure. In addition, direct growth of 1D nanostructure onto the current collector will provide additional privileges, such as direct electron conduction between materials and current collector, enhanced access to electrolyte by 1D structure arrays, and relief of insulating binders. Overall, such 1D nanostructure strategy will provide enhanced electrochemical performance at high current densities. However, many problems still exist. Most reports did not have high specific capacitances ($> 1000 \text{ F g}^{-1}$), and lots of reports show low loading mass of active materials ($< 1 \text{ mg}$). Thus, it is of great interest to explore methods to achieve high electrochemical performance of nickel and cobalt oxide/hydroxide based 1D materials with reasonable mass loading.

2.3.3 Composite/hybrid nanomaterials of for high performance supercapacitor

Carbon materials based supercapacitors have a relatively low energy density, while metal oxide/hydroxide materials exhibit low electric conductivity and some exhibits low cycling stabilities. There exists a growing effort to combine carbon materials and metal oxides/hydroxides and/or polymers together to utilize both of

their advantages and thus reduce their disadvantages. In this section, we will go through recent progress of composite/hybrid materials applied on supercapacitors. Lee et al. reported a novel CNT/MnO₂ layer-by-layer (LBL) self-assembly film that achieved a specific capacitance of 940 F g⁻¹ of MnO₂ and a specific capacitance of 290 F g⁻¹ of CNT/MnO₂ film.^[72] The surface functionalized CNTs were self-assembled from solutions. MnO₂ was reduced from the KMnO₄/K₂SO₄ solution by CNT, which leads to a uniform coating of MnO₂ on the whole network of LBL films. Due to the high electron conductivity within the network, there was only 50 % decrease of capacitance under high scan rate up to 1000 mV s⁻¹. Meanwhile, the long term stability is also improved, as only 11.6 % capacitance decrease at 200 mV s⁻¹ after 1000 cycles.

Hou et al. developed another new method to combine CNT, MnO₂ and conducting polymer PEDOT-PSS.^[73] The MnO₂ was grown on CNT and subsequently coated with PEDOT-PSS. The inner axis of CNT and an outer wrapping of PEDOT-PSS polymer could provide good electron conductivity, while the porous one dimensional structure provides facile ion diffusion path. This ternary composite gave a specific capacitance of 200 F g⁻¹ at 60 %w.t MnO₂ loading, while the capacitance maintained > 99% after 1000 cycles.

Chen et al. reported a one pot synthesis method of single crystal vanadium oxide and carbon nanotube cross linking hybrid material for supercapacitor

application.^[20] This hybrid material had a high specific capacitance of 313 F g^{-1} under a relatively high scan rate of 1 A g^{-1} . Further tests showed that, with high scan rate of 100 mV s^{-1} , the specific capacitance dropped 50%. The good performance of this hybrid material was attributed to the incorporation of CNT and V_2O_5 nanowire networks. This cross linking networks provided high surface area, effective electrolyte contact and diffusion, and good electron conduction.

Apart from the CNT based composite supercapacitor electrodes, recently, graphene/reduced graphene oxide (rGO) based composite materials also draw a lot of attention. Yan et al. recently reported a microwave assisted deposition of MnO_2 on the surface of graphene network.^[74] MnO_2 was reduced from KMnO_4 with graphene. This composite material has a large loading mass of MnO_2 as high as 72 %w.t and with a high specific capacitance of 310 F g^{-1} at 2 mV s^{-1} . What's more, it maintained a specific capacitance of 228 F g^{-1} at 500 mV s^{-1} . This material also showed excellent cycling stability. After 15000 cycles, the capacitance just slightly decreased for about 1~3%. The good performance of composite material was attributed to the increased electrode conductivity in the presence of graphene network, the increased effective interfacial area between MnO_2 and the electrolyte, as well as the contact area between MnO_2 and graphene.

Chen et al. reported an rGO- MnO_2 composite material used for supercapacitor electrode.^[75] Different from what Yan et al., Chen used the functional group on the

surface of GO as anchoring points of manganese ions. Needle like MnO_2 covered graphite oxide by the reduction of KMnO_4 with carbon. This material exhibited an improved capacitance with high loading mass of MnO_2 . The specific capacitance of this composite material was 197.2 F g^{-1} . 51.4% of C_{sp} was retained when the current density increased from 150 to $1000 \text{ mA} \cdot \text{g}^{-1}$. However, the cycling stability was not satisfactory. It maintained 84.1% after 1000 cycles.

Notably, there are limited reports on nickel cobalt oxide/hydroxide based CNT/graphene composite material. To date, only Fan et al reported a electrochemical deposition of Ni-Co mixed oxide on CNT films,^[76] in which a moderate specific capacitance of 569 F g^{-1} at a current density of 10 mA cm^{-2} can be achieved (loading mass 0.31 mg). Wang et al provided the first insight on the feasibility of $\text{NiCo}_2\text{O}_4/\text{rGO}$ composite material.^[77] A self-assembly method was applied by exfoliating Ni-Co hydroxides and assembling with GO. After heat treatment, the $\text{NiCo}_2\text{O}_4/\text{rGO}$ composite shows an initial capacitance of 835 F g^{-1} at low current density.

Another strategy for promoting the electrochemical performance is to fabricate hybrid materials of active materials with 1D conducting nanowire arrays. Similar to the benefits discussed in chapter 2.3.2, the 1D conducting nanowire arrays can provide direct electron conduction path, facile electrolyte accessibility and large area for active material growth, as shown in Figure 2.8.

Figure 2.8 (a) schematic model of indirect electron path of directly deposited sample; (b) direct electron path and easy ion diffusion path of heterostructure.

There are plenty of examples for the fabrication of 1D hybrid material arrays. For instance, the first demonstration of this idea was provided by Yan et al..^[78] The semiconducting SnO₂ nanowires were synthesized on the stainless steel substrate by CVD method. Around 10 nm thick MnO₂ was subsequently coated outside the SnO₂ nanowire. High specific capacitance of 800 F g⁻¹ was achieved at a current density of 1 A g⁻¹. Meanwhile, 255 F g⁻¹ was achieved at a current density of 50 A g⁻¹, showing an excellent rate performance. Moreover, such hybrid structured electrode material only experienced 1.2 % capacitance fading after 2000 cycles. Bao et al. further enhanced the rate performance of MnO₂ hybrid material by utilizing Zn₂SnO₄ nanowires as the conducting backbone.^[79] Zn₂SnO₄ belongs to a class of transparent conducting oxide material, which is similar to indium doped tin

oxide (ITO). The enhanced conductivity of nanowire core helped to elevate the rate performance to 413.9 F g^{-1} at 40 A g^{-1} .

The possibility of integration of metal hydroxide material has also been investigated. Yan et al. reported a growth of Co(OH)_2 using electrochemical deposition outside ITO nanowire arrays.^[80] The specific capacitance of Co(OH)_2 could maintain from 622 F g^{-1} @ 5 mV s^{-1} to 450 F g^{-1} @ 100 mV s^{-1} , showing an obvious elevation from the Co(OH)_2 deposited on stainless steel substrate. Another example is coating Ni(OH)_2 outside ZnO nanowire arrays by Liu et al..^[81] High specific capacitance of 1310 F g^{-1} was obtained at 15.7 A g^{-1} and it maintained 632 F g^{-1} at very large current of 157.2 A g^{-1} .

In summary, the strategy of fabricating composite/hybrid materials that can enhance the electron conduction will be beneficial to achieve high performance supercapacitor electrode. Yet, the reports on high performance nickel and cobalt oxide/hydroxide based composite/hybrid materials are still limited.

2.3.4 Micro electrode device for high performance supercapacitor

In above chapters, the possible strategies for enhancing the electrochemical performance of supercapacitor from the materials view have been discussed. In this chapter, the possibility of enhancing the performance of supercapacitor by electrode design level will be discussed.

As discussed in the chapter 2.1, the design of conventional supercapacitor device

involves a pair of current collectors parallel to each other. The electrode materials are coated on both electrodes. Such design, as shown in Figure 2.9a, will lead to a tortuous diffusion path of electrolyte ions and inconspicuous electron conduction path towards current collectors. These intrinsic characteristics originate from the sandwich design of the device, which could only be partly overcome by the electrode material design.

Figure 2.9 (a) schematic illustration of conventional supercapacitor device (image source: <http://www.nrel.gov/vehiclesandfuels/energystorage/ultracapacitors.html>); (b) interdigitated micro electrode design of supercapacitor current collector.

Recently, a new design of supercapacitor device, called interdigitated finger design, comes to our attention.^[82-84] As shown in Figure 2.9b, the interdigitated finger electrode design involves the comb like layout of electrodes which are parallel with each other. The cathodes and anodes of the supercapacitor device are alternatively aligned in a compact manner on a plane substrate. In general, the fabrication of these micro electrodes follows various steps patterning and

metallization processes. During the electrochemical reaction, highly efficient mass transfer between adjacent electrodes can be achieved, as the narrow gaps between the individual electrodes. Meanwhile, the interdigitated finger electrode design allows the direct electron conduction between materials and electrodes. Thus the incontinuous electron conduction in the sandwich device structure can be avoided. Overall, the interdigitated finger design of micro sized electrode provides an alternative insight into the fabrication of high performance supercapacitors.

In 2010, Pech et al. reported an ultrahigh power micro-supercapacitor device based on this interdigitated electrode design.^[82] Onion-like nanosized carbon was used as the material for EDLC. The specific capacitance of the micro device could reach 0.9 mF cm^{-2} at a very high scan rate of 100 V s^{-1} . The capacitance fading was less than 20 % when the scan rate increased from 1 V s^{-1} to 200 V s^{-1} . This suggests an instant storage of charge during the electrochemical process. Such high performance is attributed to the interdigitated electrode design and the endohedral structure carbon onions. Despite the high rate performance, the specific capacitance of the micro device is still low, due to the moderate EDLC behavior of carbon onion. Beidaghi et al. demonstrated a micro supercapacitor device using rGO/CNT composite material as electrode material.^[83] The specific capacitance of device was further improved to 2.8 mF cm^{-2} at 50 V s^{-1} , owing to the higher surface area of rGO/CNT composite electrode. Apart from the carbon material based

EDLC micro supercapacitor device, the pseudocapacitance based micro supercapacitor device is less studied. To date, only Wang et al. reported an all solid state micro-supercapacitor using polyaniline (PANI) as electrode material.^[84] Such device has a much improved areal specific capacitance of 23.3 mF cm^{-2} (c.a. 588 F cm^{-3}).

As a new concept in the design of supercapacitor device, the interdigitated finger electrode based design is of great interest. To date, only a few attempts have been made on the demonstration of concept of the device. Topics, such as the general principle of interdigitated electrode design and the elevation of specific capacitance by using pseudocapacitive materials, are of great value to investigate.

2.3.5 Summary

Based on the above literature review, we propose the following strategies to achieve better supercapacitor performance as shown in Figure 2.10.

Figure 2.10 Illustration of possible approaches for enhancing supercapacitor performance.

Chapter 3 Experimental Methods

3.1 Material synthesis

All chemicals were analytical grade and purchased from Sigma-Aldrich unless further mentioned.

3.1.1 Synthesis of polycrystalline porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires

Polycrystalline porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires in Chapter 4 were synthesized by hydrothermal method followed by heat treatment. First, nickel foam substrate (1 cm × 1 cm) was cleaned using deionized water (DI water) and 95 % ethanol in a sonication bath. Then, it was used as a substrate for the growth of materials. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, hexamethylenetetramine (HMTA) and sodium dodecyl sulfate (SDS) were added subsequently into 20 ml DI water under continuous stirring. The final concentration of each reactant was 26.5 mM, 13.5 mM, 25 mM and 5 mM respectively. After stirring for 5 minutes, the resulting solution was transferred into a 40 ml Teflon lined autoclave and kept at 140 °C for 14 hours. An illustration of an autoclave is shown in Figure 3.1.

Figure 3.1 Illustration of an autoclave.

After reaction, the nickel foam substrate was washed with DI water and ethanol

several times, then it was dried at 60 °C for 4 hours. Finally, the substrate was heated to 300 °C at a ramp of 2 °C min⁻¹ and maintained for 4 hours.

3.1.2 Synthesis of Ni_xCo_{3-x}O₄-reduced graphene oxide composite material

To synthesize materials in Chapter 5, graphene oxide (GO) was synthesized from graphite powder by modified Hummers method.^[85, 86] GO was redispersed in DI water for further use. To synthesize Ni_xCo_{3-x}O₄-rGO composite material, a solution of 0.01 M SDS in 20 ml GO (0.05, 0.1, 0.3, 0.5 and 1.0 mg ml⁻¹) was first made under magnetic stirring. Then, 0.1552 g Co(NO₃)₂•6H₂O (0.53 mmol), 0.0776 g Ni(NO₃)₂•6H₂O (0.26 mmol) and 0.56 g hexamethylenetetramine (HMTA, 4 mmol) were subsequently added into the solution. After complete dissolution and 10 minutes sonication, the solution was transferred into 40 ml Teflon lined autoclave and kept in 80 °C for 7 hours. The product was then collected by centrifuging and washed with ethanol and DI water for several times. The as prepared samples with different GO starting concentration were labeled as SG-1a, SG-2a, SG-3a, SG-4a, and SG-5a accordingly. After drying at 60°C for 6 hours, the samples were sintered at 400 °C for 6 hours. Samples after heat treatment were labeled as SG-1, SG-2, SG-3, SG-4, and SG-5 respectively. The specifics of different samples are listed below in Table 3.1.

Table 3.1 Specifics of Ni _x Co _{3-x} O ₄ -rGO		
Sample	GO starting concentration/mg ml ⁻¹	Heat treatment/°C
SG-1a	0.05	No
SG-2a	0.1	No

SG-3a	0.3	No
SG-4a	0.5	No
SG-5a	1.0	No
SG-1	0.05	400
SG-2	0.1	400
SG-3	0.3	400
SG-4	0.5	400
SG-5	1.0	400

3.1.3 Synthesis of Ni-Co layered double hydroxides Zn_2SnO_4 nanowire hybrid structure

To synthesis materials in Chapter 6, Zn_2SnO_4 nanowires were first grown in a home-made chemical vapour deposition system using a high-temperature horizontal quartz tube system, as show in Figure 3.2.

Figure 3.2 Schematic illustration of chemical vapour deposition system.

Briefly, 0.2 g of source powder ($\text{ZnO}:\text{SnO}_2$: C=2:1:5 [molar ratio]) was loaded into a small quartz tube (1.7 cm in diameter and 30 cm in length). 9-nm gold coating was sputtered onto stainless steel substrate (10 mm $\times$ 15 mm). The substrate was then placed 4.5 cm away from the small tube opening for the growth of ZTO nanowires. The furnace was heated to 1000 °C at a ramp rate of 15 °C min⁻¹ under a constant O₂ flow of 50 sccm min⁻¹ and maintained at 1000 °C for 1 hour.

Ni-Co layered double hydroxides were deposited on above Zn_2SnO_4 nanowires by

electrochemical deposition in a three electrode system. Zn_2SnO_4 nanowires coated stainless steel was applied as the working electrode. A piece of Pt plate was used as counter electrode, and Ag/AgCl in KCl was used as reference electrode. The electrochemical deposition was carried out at a constant current density of 0.5 mA cm^{-2} in a $0.1 \text{ M Ni}^{2+}/\text{Co}^{2+}$ nitrate solution for 600 s. The ratio of $\text{Ni}^{2+}/\text{Co}^{2+}$ was 1:2, 1:1 and 2:1.

3.1.4 Synthesis of defective Ni-Co-Al layered hydroxides

The following experiments were carried out to synthesis the materials studied in Chapter 7.

Synthesis of Ni-Co-Al layered hydroxides

Ni-Co-Al layered hydroxides were synthesized similar with reported literature with minor modifications.^[87] Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ were dissolved subsequently in a flask containing 100 ml DI water to give a total metal ion concentration of 20 mM. Urea was then added into the flask to give a concentration of 0.1 M. After complete dissolution, the flask was heated in an oil bath and refluxed at 100°C for 14 hr. After reaction, the samples were collected by centrifuge and were washed with DI water for several times. The samples were dried in oven at 60°C . The starting ratio of $\text{Ni}^{2+}/\text{Co}^{2+}$ was fixed at 1:2, while the ratio between M^{2+} ($\text{M} = \text{Ni}^{2+}$ and Co^{2+}) and Al^{3+} varied from 3:1, 5:1 to 7:1 respectively. The products were labeled as NCA 3-1, NCA 5-1 and NCA 7-1

accordingly.

The dried layered hydroxide samples were first grinded and then dispersed in 2 M NaOH with vigorous stirring for 2 days to ensure complete reaction. The samples were collected by centrifuge and washed extensively with DI water for several times. The samples were then dried in oven at 60 °C. The samples after NaOH treatment were labeled as NCA 3-1T, NCA 5-1T and NCA 7-1T.

Table 3.2 Specifics of Ni-Co-Al LDH samples		
Sample	Ni : Co concentration ratio	(Ni+Co):Al concentration ratio
NCA 3-1	1:2	3:1
NCA 5-1	1:2	5:1
NCA 7-1	1:2	7:1
NCA 3-1T	1:2	3:1
NCA 5-1T	1:2	5:1
NCA 7-1T	1:2	7:1
NCA 7-1b	1:1	7:1
NCA 7-1c	2:1	7:1

To further optimize the Ni/Co ratio in Ni-Co-Al layered hydroxides, the M (M=Ni and Co)/Al ratio was fixed at 7:1. The Ni/Co ratio in the starting solution varies from 1:2 to 1:1 and 2:1. After NaOH treatment, the samples were labeled as NCA 7-1Tb and NCA 7-1Tc, respectively.

3.1.5 Fabrication of MnO_x-Polyaniline micro-supercapacitor

The fabrication process of MnO_x-polyaniline micro supercapacitor in Chapter 8 can be illustrated in Figure 3.3.

Figure 3.3 Schematic illustration of fabrication process of micro supercapacitor on a paper.

a. Fabrication of interdigital finger electrodes

Table 3.3 Specifics of interdigital finger electrode				
Design/Pattern	Electrode length/ μm	Electrode width/ μm	Gap/ μm	Total Area/ cm^2
MC-1	5000	500	300	0.15
MC-2	5000	300	300	0.15
MC-3	5000	100	300	0.15
MC-4	5000	100	500	0.08
MC-5	5000	100	300	0.08
MC-6	5000	100	100	0.08

Interdigital finger electrodes were fabricated using contact lithography method. Briefly, Parylene was first thermally evaporated onto $1.5 \text{ cm} \times 1.5 \text{ cm}$ photo paper substrate. 200 nm gold patterns were then directly thermally evaporated onto the parylene passivated paper using different hard masks. The specifics of electrode patterns are listed in Table 3.2. The electrode patterns are labelled as sample MC-1,

MC-2, MC-3, MC-4, MC-5, and MC-6, respectively.

b. Electrochemical deposition of polyaniline-manganese oxide composite material

Manganese oxide-polyaniline ($\text{MnO}_x\text{-PANI}$) was electrochemically deposited onto the interdigital electrode pattern in a three electrode cell setup similar in chapter 3.1.2. A mixed solution of 0.1 M aniline, 0.12 M manganese acetate and 0.5 M sulfuric acid using Ag/AgCl was used for potentially dynamic deposition (cyclic voltammetry (CV) deposition). The CV deposition was carried out at a scan rate of 0.2 V s^{-1} from -0.2 to 0.9 V with appropriate cycles.

3.2 Materials characterizations

3.2.1 Structural and elemental characterizations

The structural and elemental characterizations of different materials during the course of study generally involves the following technologies.

X-ray diffractometer Shimazu XRD-6000 and Bruker D8 advance, (voltage 40 kV, current 40 mA) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) were used for characterize the crystal structure of the samples. Indexing of the as-obtained diffraction data can be performed using software like “Match” with ICDD database (International Centre for Diffraction Data).

Field emission scanning electron microscopy (FESEM; JEOL, JSM-7600F, 5 kV) was used to characterize the morphology of different samples. For Ni-Co layered double hydroxides- Zn_2SnO_4 related studies, the samples were directly used for

inspection. The other samples were first dispersed in ethanol and then dropped cast on silicon wafer. 30 seconds of Pt plasma coating was required for preventing the sample charging.

Transmission electron microscopy (TEM; JEOL, JEM-2010 and JEM-2100F, 200 kV) was used to investigate the detailed morphologies and structures of the samples. The samples were first dispersed in the ethanol and then drop onto the TEM specialized copper grids with carbon membrane.

Electron dispersive X-ray spectroscopy (EDX; 20 kV for FESEM, JSM-7600F; 200 kV for TEM, JEM-2100F) was used for both qualitatively and quantitatively determine the elemental composition of the samples. The sample preparations are the same with the preparations for SEM and TEM samples.

X-ray photoelectron spectroscopy (XPS) was carried out in the VG ESCALAB 220I-XL system to analyze the surface chemical state of the elements. Monochromatized Al K α X-ray source (1486.6 eV) on Kratos Analytical AXIS HSi spectrometer, with constant dwell time of 100 ms and a pass energy of 40 eV were used during XPS measurement. The sample were mounted on silicon wafer for the test. The raw data of XPS was deconvoluted and fitted using CasaXPS software.

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer FTIR system) was carried out to analyze the chemical bonding of functional groups in the samples.

The sample was prepared by grinding the mixture of desiccative optical pure KBr and sample. After grinding, the powder was pressed into a transparent pellet for testing.

Brunauer–Emmett–Teller (BET) measurements (TriStar II surface area and porosity analyzer) were used to determine the N₂ adsorption/desorption surface area of samples.

Inductively coupled plasma mass spectroscopy (ICP-MS, Perkin Elmer Elan DRC-e) was used to perform quantitative analysis of elementary composition of Ni-Co-Al layered hydroxides. The sample was first dissolved 1 % w.t. HNO₃ and diluted till the ion concentration was below 200 ppb.

Conductivity meter (Tencor) with four point probe head was employed to measure the conductivity of Ni-Co-Al layered hydroxides. The material was pressed into a 1 cm² pellet for the test.

3.2.2 Electrochemical characterizations

For Ni_xCo_{3-x}O₄-rGO composite material and Ni-Co-Al layered hydroxides, the working electrode was prepared by mixing 85 wt. % active material, 10 wt. % carbon black, and 5 wt. % polyvinylidene fluoride (PVDF) in NMP. The mixture was then stirred overnight and the slurry was loaded on the nickel foam (1 cm × 1 cm in area) and dried in air at 80 °C for 6 hours. The electrode was pressed under 40 MPa and dried overnight. For Ni_xCo_{3-x}O₄ on nickel foam and Ni-Co layered

double hydroxide on Zn_2SnO_4 , the samples were directly used for tests. The loading mass of active material was acquired by measuring electrode with a microbalance with accuracy of 0.01 mg.

The electrochemical characterizations were carried out using cyclic voltammetry, galvanostatic charge-discharge test, and electrochemical impedance spectrum. Electrochemical working station (Autolab PGSTAT 30 potentiostat) was utilized for providing electrical signals and recording data. The electrochemical tests of various samples were conducted using a three electrode system in appropriate electrolyte using Ag/AgCl in 3 M KCl as the reference electrode and Pt plate as counter electrode.

The cyclic voltammetry was carried out to investigate the redox behavior of the samples.

The galvanostatic charge-discharge test was carried out to determine the specific capacitance of the samples. In galvanostatic charge-discharge test, the current of measured device/electrode is constant. The specific capacitances of different samples can be calculated from galvanostatic charge-discharge based on the following equation:

$$C_{sp} = I\Delta t / m\Delta V \text{ (eq. 3.1)}$$

where I is the discharge current, Δt is the discharge time, m is the active material mass, and ΔV is the potential window.

The electrochemical impedance spectrum (EIS) was carried out at 0 V with AC amplitude of 10 mV. The frequency ranges from 0.1 Hz to 10^5 Hz. It helps to understand the resistance and mass transfer behavior of the electrochemical system. Long term cycling tests were performed using either cyclic voltammetry or galvanostatic charge-discharge test. It is to examine the long term stability of the electrode materials

3.2.3 Prototype device test

The prototype supercapacitor device was assembled into a CR 2032 type coin cell using active materials as the cathode and activated carbon as the anode with a filter paper as separator. For the micro-supercapacitor device, the device was simultaneously formed on the substrate. The electrochemical tests of the device were similar as the techniques stated above. The specific capacitance of device can be calculated from both cyclic voltammetry and galvanostatic charge-discharge test.

For cyclic voltammetry, the average specific capacitance of the device can be expressed by the following equation:

$$C_{sp} = [q/MV] \text{ (eq. 3.2)}$$

where q is the time-dependent charge stored in the device, M is the total mass of positive and negative electrode material, and V is the working potential window of the device.

For galvanostatic charge-discharge test, the sepcific capacitance can be expressed as:

$$C_{sp}=I\Delta t/M\Delta V \text{ (eq. 3.3)}$$

where I is the discharge current, Δt is the discharge time after IR drop, M is the total mass of both positive and negative electrodes, and ΔV is the potential window of device.

Additionally, the energy density and power density were calculated to illustrate the energy delivery characteristics of the device, which was eventually plotted as Ragone plot. The energy and power density of the device can be calculated based on the following equations:

$$E=1/2C_{sp}V^2 \text{ (eq. 3.4)}$$

$$P=E/t \text{ (eq. 3.5)}$$

where C_{sp} is the specific capacitance of device, V is the working potential, and t is the discharge time.

Chapter 4 Polycrystalline porous nickel cobalt oxide nanowires for asymmetric supercapacitor

4.1 Motivation

Nickel cobalt oxide ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$, $0 < x \leq 1$) with spinel crystal structure is of great interest for supercapacitor application due to the following several aspects: 1) abundant electrochemical reaction; 2) high electrical conductivity ($\sim 10^{-1}$ – 10 S cm^{-1}); 3) low cost and 4) environmental benignity.^[33, 34] The fabrication of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ supercapacitor electrode materials in previous reports have encountered several major problems such as low capacitance,^[88, 89] poor cycling stability,^[39] and low active material loading mass.^[38] In previous studies, the supercapacitor electrodes were prepared using conventional slurry based method, in which the electric conductivity is affected by the random stacking of electrode materials and insulating binders. Meanwhile, the thick slurry layer in electrode fabrication process could lead to peeling of active material during cycling. On the other hand, one dimensional (1D) nanomaterial directly grown on current collector contact is advantageous for electrochemical applications, owing to its fast redox reaction as well as short electrolyte diffusion path.^{[78], [80, 90]} Furthermore, the exclusion of insulating binders greatly enhances the rate performance. Thus, to fabricate the one dimensional nanostructure of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is of great interest to fully exploit their potential in electrochemical energy storage (theoretical specific capacitance over 3000 F g^{-1}).

Based on above considerations, we propose to exploit the merit of $\text{Ni}_x\text{Co}_{1-x}\text{O}_4$ by constructing one dimension nanowire structures to enable facile electron conduction and electrolyte diffusion. The synthesis method of 1D structure of $\text{Ni}_x\text{Co}_{1-x}\text{O}_4$ in previous literatures are quite limited. For example, Li et al. synthesized Co_3O_4 and $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ microwires with diameters over 500 nm using a chemical bath method by the evaporation of ammonia.^[36, 91] However, the large diameter of 1D structure leads to a low aspect ratio of material. The bulky structure reduces the surface area of material, meanwhile it also limits the ion diffusion. Xiao et al. reported the other chemical bath method for the synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ polycrystalline nanowire.^[92] The bimetallic carbonate hydroxide nanowire precursor was induced by the hydrolysis of urea. Post annealing leads to the formation of polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire structure. The diameter of nanowire is 70~100 nm, while the length is only 1~2 microns. Additionally, well-separated nanowires could be grown on various substrates.^[93] However, this method yields an unsatisfactory specific capacitance of 658 F g^{-1} at 1 A g^{-1} . Based on above discussion, the reports on the fabrication of 1D $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanostructures show unsatisfactory large diameter with bulky structure, or low aspect ratio, which hinders electron conduction and electrolyte diffusion. Therefore, developing an effective method for the synthesis of high performance $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ 1D material is intriguing for the achieving better electrochemical performance.

In this chapter, we introduce the synthesis of high aspect ratio porous polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ ($x=0.6$) nanowires and their electrochemical properties. Ni Co bimetallic carbonate hydroxide nanowires were first formed by a crystallization-dissolution-recrystallization process from single crystalline Ni-Co layered double hydroxides. Post annealing process yielded the porous polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires. Nickel foam (NF) was used as current collector for the support of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires. The specific capacitance of binder free $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ electrode can reach 1479 F g^{-1} at 1 A g^{-1} and 792 F g^{-1} at 30 A g^{-1} . Moreover, a prototype of asymmetric supercapacitor device was assembled $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF and activated carbon (AC). It shows a high specific capacitance of 105 F g^{-1} at a current density of 3.6 mA cm^{-2} , while it maintains 58.7 F g^{-1} at 89.4 mA cm^{-2} . In addition, the asymmetric device shows good long term cycling stability. Comparing to other material systems, such as MnO_2 , Co_3O_4 and its composite material, the device shows enhanced energy density at high power density.

4.2 Structural characterization

XRD was used to examine the crystal structure and phase of the porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$. The diffraction peaks of nanowire sample are shown in Figure 4.1a. They match well with the spinel structure of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ (PDF card No.200781). In Figure 4.1b, TEM based EDX confirmed the co-existence of Ni and Co elements in the spinel

structure. On the other hand, the C and Cu elements are from carbon film covered copper grid sample holder. In addition, the Ni/Co atomic ratio was determined to be 0.23 by TEM based EDX, corresponding to $x=0.6$ in $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$. SEM was used to examine the micro range morphologies of the $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires, as shown in Figure 1c and d. In Figure 4.1c, nanowires of porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires with over 10 μm in length can be observed. Meanwhile, the nanowires are uniformly grown on the nickel foam substrate with plenty of space in between. It is beneficial for the material-electrolyte contact as well as the diffusion of electrolyte. The BET surface area is measured to be $77.339 \text{ m}^2 \text{ g}^{-1}$. As shown in Figure 4.1d, uniform nanowires can be observed under higher magnification under SEM. TEM was used for further investigation of the micro structure of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire. The polycrystalline nature is confirmed by SAED as shown in Figure 4.1e. As shown in Figure 4.1f, the polycrystalline porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire is assembled by small nanocrystals with the diameter below 10 nm. The diameter of the nanowire is around 80 nm. In Figure 4.1g, the crystal lattice spacing is determined to be 0.242 nm under high magnification, matching with the spacing between (311) planes in $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ spinel structure.

Figure 4.1 (a) XRD patterns of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire (blue line: standard diffraction peaks of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$, PDF No.200781); (b) EDX spectrum of sample $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire; (c) and (d) SEM images of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire on nickel foam of different magnifications; (e) select area electron diffraction pattern of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire; (f) low magnification TEM images of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire, inset is the low magnification of observed nanowire ; (g) HRTEM image of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire. Reprinted from Nano Energy, 3, Wang, Xu Yan, Chaoyi Sumboja, Afriyanti Lee, Pooi See, High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor, 121, Copyright (2014), with permission from Elsevier.

4.3 Growth mechanism of Ni Co bimetallic carbonate hydroxide nanowire

The evolution of Ni Co bimetallic carbonate hydroxide nanowire (NiCo cNW) during growth process is investigated to elucidate the growth mechanism. Time dependant experiment with reaction time of 2h, 6h, 10h and 14h were performed to check the morphology evolution of nanowire structure. The samples were labeled as NW-2h, NW-6h, NW-10h and NW-14h respectively. Obvious morphology changes can be observed at different stages of reaction. As shown in Figure 4.2a~b, micro-sized sheet-like structure forms at the early stage of reaction and no nanowires can be observed in sample NW-2h. In Figure 4.2c, nanowires can be observed around the micro sheet after 6 hours reaction. Detailed inspection under high magnification in Figure 4.2d shows that the nanowires grow from the micro sheet. The amount of nanowires increases while the size and amount of micro sheet decrease after 10 hours reaction (Figure 4.2d~e). This indicates a process where micro sheet dissolves and recrystallizes into nanowire. After 14 hours reaction, the nanowires are the dominant product and only a few particles are observed.

Figure 4.2 (a) Low magnification SEM images of sample NW-2h; (b) high magnification SEM images of sample NW-2h; (c) low magnification SEM images of sample NW-6h; (d) high magnification SEM images of sample NW-6h; (e) low magnification SEM images of sample NW-10h; (f) high magnification SEM images of sample NW-10h; (g) low magnification SEM images of sample NW-14h; (h) high magnification SEM images of sample NW-14h. Reprinted from Nano Energy, 3, Wang, Xu Yan, Chaoyi Sumboja, Afriyanti Lee, Pooi See, High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor, 122, Copyright (2014), with permission from Elsevier.

The crystal structures of sample NW-2h and sample NW-14 were examined by XRD in order to track the phase change during different stages of reaction. As shown in Figure 4.3, typical diffraction peaks of layered double hydroxides (LDHs) were observed in sample NW-2h at the early stage of reaction.^[94] However, in Figure 4.3b, the product at the final stage of reaction (sample NW-14h) agree with previous report on nickel cobalt bimetallic carbonate hydroxides.^[95] On the contrary, the sample prepared without the use of SDS shows a rectangular nanosheet structure, as shown in Figure 4.3c. It strongly proves that the nanowire structure is produced from SDS induced a phase evolution process.

Figure 4.3 (a) XRD pattern of sample NW-2h; (b) XRD pattern of sample NW-14h; (c) SEM image of sample prepared without SDS synthesized at the same condition as sample NW-14h.

The elemental composition change during the reaction process is monitored by EDX. As shown in Table 4.1, the presence of high sulfur content in the micro sheet structures from sample NW-2h, NW-6h and NW-10h confirm the intercalation of dodecyl sulfate anion into the LDHs. The high content of Ni in the initial sample suggests that Ni rich LDHs were first formed at the early stage, while a much faster dissolution of Ni than Co from LDHs occurred. Additionally, the TEM based EDX analysis was performed on carbonate hydroxide nanowires of sample NW-10h and NW-14h. There is an increasing of Ni content in nanowire during growth. It suggests a faster recrystallization of Ni than Co into carbonate hydroxide nanowire.

Table 4.1EDX analysis in LDH flakes and Ni-Co cNWs

Element	LDH flakes			Ni-Co cNWs	
	NW-2h	NW-6h	NW-10h	NW-10h	NW-14h
S %	21.64	18.69	16.76	5.34	2.7
Co %	40.28	49.85	53.17	82.25	78.9
Ni %	38.08	31.47	30.07	12.41	18.27

Based on above results, we propose a growth mechanism of NiCo cNW as illustrated in Figure 4.4. At the early stage of reaction, Ni rich dodecyl sulfate intercalated LDHs form at first with 2 dimensional sheet like structure. Meanwhile, the hydrolysis of HMTA during the hydrothermal reaction yields carbeneous species. As a result, the bimetallic carbonate hydroxide seeds form on the surface

of LDHs. On the other hand, carbonate anion intercalated hydroxide is a more thermodynamically stable phase.^[96, 97] The interlayer dodecyl sulfate anion hereby tends to exchange with carbonate anion. Thus, a driving force promotes the dissolution of LDHs and recrystallization into carbonate hydroxide. Meanwhile, the dodecyl sulfate anion in the solution may also act as a structure direct agent for carbonate hydroxide growth. In this way, the NiCo cNW continues to grow as reaction proceeds. Finally, the major product is the thermodynamically favorable NiCo cNW. However, direct formation of bimetallic carbonate hydroxide at early stage will not lead to the nanowire growth as induced by SDS.

Figure 4.4 Schematic illustration of the growth mechanism of NiCo cNW. Reprinted from Nano Energy, 3, Wang, Xu Yan, Chaoyi Sumboja, Afriyanti Lee, Pooi See, High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor, 122, Copyright (2014), with permission from Elsevier.

4.4 Electrochemical characterizations

4.4.1 Electrochemical characterizations of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -nickel foam electrode

The electrochemical redox reaction of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ NW-nickel foam ($\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -NF) electrode was first investigated using cyclic voltammetry (CV). As shown in

Figure 4.5a, the redox peaks at 0.4 V and 0.12 V belong to the faradic reactions of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ in the alkaline electrolyte.^[98, 99] The possible redox reactions are based on equations 4.1 and 4.2:

The specific capacitances of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-NF}$ were determined by galvanostatic charge-discharge tests. Figure 4.5b and c show the galvanostatic discharge curves and the relationship between specific capacitances and current densities, respectively. The calculation of the specific capacitance is based on equation 3.1.

The $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-NF}$ electrode shows a high capacitance of 1479 F g^{-1} at a current density of 1.0 A g^{-1} , while the capacitance remains 792 F g^{-1} at 30 A g^{-1} , showing an excellent rate performance. Electrochemical impedance spectrum (EIS) is carried out to further investigate the electrochemical property of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-NF}$ electrode. The Nyquist plot is shown in Figure 4.5d. The first intercept of the impedance curve with real axis is 1.3 ohm, indicating a low equivalent series resistance (ESR).^[100] In addition, no obvious semicircle in higher frequency region is observed, suggesting the negligible charge transfer resistance from electrochemical reaction.^[101] Therefore, the direct highly conductive material to current collector design is favorable for high performance electrochemical application.

Figure 4.5 (a) CV curves of sample $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-NF}$ and pure NF sintered at 300°C in 2 M KOH electrolyte at a scan rate of 10 mV s^{-1} ; (b) Galvanostatic discharge curves of porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF at different current densities; (c) Specific capacitance of porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF at different current densities; (d) Nyquist plot of porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ on NF. Reprinted from Nano Energy, 3, Wang, Xu Yan, Chaoyi Sumboja, Afriyanti Lee, Pooi See, High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor, 122, Copyright (2014), with permission from Elsevier.

4.4.2 Supercapacitor device based on $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-NF}$ //Activated carbon

Activated carbon (AC) is a prevalent electrode material in asymmetric supercapacitor devices.^[102, 103] The activated carbon in our study is commercially available, which has a BET surface area of $2084.15 \text{ m}^2 \text{ g}^{-1}$ and a narrow pore

distribution around 1.9 nm. The electrochemical property of activated carbon was first characterized before cell assembly. As shown in Figure 4.6a, activated carbon shows well-defined rectangular CV curves, indicating an electrical double layer behavior. The specific capacitance determined by charge-discharge tests is 186.5 F g⁻¹ at 1 A g⁻¹ and remains as high as 155.5 F g⁻¹ at 20 A g⁻¹. The optimization of activated carbon and Ni_xCo_{3-x}O₄ mass ratio is based on the equation 4.3:

$$C_{sp+} \times \Delta E_+ \times m_+ = C_{sp-} \times \Delta E_- \times m_- \quad (\text{eq.4.3})$$

Where the $C_{sp\pm}$ is the specific capacitance of positive/negative electrode; $\Delta E_{\pm}$ is the potential window of positive/negative electrode; $m_{\pm}$ is the active material mass of cathode/anode. Asymmetric supercapacitor is assembled into a coin cell using porous Ni_xCo_{3-x}O₄ nanowires on NF as cathode and AC as anode. A common filter paper (Advantech, cellulose, 100 circles) is applied as the separator.

Figure 4.6 (a) CV curves of activated carbon in 2 M KOH; (b) relationship between specific capacitance of activated carbon and discharge current density.

A prototype asymmetric supercapacitor was assembled based on the optimized $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire/AC mass ratio. As shown in Figure 4.7a, the CV curves from 0~1.5 V and 0~1.6 V preserve good rectangular shapes. When operation voltage exceeds 1.6 V, there is a distortion around 1.7 V in the CV curve, which suggests some irreversible reactions happen. Therefore, the ideal operation voltage range for this asymmetric supercapacitor device is from 0~1.6 V. The specific capacitance of the asymmetric supercapacitor device was determined by galvanostatic charge-discharge tests. As shown in Figure 4.7b, the typical symmetric triangle shape charge-discharge curves indicate the well matched charge storage of cathode and anode. The specific capacitance of the device is calculated based on equation 3.3.

Figure 4.7 (a) CV curves of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires on NF/AC device measured at different potential window in 2M KOH electrolyte at a scan rate of 10 mV s^{-1} ; (b) charge-discharge curves of different current densities; (c) relationship between specific capacitance vs discharge current density; (d) Nyquist plot of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires on NF/AC asymmetric supercapacitor. Reprinted from Nano Energy, 3, Wang, Xu Yan, Chaoyi Sumboja, Afriyanti Lee, Pooi See, High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor, 124, Copyright (2014), with permission from Elsevier.

In Figure 4.7c, the specific capacitance is measured to be 105 F g^{-1} at 3.6 mA cm^{-2} and 58.7 F g^{-1} at 89.4 mA cm^{-2} , showing a good rate performance. This indicates the high energy density delivery ability of the device at high power density.^[101, 104]

The Nyquist plot of the asymmetric device is shown in Figure 4.7d, the ESR of

corresponding asymmetric cell is 5.36 ohm, while it shows negligible charge transfer resistance.

The evaluation of cycling stability is critical for real supercapacitor application. The cycling test of the device was performed using CV test at 20 mV s^{-1} for 3000 cycles. The relationship between normalized capacitance and cycle number is shown in Figure 4.8a. As can be seen, the capacity first has a slight increase within the first 50 cycles and finally maintains 82.8 % after 3000 cycles, comparing with the second cycle. This indicates a stable device performance towards long time usage. Ragone plot is plotted according to equations 3.4 and 3.5 to illustrate the characteristics of the supercapacitor device.

Figure 4.8 (a) Cycling test of the $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire on NF/activated carbon asymmetric device at 20 mV s^{-1} for 3000 cycles in 2 M KOH. (b) Ragone plot of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire on NF/activated carbon asymmetric device. Reprinted from Nano Energy, 3, Wang, Xu Yan, Chaoyi Sumboja, Afriyanti Lee, Pooi See, High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor, 125, Copyright (2014), with permission from Elsevier.

As shown in the Ragone plot in Figure 4.8b, the asymmetric device shows an energy density of 37.4 Wh kg^{-1} at a power density of 163 W kg^{-1} , while maintains a high energy density of 20.9 Wh kg^{-1} at a power density of 4.1 kW kg^{-1} . This result shows an enhanced energy density at high power density comparing with Graphene-MnO₂//Graphene asymmetric device (10.03 Wh kg^{-1} at 2.53 kW kg^{-1}),^[105] MnO₂-functional CNT (FCNT)//FCNT asymmetric device (10.4 Wh kg^{-1} at 2.0 kW kg^{-1}),^[106] and Ni-Co oxide//AC asymmetric device (7.4 Wh kg^{-1} at 1.90 kW kg^{-1}).^[107] Moreover, in this work, the Ni_xCo_{3-x}O₄ nanowire on NF shows superior energy density at high power density than the recently published Co₃O₄ nanowire-Ni(OH)₂ on NF (2013). This strongly indicates the advantage of more conductive Ni_xCo_{3-x}O₄.^[108] Apart from that, a significant improvement of energy density was made by Wang et al. in their Ni-Co oxide//PANI derived carbon asymmetric supercapacitor.^[109] The advantage of PANI derived carbon is to provide additional redox reaction originating from N group. Such improvement of charge storage ability in carbon will help to enhance the overall energy density in device.

4.5 Summary

In this chapter, a novel method to synthesis polycrystalline porous Ni_xCo_{3-x}O₄ nanowires on nickel foam is successfully demonstrated. Nickel cobalt bimetallic carbonate hydroxide nanowires precursors were formed through dodecyl sulfate intercalated layered double hydroxides via crystallization-dissolution-

recrystallization process. The porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires can be obtained by thermal sintering.

The binder free electrode design of porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires on nickel foam offers a high specific capacitance of 1479 F g^{-1} at 1 A g^{-1} and 792 F g^{-1} at 30 A g^{-1} .

The one dimension conducting nanowire together with direct material-electrode contact offers the following advantages: 1) high rate performance due to enhanced electric conductivity; 2) facile electrolyte contact and diffusion; 3) small nanocrystal shortened electrolyte ion diffusion length.

Moreover, asymmetric supercapacitor device based on the porous $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires on nickel foam and activated carbon was successfully fabricated. Due to the merit of one dimensional nanostructure, the asymmetric device delivers a high energy density of 37.4 W h kg^{-1} at a power density of 163 W kg^{-1} . Furthermore, it can operate at a high power density of 4.1 kW kg^{-1} with an energy density of 20.9 Wh kg^{-1} . Additionally, this asymmetric device also exhibits stable performance over a long period. The character of such device will be suitable for high power heavily duty applications, such as automotive subsystems, hybrid vehicles, heavy industrial equipments and so on. This new strategy of synthesizing $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ provides a perfect platform for further electrochemical applications in energy storage, electrochemical catalysis and so on.

Chapter 5 Enhanced fast faradic reaction in $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -reduced graphene oxide composite material

5.1 Motivation

In chapter 4, the synthesis of one dimensional $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire material has been demonstrated, which shows impressive rate capability and high specific capacitance. In that study, structure engineering of nano material was applied so as to provide facile electron conduction path. In this way, the electron conduction from redox reaction to the current collector is facilitated by reducing the random electron conduction path. Apart from creating beneficial material structure for electron conduction, the electric conductivity of electron conduction path can be further improved by adding conductive additives into the electrode matrix. In order to facilitate the electric conductivity of the electron conduction path, we propose to fabricate a hybrid material of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ with conductive carbon material.

Graphene oxide has attracted plenty of interests of research due to its unique properties.^[110] Unlike carbon nanotube, graphene oxide can be readily homogeneously dispersed in water without any aid of surfactant. This property is particularly useful for us to avoid unnecessary agglomeration of material at the beginning of synthesis process. Especially for supercapacitor application, numerous reports on metal oxide/reduced graphene oxide (GO) composite materials has shown enhanced electrochemical performance, such as MnO_2/rGO ,^[111, 112] NiO/rGO ,^[113, 114] $\text{Co}_3\text{O}_4/\text{rGO}$,^[115] and so on. It has been well

established that the relatively high conductivity of rGO gives rise to enhanced electrochemical performance. Most of previous reports focus on synthesizing binary metal oxide with various morphologies on rGO. However, little work has been reported dealing with enhancing the conductivity of metal oxides. As discussed in chapter 2, $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ has much higher electron conductivity compared with the above metal oxides.^[116] Thus, it is a perfect subject for metal oxide/rGO composite material study. To date, there are limited reports on $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite materials for supercapacitor application. Until recently, Wang et al.^[77] reported a self-assembly method by exfoliating Ni-Co hydroxides and assembling with GO. After heat treatment, the capacitance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ can reach 835 F g^{-1} . This method provides the first insight into $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material. The electrochemical stability of the composite material is good. However, the preparation method is tedious and the specific capacitance is low comparing with early reports on pure $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ by Wei et al.^[38] and Hu et al.^[39] Thus, developing a $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite with high capacitance and high stability is of great value for practical application.

In this chapter, we present a facile synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material by conversion from dodecyl sulfate intercalated Ni-Co LDH/GO composite. Dodecyl sulfate is proved to induce a faster faradic reaction within the $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material. As a result, this composite material shows a high

capacitance of 1222 F g^{-1} at 0.5 A g^{-1} and maintains 768 F g^{-1} at 40 A g^{-1} , demonstrating an elevated rate performance than $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires. Moreover, a prototype of asymmetric supercapacitor device is assembled using $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ and activated carbon for the first time. It shows a high experimental energy density of 23.32 Wh kg^{-1} and a maximum experimental power density of 12.99 kW kg^{-1} . Additionally, the asymmetric device shows a good stability towards multistage current charge-discharge cycles. When comparing with the previously reported systems, such as MnO_2 , Co_3O_4 and their composite materials, this study shows superior energy density at high power density owing to the high rate performance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$.

5.2 Structural characterization

Different concentration of GO has been investigated, among them the sample prepared in 0.1 mg ml^{-1} GO was labelled as SG-2a. The sample after the sintering process of SG-2a was labelled as SG-2 (please refer to Chapter 3.1.3 for detailed information). The crystal structure and phase of sample SG-2a and sample SG-2 are investigated by XRD measurements. The X-ray diffraction patterns are shown in Figure 6.1a. Sample SG-2s shows a typical XRD pattern of dodecyl sulfate anion intercalated Ni-Co layered double hydroxides (LDHs).^[94] Meanwhile, the significant peak shift of (003) and (006) faces in the diffraction pattern, suggesting the enlarged lattice spacing and the incorporation of dodecyl sulfate anion into the

Ni-Co LDHs lattice. The X-ray diffraction pattern of sample SG-2 was indicated in red as shown in Figure 5.1a. After heat treatment, the Ni-Co LDHs transfers into $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ spinel structure (PDF card No.200781). It is noteworthy to mention that the GO or rGO peaks are not present in both samples. This may be due to the low carbon weight ratio in the composite material. The XRD signals are suppressed by Ni-Co LDHs and $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$.

FTIR is performed to confirm the presence of dodecyl sulfate anion in sample SG-2a, as shown in Figure 5.1b. The typical peaks at 2920 cm^{-1} , 2851 cm^{-1} , 1468 cm^{-1} and 1215 cm^{-1} can be attributed to the alkyl group in dodecyl sulfate. Further heat treatment leads to the full decomposition of dodecyl sulfate, as no alkyl group signals are detected in sample SG-2, shown in Figure 5.1b. Microstructures of sample SG-2a and sample SG-2 are examined by SEM, presenting in Figure 5.1 c~f. In Figure 5.1c and 5.1d, disk like Ni-Co LDHs sheets are found uniformly grown on the GO sheet, forming a 2 D sheet on sheet structure. It helps to expose the surface of composite material by preventing the stacking of GO. In Figure 5.1e and Figure 5.1f, the disk like Ni-Co LDHs sheet disappears and transfers into a more compact structure after sintering.

Figure 5.1 (a) X-ray diffraction patterns of sample SG-2a and sample SG-2; (b) FTIR spectrums of sample SG-2a and sample SG-2; (c) and (d) SEM images of sample SG-2a at different magnifications; (e) and (f) SEM images of sample SG-2 at different magnifications.^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

The chemical composition of sample SG-2 was further examined by EDX, as shown in Figure 5.2a~c. The EDX mapping in Figure 5.2b shows that the $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ is relieved from sulfur, indicating the full decomposition of dodecyl sulfate. The EDX spectrum of the SG-2 in Figure 5.2c confirms that the composite material is composed of O, C, Ni and Co.

Figure 5.2 (a) Micrograph of sample SG-2; (b) EDX elements mapping of Co K α , Ni K α and S K α ; (c) EDX of sample SG-2.

Detailed TEM study is performed to further elucidate the structure of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material. In Figure 5.3a, it reveals that the ultrasmall NiCo_2O_4

nanocrystals are homogeneously anchoring on the surface of rGO in sample SG-2. Moreover, HRTEM image in Figure 5.3b shows that the diameter of NiCo_2O_4 nanocrystals is only around 5 nm, which is beneficial for enhancing electrochemical performance.^[118] In addition, due to the decomposition dodecyl sulfate, it creates various voids in the NiCo_2O_4 , making it more accessible for electrolyte.

Figure 5.3 (a) High magnification TEM image of sample SG-2; (b) HRTEM image of sample SG-2.^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

5.3 Electrochemical characterization

5.3.1 Characterization of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material

The influence of SDS concentration on the specific capacitances of different samples was investigated by galvanostatic charge-discharge method. As shown in Figure 5.4a, the addition of SDS in during synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite

materials greatly promotes the specific capacitances. For the sample without SDS, the maximum specific capacitance is only 410.8 F g^{-1} . However, when SDS is incorporated, the electrochemical performance greatly improved to above 1000 F g^{-1} at the same current density. Meanwhile, the concentration of SDS concentration doesn't give a dramatic difference in the specific capacitance. This indicates that addition of dodecyl sulfate is crucial for the electrochemical redox reaction in $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-rGO}$ composite, which will be elaborated later. In addition, according to Figure 5.4a, 0.01 M SDS during synthesis is the optimum concentration for further study. The effect of GO concentration is explored as well. In Figure 5.4b, there shows an optimum 0.1 g ml^{-1} GO concentration to achieve the best specific capacitance. Thus, we focus on investigating the electrochemical properties of sample SG-2 for the following study.

Figure 5.4 (a) Relationship between specific capacitance and different SDS concentrations; (b) relationship between specific capacitance at 0.5 A g^{-1} and GO concentration in the stating solutions.^[117] Reproduced from Ref. 114 with

permission from The Royal Society of Chemistry.

The comparison between the electrochemical behavior of sample SG-2 and sample without SDS are shown in Figure 5.5a. The integration CV curve area of sample SG-2 shows a much larger area and much higher current density. This indicates a better pseudocapacitive behavior of SG-2. Both curves show a pair of broad redox peaks around 0.35 V and 0.15 V. It is the result from the faradic reaction between $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and alkaline electrolyte.^[98, 99] The possible redox reactions are based on equations 5.1~5.2:

Galvanostatic charge-discharge tests were carried out to examine the specific capacitance of the sample SG-2. Galvanostatic discharge curves are shown in Figure 5.5b, while the relationship between specific capacitances discharge current densities are shown in Figure 5.5c. Sample SG-2 shows a high capacitance of 1222 F g^{-1} at a current density of 0.5 A g^{-1} , while it maintains 768 F g^{-1} at 40 A g^{-1} , showing a great rate capability of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO composite material. It strongly suggests the merit of rGO in the composite materials by creating fast electron conduction path, which has been well demonstrated by many reports.^[119-122] The stability of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO composite material was further examined using CV test. The relationship between specific capacitance and cycle number is shown in

Figure 5.5d. Sample SG-2 exhibits an excellent stability towards long time cycling. After a short activation process about 50 cycles, there shows a maximum 949 F g⁻¹. After 3000 cycles, the specific capacitance retains 91.6%, c.a. 870 F g⁻¹.

Figure 5.5 (a) CV curves of sample SG-2 and sample without SDS synthesized at the same condition as SG-2 at 20 mV s⁻¹ in 2 M KOH; (b) discharge curves of sample SG-2 at different current densities; (c) relationship between the specific capacitance and current density of sample SG-2; (d) relationship between specific capacitance and cycling number at 20 mV s⁻¹ for 3000 cycles.^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

5.3.2 Role of dodecyl sulfate on electrochemical performance

As motioned above, the presence of dodecyl sulfate has a direct effect on the electrochemical performance of NiCo₂O₄-rGO composite. To study this effect in detail, we first apply an electrochemical impedance spectrum (EIS) study on sample SG-2 and the sample without SDS. The equivalent circuit for fitting the Nyquist plots are shown in Figure 5.6a.^{[55],[123]} The symbols represent the following factors: R_s (equivalent series resistance), R_f (Faradic charge transfer resistance), C_{dl} (electric double layer capacitance), W (Warburg impedance) and C_f (limit capacitance). The values of corresponding segments in sample SG-2 and sample without SDS are shown in Table 5.1.

Table 5.1 Calculated values of R_s , R_f , W , C_{dl} , C_f from the equivalent circuit.^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

	$R_s /$	$R_f /$			
	Ω	Ω	W	C_{dl} / mF	C_f / F
Without SDS	1.675	0.358	7.97	1.73	0.015
SG-2	0.621	0.214	1.75	0.5	0.142

In high frequency region of Nyquist plot, sample SG-2 exhibits a much lower real axis intercept in Figure 5.6a,, indicating a lower interfacial resistance,^[100] which is also confirmed in the simulation results. While the semicircles of two samples

show similar diameters, this indicates the charge transfer resistance during the electrochemical reaction is comparable.^[55] According to the EIS result, the first effect of SDS is to reduce the electrical resistance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material. This directly affects the rate capability in the composite material. The capacitance retention of sample SG-2 and sample without SDS are 63.8 % and 48.6 % from 0.5 A g^{-1} to 40.0 A g^{-1} , respectively. By comparing the microstructures of sample SG-2 and sample without SDS, we may get more insight. As shown in Figure Appendix 1, contrary to the small nanocrystals on rGO in sample SG-2, the sample without SDS has a wrinkled surface. It consists of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ flakes randomly aligned on the rGO surface, which reduces the contact of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ with rGO. This will increase the resistance of composite material.

To further elucidate the cause of the raise in the capacitance, the Trasatti procedure is performed.^{[124],[125]} This allows to discriminate charge storage due to easily accessible surface (outer, q_o) and not easily accessible surface (inner, q_i). The specific charge (q^*) is the total charge exchanged between electrode and electrolyte including both inner and outer charge storage, as shown in equation 5.3.

Figure 5.6 (a) Nyquist plots of sample SG-2 and sample without SDS synthesized under the same condition; (b) total charge stored charge vs scan rate of sample SG-2 and sample without SDS; (c) relationship between specific charge stored and the inverse of square root of the scan rate; (d) inner and outer charge storage comparison between sample SG-2 and sample prepared without SDS. ^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

$$q^* = q_i + q_o \text{ (eq. 5.3)}$$

The inner charge is diffusion controlled, which is more difficult as scan rate increases. Whereas, the outer charge storage is assumed not dependent on scan rate. Thus there gives the relationship of charge stored with scan rate: ^[57]

$$q^* = q_{\infty} + \frac{k}{\sqrt{v}} \text{ (eq.5.4)}$$

When scan rate $v \rightarrow \infty$, q_{∞} is the charge stored instantly at the outer and easily accessible surface, which equals with q_o . On the other hand, when scan rate $v \rightarrow 0$, the access to all electrochemically active sites is fully available and q includes both q_i and q_o . To calculate q_o , a set of CV experiments have been conducted from 2 to 150 mV s^{-1} , as shown in Figure 5.6b and Figure 5.6c. The q_o can be derived from the extrapolated value of q^* vs $v^{-1/2}$. The outer and inner charges for sample SG-2 and sample without SDS are shown in Figure 5.6d. If we take assumption that the electrical double layer capacitance reaches a maximum value of $50 \mu\text{C cm}^{-2}$.^[126] The sample without SDS is estimated to have an electrical double layer capacitance around 65 C g^{-1} based on a surface area of $136.01 \text{ m}^2 \text{ g}^{-1}$. Meanwhile, sample SG-2 only has 45.3 C g^{-1} based on a surface area of $94.91 \text{ m}^2 \text{ g}^{-1}$. Apart from readily formed electrical double layer on the material surface, the fast redox reaction of the metal oxide within the near surface also contributes to the instantly stored charge. In this view, SDS has induced a better accessibility of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ in the electrolyte. That may result in a higher mobility of OH^- or oxygen ion in the $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals.

5.3.3 $\text{NiCo}_2\text{O}_4/\text{rGO}$ -Activated Carbon device

Activated carbon (AC) is a prevalent electrode material in asymmetric supercapacitor devices.^[55, 102] The commercial available activated carbon was the

same with the one used in chapter 4. Based on the charge balance principle,^[127] the recommend mass ratio of composite/AC is 0.28. Asymmetric supercapacitor was assembled into a coin cell using $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO composite material as cathode and AC as anode. 2 M KOH aqueous solution was used as electrolyte and a piece of common filter paper was applied as the separator.

Figure 5.7 (a) CV curves of different potential windows of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO/AC asymmetric supercapacitor cell; (b) galvanostatic charge-discharge curves at different current densities; (c) Nyquist plot of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO/AC asymmetric supercapacitor; (d) Ragone plot of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO/AC asymmetric supercapacitor.^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

Figure 5.7a presents the CV curves of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-rGO/AC}$ asymmetric device with optimum mass ratio at different potential windows. From 0.3 V ~ 1.6 V, the CV curves show typical rectangular shapes, indicating a well-defined capacitive behavior. When the potential window increases to 0.3 ~1.7 V, there shows a distortion at 1.7 V in the CV curve. There is also a slight hump at the anodic sweeping around 1.4 V. The abnormal distortion and hump suggest some irreversible reactions occur when the device potential is charged higher than 1.6 V. Therefore, 0.3 to 1.6 V is the optimum operation range for this asymmetric supercapacitor device. As shown in Figure 5.7b, galvanostatic charge-discharge tests are preformed to examine the specific capacitance of the asymmetric cell. The charge-discharge curves all show well symmetric triangle shapes suggesting well matched masses between cathode and anode. Meanwhile, the specific capacitance reaches 99.4 F g^{-1} at 0.5 A g^{-1} and maintains 44.6 F g^{-1} at 20 A g^{-1} . This indicates a good rate performance at high current density. Due to the benefit of SDS induced high performance $\text{Ni}_x\text{Co}_{3-x}\text{O}_4\text{-rGO}$ composite material, the ESR of corresponding asymmetric cell is quite low as well, as shown in Figure 5.7c. This also suggests a good ability to undertake high power delivery applications.^[55, 128] The Ragone plot of $\text{NiCo}_2\text{O}_4\text{-rGO/AC}$ asymmetric device is shown in Figure 5.7d. The energy density of device can reach 23.3 Wh kg^{-1} at a power density of 324.9 W kg^{-1} , while it maintains a high energy density of 10.5 Wh kg^{-1} at a power density of 12.99 kW

kg^{-1} . This result shows a much enhanced energy density output at high power density comparing with Graphene- MnO_2 /Graphene asymmetric device (10.03 Wh kg^{-1} at 2.53 kW kg^{-1}).^[105] MnO_2 -functional CNT (FCNT)/FCNT asymmetric device (10.4 Wh kg^{-1} at 2.0 kW kg^{-1}),^[106] Ni-Co oxide//AC asymmetric device (7.4 Wh kg^{-1} at 1.90 kW kg^{-1}),^[107] and recently published Co_3O_4 nanowire-Ni(OH)₂ on NF (2013).^[108] It is evident that the power density of previous work (less than 3 kW kg^{-1}) is much inferior to our current work (13 kW kg^{-1}), when the energy density is comparable ($\sim 10 \text{ Wh kg}^{-1}$). This strongly indicates the advantage of high rate capability $\text{Ni}_x\text{Co}_{3-x}\text{O}_4/\text{rGO}$ composite material, as discussed in section 5.3. Apart from that, a significant improvement of energy density was made by Wang et al. in their Ni-Co oxide//PANI derived carbon asymmetric supercapacitor (2014).^[109] The advantage of PANI derived carbon is to provide additional redox reaction originating from N group. Such improvement of charge storage ability in carbon will help to enhance the overall energy density in device.

Figure 5.8 Cycling test of NiCo₂O₄-rGO/AC device at various current densities.
^[117] Reproduced from Ref. 114 with permission from The Royal Society of Chemistry.

The cycling stability of supercapacitor is another concern for practical application. Here we demonstrate a multistage charge-discharge cycling test for our asymmetric device, as shown in Figure 5.8. In the first 500 cycles, there is only 5 % capacity fading and 7 % capacity drop after 1000 cycles at 1.0 A g⁻¹. Moreover, the capacity fading is less than 1 % for the rest 3 stages. After a total 2500 cycles, the capacity at 2.0 A g⁻¹ retains 83 % of the first cycle, which indicates a good long time stability. Meanwhile, the stable output during each charge-discharge stages suggests the ability to store and deliver with desired power and energy densities.

5.4 Summary

In summary, we have successfully synthesized Ni_xCo_{3-x}O₄-rGO composite material by the aid of sodium dodecyl sulfate using hydrothermal method. The composite

material shows good electrochemical performance with high specific capacitance, high rate performance and high cycling stability. Due to the merit of rGO, the rate performance is greatly enhanced comparing to the $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire.

Dodecyl sulfate plays a crucial role in the enhancement of electrochemical properties. It helps to create ultra-small nanocrystals of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ to increase the material utilization. More importantly, the resulting $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals have more easily assessable redox active sites for faradic reaction. This greatly enhances the specific capacitance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO composite material.

A prototype supercapacitor device using $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -rGO composite material and activated carbon shows a specific capacitance of 99.4 F g^{-1} (0.397 F cm^{-2}) at 0.5 A g^{-1} and maintains 44.6 F g^{-1} (0.178 F cm^{-2}) at 20 A g^{-1} . Such device is able to deliver a high energy density of 23.32 Wh kg^{-1} and a high power density of 12.99 kW kg^{-1} . Meanwhile, this asymmetric supercapacitor exhibits good stability towards multistage charge-discharge cycling. Such asymmetric supercapacitor is promising for future high power heavy duty applications, such as automotive subsystems, hybrid vehicles, heavy industrial equipments and so on.

Chapter 6 Ni-Co layered double hydroxide-Zn₂SnO₄ nanowire hybrid material for high performance supercapacitor

6.1 Motivation

Apart from Ni_xCo_{3-x}O₄, Ni-Co layered double hydroxide is another interesting material with high theoretical specific capacitance. Unlike Ni_xCo_{3-x}O₄, Ni-Co layered double hydroxide is insulating in nature and the rate performance of this material is not satisfactory as discussed in Chapter 2. In this sense, to enhance the rate performance of Ni-Co layered double hydroxide is of great importance for developing Ni-Co LDH based supercapacitor. Here, we propose to fabricate a nanowire-LDH hybrid structure to facilitate the electron conduction from LDH to current collector during electrochemical process. In previous studies, hybrid materials using conducting nanowires are highly important in energy related research for the development of high rate performance electrodes. It has been shown that 1D conducting nanowires are crucial for enabling direct electron conduction along the nanowire for energy storage applications.^[78, 129-131] Previous reports on heterostructure electrodes, such as MnO₂ on SnO₂,^[78] MnO₂ on ZTO,^[79] Co(OH)₂ on ITO,^[80] and Ni₃(NO₃)₂(OH)₄ on ZnO,^[132] have demonstrated their superior rate performance due to facile electron conduction, particularly in supercapacitors. As to these heterostructure electrodes, the key factors other than their superior electron conduction properties are poorly understood. Moreover, previous studies have focused on the evaluation of a single electrode, while two-

electrode devices are more important in the case of real applications. Therefore, it is critical to elucidate the detailed electrochemical behaviour of the unique heterostructure architecture. It is also important to develop a highly conductive 1D supercapacitor electrode to construct devices capable of ultrahigh power delivery and high energy storage.

In this chapter, we present the design of a novel heterostructure based on electrochemically deposited ultrathin $\text{Ni}_x\text{Co}_{1-x}$ LDH nanoflakes on conducting ZTO nanowires prepared by chemical vapour deposition (CVD). Unlike semiconducting SnO_2 and ZnO , ZTO is a highly conductive ternary oxide ($10^2\sim 10^3 \text{ S cm}^{-1}$) with great potential to replace ITO as a transparent conducting oxide material.^[133] Although the maximum conductivity of ITO is 10^5 S cm^{-1} , indium is a rare metal, and the conductivity of ITO is strongly affected by the partial pressure of O_2 during synthesis.^[133, 134] Therefore, ZTO represents an alternative, low-cost highly conducting ternary oxide material, which makes it ideal for conducting scaffolds. The effects of electrochemical deposition conditions on the presence of electrochemically active sites are elucidated for the first time. The results provide rational guidelines and a protocol for the future design of similar heterostructures for different applications, such as batteries and photoelectrodes. Apart from the fundamental electrochemical study, prototype asymmetric supercapacitor device was fabricated using this LDH/nanowire heterostructure as the cathode and

commercially available activated carbon as the anode. The device exhibits excellent electrochemical performance within 1.2 V working potential range. It can deliver an energy density of 23.7 W h kg⁻¹ at a power density of 284.2 W kg⁻¹ and a high energy density of 9.7 W h kg⁻¹ at 5.81 kW kg⁻¹. The LDH/nanowire heterostructure enables high energy density at high power density comparing with the pure Ni(OH)₂, Co(OH)₂ or Ni-Co LDH systems, meanwhile, it also shows superior energy density than other material systems such as K_{0.27}MnO₂. More importantly, this device shows an excellent long term cycling stability.

6.2 Structural characterization of Ni_xCo_{1-x} LDHs on ZTO nanowires

Electrochemically deposited Ni_xCo_{1-x} LDHs on ZTO nanowires were structurally characterized. The X-ray diffraction peaks of the deposited LDHs with Ni/Co=1:1 shows the presence of ZTO peaks that fit well with the standard peaks of PDF # 00-024-1470 (blue line, Figure 6.1a) and literature reports.^[135, 136] The XRD pattern also shows the presence of Ni_xCo_{1-x} LDH peaks as labelled in Figure 6.1a, which matches well with previous reports.^[98, 137] The FESEM image in Figure 6.1b shows that ZTO nanowires exist in the form of a dense forest. Figure 6.1c clearly shows that small nanoflakes form a uniform coating around the well-separated ZTO nanowires, a feature that is beneficial for electrolyte diffusion. On the other hand, dense nanowalls with obvious overlaps can be observed for Ni_xCo_{1-x} LDHs electrochemically deposited on stainless steel (Figure 6.1d). The size of

electrochemically deposited $\text{Ni}_x\text{Co}_{1-x}$ LDHs is over 500 nm as shown in Figure 6.1e.

Figure 6.1 (a) XRD diffraction peaks of the Ni/Co 1:1 sample (labelled peaks represent $\text{Ni}_x\text{Co}_{1-x}$ LDHs); (b) FESEM image of ZTO nanowires; (c) FESEM image of $\text{Ni}_x\text{Co}_{1-x}$ LDHs on ZTO nanowires, sample Ni/Co 1:1; and (d) FESEM image of $\text{Ni}_x\text{Co}_{1-x}$ LDHs deposited on stainless steel from a $\text{Ni}^{2+}/\text{Co}^{2+}=1:1$ solution (e) TEM image of $\text{Ni}_x\text{Co}_{1-x}$ nanoflakes deposited on stainless steel.^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

The nanostructure of the Ni/Co 1:1 material was studied in detail using TEM and

EDX, as shown in Figure 6.2. Uniform coating of ultrathin nanoflakes are deposited onto ZTO nanowires. The thicknesses of nanoflakes is approximately 10~15 nm (Figure 6.2a and Figure 6.2b). The HRTEM image in Figure 6.2c reveals the poor crystalline nature of $\text{Ni}_x\text{Co}_{1-x}$ LDHs on single crystalline ZTO nanowires (confirmed by SAED in Figure 6.2d). A random lattice fringe direction was observed within the $\text{Ni}_x\text{Co}_{1-x}$ LDHs coating shell. The ZTO nanowire exhibited a continuous lattice fringe in one direction, indicating the single crystalline nature of this nanowire. EDX was performed to further confirm the elemental composition of the heterostructure. Figure 6.2e presents the EDX spectrum of an entire heterostructure, clearly showing the presence of Ni and Co from $\text{Ni}_x\text{Co}_{1-x}$ LDHs, as well as Zn and Sn from the nanowire. The x in $\text{Ni}_x\text{Co}_{1-x}$ LDHs is estimated to be 0.6 by the relative ratio of Ni/Co. The carbon and copper signals are from the copper grid used for TEM sample holder. EDX line scanning further reveals the distributions of different elements. The scanning path is indicated as the white line in Figure 6.2f. Zn and Sn exhibit identical signals and are only present in the core part of the heterostructure, while the Co and Ni signals are present in the surrounding area.

Figure 6.2 (a) Low magnification TEM image of sample Ni/Co 1-1; (b) high magnification TEM image of sample Ni/Co 1-1; (c) HRTEM image of the sample Ni/Co 1-1; (d) select area electron diffraction pattern of ZTO nanowire; (e) EDS of sample Ni/Co 1-1; and (f) EDX line scan of sample Ni/Co 1-1. ^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

6.3 Electrochemical characterization of $\text{Ni}_x\text{Co}_{1-x}$ LDHs on ZTO nanowires

To further examine the electrochemical redox behavior of the $\text{Ni}_x\text{Co}_{1-x}$ -ZTO heterostructure, cyclic voltammetry (CV) was first performed in a three-electrode cell configuration. Figure 6.3a shows the CV curves of pristine ZTO on stainless steel and of $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO hybrid materials prepared from the solutions with different $\text{Ni}^{2+}/\text{Co}^{2+}$ concentration ratio. In contrast to pristine ZTO nanowires, which do not exhibit any electrochemical response, $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO hybrid material exhibits significant redox peaks from -0.1 to 0.3 V vs Ag/AgCl. The redox peak positions vary with the Ni ratio in the $\text{Ni}_x\text{Co}_{1-x}$ LDHs. With the increasing of Ni ratio in $\text{Ni}_x\text{Co}_{1-x}$ LDH, the anodic peaks shift to a higher potential, which has also been observed in previous literature reports.^[98] The redox peaks of $\text{Ni}_x\text{Co}_{1-x}$ LDHs mainly originated from the faradaic reactions of Ni and Co species in alkaline electrolyte, as shown in equations 6.1-6.3:^[98, 99]

The difference of redox peaks' positions is the result of the higher redox potential of the $\text{Ni}(\text{OH})_2$ species, which is approximately 0.4-0.5 V vs. SCE,^[139-141] while the

redox potential of Co(OH)_2 is approximately 0.1-0.3 V vs. SCE.^[142]

Figure 6.3 (a) CV curves of sample Ni/Co 1:2, sample Ni/Co 1:1, sample Ni/Co 2:1 and pure ZTO samples at 20 mV s⁻¹; (b) relationship between specific capacitance and discharge current density for sample Ni/Co 1:2, sample Ni/Co 1:1 and sample Ni/Co 2:1.^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

The specific capacitances (C_{sp}) of $\text{Ni}_x\text{Co}_{1-x}\text{-ZTO}$ heterostructures were examined by galvanostatic charge-discharge tests. The C_{sp} was calculated using equation 3.1.

Figure 6.3b shows the C_{sp} of each sample at different discharge currents. The Ni/Co 1:1 sample exhibited the highest C_{sp} of 1805 F g⁻¹ among the three samples at 0.5 A g⁻¹. The hybrid structured $\text{Ni}_x\text{Co}_{1-x}\text{-ZTO}$ material demonstrates a greatly improved specific capacitance compared with conventional electrochemically deposited materials^[143-145] and the nickel hydroxidenitrate-ZnO nanowire heterostructure.^[132] In addition to exhibit the highest C_{sp} among the three samples, the Ni/Co 1:1 sample demonstrated the best rate capability with a high C_{sp} retention of 74.2 % at a high current density of 80 A g⁻¹, superior to that of

previously reported hybrid materials.^[132, 146]

6.4 Relationship between Faradic reaction active sites and electrochemical deposition

The electrochemically active sites within $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructures were examined in detail by cyclic voltammetry. It is well established that in a diffusion-controlled electrochemical redox reaction, the peak current i_p is determined by the Randles-Sevcik equation: $i_p \sim n^{3/2} A C D^{1/2} \nu^{1/2}$,³³ where n is the number of electrons transferred in the redox reaction, A is the electrochemically active area in cm^2 , D is the diffusion coefficient of electrolyte in $\text{cm}^2 \text{ s}^{-1}$, C is the concentration of electrolyte in mol cm^{-3} and ν is the scan rate of the CV test. As the bulk diffusion coefficient and electrolyte concentration are the same for both $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructures and $\text{Ni}_x\text{Co}_{1-x}$ LDHs on stainless steel samples, the peak current i_p is mainly affected by the effective electrode area A . Figure 6.4a shows the relationship between different CV scan rate and corresponding anodic peak currents of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure Ni/Co 1:1 and $\text{Ni}_x\text{Co}_{1-x}$ LDHs. During discharge, the effective electrode area of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure is 1.82 times larger than that of $\text{Ni}_x\text{Co}_{1-x}$ LDH on stainless steel, as shown in Figures 6.4a. Considering both the $\text{Ni}_x\text{Co}_{1-x}$ LDH studied are nanosheets, the geometry change in the currently will definitely affect the redox active sites in these nanosheets. The TEM images of the two structures in Figure 6.1d and Figure 6.2b also confirm the highly ordered open structure of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO

heterostructure. It is reasonable to conjecture that a much larger active reaction area can be achieved by reducing the overlapping of nanoflakes during deposition on ZTO nanowires.

Figure 6.4 (a) The relationship between difference CV scan rates and anodic peak current densities fitted using the Randles-Sevcik equation for sample Ni/Co 1:1 (red) and Ni_xCo_{1-x} LDHs on stainless steel (black, prepared from a Ni²⁺/Co²⁺=1:1 solution). The total charge during deposition for both is 0.3 C; (b) the relationship between different CV scan rates and anodic peak current densities fitted by the Randles-Sevcik equation for Ni/Co 1:1 0.6 C (black) and Ni/Co 1:1 0.9 C (red).^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

The influence of the Ni_xCo_{1-x} LDH structure on ZTO nanowires was further studied by varying the deposition time for the Ni/Co 1:1 sample. The total charges during constant current deposition were set to 0.6 and 0.9 C, and these samples are labeled as Ni/Co 1:1 0.6 C and Ni/Co 1:1 0.9 C, respectively. Figure 6.4b shows dramatically decreases in the slope of the fitting curves, indicating that the active Faradic reaction sites for energy storage are reduced. It is well known that the active material mass also influences the peak discharge current. Hereby, the normalized Faradic reaction active area ratio between 0.3: 0.6: 0.9 C is C=5.19:

1.63: 1. Based on this result, we suggest that prolonged electrochemical deposition is not favourable for high-performance electrochemical applications. The active reaction sites are greatly reduced during prolonged deposition due to the stacking of LDHs (or other active materials in general cases of electrochemical deposition). There are several other disadvantages: 1) the facile electrolyte diffusion of the heterostructure is hindered because of the stacking of thick LDH layers; 2) the electron conduction is adversely affected by the increase in the insulating LDH layers; and 3) the electrochemical behavior deviates from the ideal diffusion-controlled scenario, as the standard deviation of the Randles-Sevcik fit increases in 0.6 and 0.9 C cases.

Thus, we attribute the superior electrochemical performance of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure to the benefits of conductive ZTO nanowires and the unique growth direction of $\text{Ni}_x\text{Co}_{1-x}$ LDH. In contrast to the direct electrochemical deposition of the active material on a flat substrate, the single crystalline ZTO nanowires in $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructures provide direct electron conduction paths from the nanowires to the current collector. In addition, the wide spacing between nanowires facilitates the diffusion of the electrolyte to the active material surfaces. Furthermore, high-aspect-ratio nanowires provide rigid and large area support to ultrathin $\text{Ni}_x\text{Co}_{1-x}$ LDH nanoflakes, and the nearly parallel growth of $\text{Ni}_x\text{Co}_{1-x}$ LDHs prevents overlap after electrochemical deposition. The exclusion

of binder and carbon black effectively reduces the internal resistance. All of the above factors contribute to the superior performance of this heterostructure material.

6.5 Asymmetric supercapacitor device

As discussed in Chapter 4.4.2, the optimization of mass ratio between cathode and anode is based on balancing the charge storage.^[127] Based on this principle, the mass ratio of $\text{Ni}_x\text{Co}_{1-x}$ LDHs/AC=0.23 is recommended for the asymmetric supercapacitor device developed here. A two electrode test in 2 M KOH electrolyte was first carried out to check the optimum working potential range of the device, as shown in Figure 6.5a. The CV curves show a distinct distortion and sharp increase of current at potential windows of 1.3 V and 1.4 V, which may result from the H_2 evolution at negative electrode in alkaline electrolyte. From Figure 6.5b, a C_{sp} around 90 F g^{-1} can be achieved from 1 V to 1.3 V, meanwhile, the C_{sp} reaches the maximum value of 92.6 F g^{-1} at 1.4 V. Considering both the requirement of high energy density and the safety of device, we take 1.2 V as the optimum working potential of our asymmetric device.

Figure 6.5 (a) CV curves of $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO/Activated carbon two electrode cell measured at different potential windows in 2M KOH electrolyte at a scan rate of 20 mV s^{-1} ; (b) specific capacitance of $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO/Activated carbon two electrode cell at a scan rate of 20 mV s^{-1} .^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

A prototype of asymmetric supercapacitor device comprising of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure (sample Ni/Co 1:1) as cathode and activated carbon as anode was fabricated in a Swagelok. Common filter paper (Advantech) was soaked in 2 M KOH electrolyte solution before use and was applied as the separator. Based on the optimized working potential, CV tests and galvanostatic charge-discharge tests were performed to investigate the electrochemical performance of the asymmetric device. Figure 6.6a presents different CV curves ranging from a scan rate of 2 to 200 mV s^{-1} . As can be observed, the CV curves show typical rectangular shapes without obvious distortion, indicating well defined capacitive behaviour of this device. The average specific capacitance of the device based on the CV test is expressed by equation 3.2.^{35, 36}

As shown in Figure 6.6b, at a scan rate of 5 mV/s, the device shows a high specific capacitance of 118.4 F g⁻¹. It is much higher than the previous reports on Co(OH)₂/AC asymmetric devices ^[147] and Co_{0.56}Ni_{0.44} oxide/AC (two-electrode test).^[148] Most importantly, the C_{sp} retains 40.9 % of the charge at 200 mV s⁻¹ (54.5 % at 100 mV s⁻¹), demonstrating an excellent rate capability.

Figure 6.6 (a) CV curves of Ni_xCo_{1-x} LDH-ZTO/activated carbon asymmetric supercapacitor at different scan rates from 2 to 200 mV s⁻¹ in 2 M KOH electrolyte; (b) specific capacitance vs. scan rate of the Ni_xCo_{1-x} LDHs-ZTO/activated carbon asymmetric supercapacitor device; (c) charge-discharge curves of Ni_xCo_{1-x} LDH-ZTO/activated carbon asymmetric supercapacitor at different current densities; and (d) 8 charge-discharge cycles of the Ni_xCo_{1-x} LDH-ZTO/activated carbon asymmetric device at 1.76 A g⁻¹. ^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

To further examine the performance of the device, galvanostatic charge/discharge tests were performed as shown in Figure 6.6c. The charge/discharge curves at different current densities show the typical symmetric triangular shape, indicating a balanced charge between cathode and anode (Figures 6.6c and 6.6d). The C_{sp} is at 0.88 A g^{-1} calculated to be 125.2 F g^{-1} , which is similar with the CV tests.

The cycling stability is an important requirement for a supercapacitor device. As shown in Figure 6.7, the capacitance of $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure/activated carbon asymmetric supercapacitor device retains 92.7 % capacity after 5000 consecutive CV cycles. The slight capacitance increase during the first 1000 cycles may be due to the variation of room temperature during testing.^[149] The long-term stability of the cell is superior compared with other asymmetric devices, such as $\text{Co}(\text{OH})_2/\text{AC}$,^[147] $\text{CNTs}/\text{MnO}_2//\text{CNTs}/\text{SnO}_2$,^[150] and $\text{LiTi}_2(\text{PO}_4)_3/\text{AC}$.^[151]

Figure 6.7 Cycling test of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO/activated carbon asymmetric device at 50 mV s^{-1} .^[138] Reproduced from Ref. 135 with permission from The Royal Society of Chemistry.

The energy density and power density of supercapacitor device are two major concerns for practical application. The relationship between energy densities and average power densities of the asymmetric supercapacitor device according to CV tests was calculated based on equation 3.4 and 3.5.^[101, 152]

The Ragone plot of the device is shown in Figure 6.8. A maximum energy density of 23.7 W h kg^{-1} at a power density of 284.2 W kg^{-1} can be achieved. The device can also achieve a high power density of 5.82 kW kg^{-1} at an energy density of 9.7 W h kg^{-1} . The energy density and power density of the asymmetric device shows superior performance comparing with previously reported devices, including $\text{MnFe}_2\text{O}_4//\text{LiMn}_2\text{O}_4$ (10 W h kg^{-1}),^[153] $\text{K}_{0.27}\text{MnO}_2//\text{AC}$ (25.3 Wh kg^{-1} at 140 W kg^{-1}),^[154] $\text{Fe}_3\text{O}_4//\text{AC}$ (7 W h kg^{-1}),^[155] $\text{Co}(\text{OH})_2//\text{USY}//\text{AC}$ (16.8 W h kg^{-1}),^[156]

$\text{Ni}(\text{OH})_2/\text{GNs}/\text{NF}//\text{AC}$ ^[157] and $\text{Ni-Co LDH}/\text{rGO}$.^[158] More detailed discussion of projective technology development will be in Chapter 9.

Figure 6.8 Ragone plot of the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO/activated carbon asymmetric device.

We attribute the improved electrochemical performance of the asymmetric device to the following points. (1) Conductive ZTO nanowires provide direct paths for electron conduction. In this case, the device shows a high rate performance. (2) The solid-liquid interfacial contact of electrode material and the electrolyte is greatly improved benefitting from the ultrathin $\text{Ni}_x\text{Co}_{1-x}$ LDH nanoflake structure. (3) ZTO nanowires provide rigid scaffolds to maintain mechanical strength, while the wide spacing between nanowires facilitates electrolyte diffusion. Additionally, the conductivity of ZTO may be further improved if the oxygen vacancy density is carefully tuned during synthesis. We also believe that the performance of the asymmetric device could be improved by making a fully sealed device.

6.6 Summary

In summary, a novel $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure was successfully synthesized through a combined CVD and electrochemical deposition method. Uniform coating of LDHs outside ZTO nanowires were achieved and can be controlled by simply varying the electrochemical deposition time. It is found that the Ni/Co ratio in the LDHs can greatly affect the specific capacitance of the hybrid material. Ni/Co=1:1 is the best ratio for high specific capacitance of hybrid material. The rate performance of LDHs is greatly improved by using conducting ZTO nanowires as the electron conduction channels.

Meanwhile, the intricate connection between heterostructure fabrication parameters on nanowires and the electrochemical active area was explored. The prolonged electrochemical deposition will cause the overlapping of LDH nanosheets and the electrochemical active area per mass will be greatly reduced. In addition, such one dimensional hybrid material design can also improve the electrochemically active material comparing with the conventional planar electrode. Such fundamental study provides the quantitative insight into the rational design of one dimensional hybrid material for electrochemical application.

Furthermore, an optimized asymmetric supercapacitor device was successfully fabricated based on the $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO heterostructure and activated carbon. The asymmetric device shows superior energy density and power density comparing with previous reports. More importantly, the asymmetric device

exhibits stable performance over a long period. These properties make this asymmetric device promising for future energy storage applications.

Chapter 7 Chemically etched layered hydroxides with enhanced pseudocapacitive performance

7.1. Motivation

In the previous chapters, we have discussed a few methods to enhance the overall electron conduction of the pseudocapacitive electrode by designing one dimensional nanostructures in Chapter 4 and Chapter 6, and by synthesizing composite material with reduced graphene oxide in Chapter 5. These methods either involve the creation of specific morphology of electrode material, or hybridizing active material with conducting component. In this sense, the electric conductivity of active material itself remains unchanged in these studies. In previous studies, the enhancement of the electric conductivity of material itself has never been demonstrated before. Therefore, it is of great value to investigate the possibility to achieve the better inherent electron conductivity of material itself.

As discussed in Chapter 2, LHs are a class of layered inorganic material with both M^{2+} and M^{3+} cations, meanwhile, the large lattice spacing along the c axis allows the facile electrolyte diffusion within the materials. However, the insulating nature of LHs always leads to a poor rate performance reported in the literatures.^[50, 98, 143]

From previous literatures, it is found that Co (III) can greatly enhanced the electrochemical performance of $Ni(OH)_2/NiO$.^[159-161] $Ni(OH)_2/NiO$ have been studied as the cathode materials for nickel-hydrogen battery. The original poor conductivity of $Ni(OH)_2/NiO$ can be overcome by addition of Co or $Co(OH)_2$ into

the electrode materials. During the electrochemical process, Co or Co (II) will be oxidized into Co (III), which has higher conductivity than $\text{Ni(OH)}_2/\text{NiO}$. Moreover, when Co(II) is chemically oxidized into Co (III), the resulting Co (III) will be more conductive than the electrochemically oxidized Co (III).^[159] Pralong et al. further pointed out that the chemical oxidization leads to nonstoichiometric $\text{Co}_x^{4+}\text{Co}_{1-x}^{3+}\text{OOH}_{1-x}$, which has elevated conductivity due to Co^{4+} ions (the band filling of $t_{2g}^5 e_g^0$ in Co^{4+}).

Inspiring by the previous studies, we propose a simple chemical etching of Ni-Co-Al layered hydroxides (LHs) in NaOH for enhanced pseudocapacitive performance in this chapter. The unique crystal structure of LHs makes it perfect for the study of transforming Co (II) to Co (III). Variable ratio between M^{2+} and M^{3+} in the hydroxide single layer can tolerant the change in the chemical state of cobalt and loss of Al without changing the phase of the material. Meanwhile, the chemical etching of Al from LHs can provide additional defects in the LHs, which may be helpful in the electrochemical reaction.

7.2 Structural characterizations

The Ni-Co-Al LHs were synthesized using a simple chemical bath reaction using metal nitrates and urea as reactants.^[96] The starting ratio of $\text{Ni}^{2+}/\text{Co}^{2+}$ was fixed at 1:2, while the ratio between M^{2+} ($\text{M} = \text{Ni}^{2+}$ and Co^{2+}) and Al^{3+} varied from 3:1, 5:1 to 7:1 respectively. The products were labeled as NCA 3-1, NCA 5-1 and NCA 7-1

accordingly. X-ray powder diffraction (XRD) was used to investigate the phase of the as-prepared samples. As shown in Figure 7.1a, sample NCA 3-1, NCA 5-1 and NCA 7-1 show typical diffraction peaks of (003) and (006) in layered hydroxides, which correspond well with previous studies.^[94, 96] The well-defined diffraction peaks with small widths are observed for all the samples, which indicate well crystallized products are obtained. The XRD patterns of chemically treated sample NCA 7-1T and sample NCA 7-1 are shown in Figure 7.1b. Despite the chemical treatment in the NaOH, sample NCA 7-1T preserves the characteristic diffraction patterns of LHs without any impurities. As it is known that aluminum hydroxide is an amphoteric hydroxide. Strong alkaline environment like NaOH solution will dissolve the $\text{Al}(\text{OH})_3$ from the LHs. Therefore, based on the evidence in Figure 1b, the loss of composition material will not lead to any phase change in the LHs.

Field emission scanning electron microscopy (FESEM) was carried out to investigate micro scale morphologies of LHs samples before and after chemical treatment. All the samples show a sheet like structure with several microns in lateral dimension (shown in Appendix Figure 2). Representatively, in Figure 7.1c and d, micro sheets of LHs can be observed in sample NCA 7-1. The lateral dimensions of sheet structures are not uniform, but the sizes are mostly larger than 1 micron. Meanwhile, the thickness of the sheet structure is estimated to be less than 50 nm, as shown in Figure 7.1d. The typical hexagonal shape sheet structure

of LHs is also observed as indicated in Figure 7.1d.^[94, 96] Figure 7.1e and f present the morphologies of sample NCA 7-1T. No obvious change in morphology can be observed after chemical etching of NaOH. Considering that the phase of treated sample remains unchanged, therefore it can be assure that the phase and micro morphologies of LHs won't be affected by NaOH treatment.

Figure 7.1 (a) XRD patterns of sample NCA 3-1, NCA 5-1 and NCA 7-1; (b) XRD

patterns of NCA 7-1 and NCA-7-1T; (c) and (d) SEM images of sample NCA7-1; (e) and (f) SEM images of sample NCA 7-1T.

Transmission electron microscope (TEM) was performed to check the nano-scale morphology changes of sample NCA 7-1 and NCA 7-1T. Under the low magnification TEM in Figure 7.2a, it is clearly that sample NCA 7-1 possesses a sheet like structure, which is the same with the observation under SEM. However, sample NCA 7-1 doesn't show a clear lattice fringes even under high magnification TEM, as shown in Figure 7.2b. As the LHs have abundant structural water and intercalated anions, the high energy electron beam may cause the damage and localized heat effect to the crystal structure. Selected area electron diffraction (SAED) was carried out to check the overall crystallinity of sample NCA 7-1. As shown in Figure 7.2c, the multiple diffraction rings indicate the crystalline nature of pristine LH sample. The sheet like structure of sample NCA 7-1T is also observed under low magnification of TEM in Figure 7.2d. Interestingly, the chemical etching of LHs leads to random defects on the micro sheet, as shown in Figure 7.2e. The defects resemble holes with random diameters. Due to the amphoteric property of aluminum hydroxide, it can be deduced that the defects come from the etching of Al from the LHs. Moreover, the crystal structure remains intact after NaOH treatment, while the lattice fringes can be clearly observed in Figure 7.2e. The crystalline nature of sample NCA 7-1T is also confirmed by SAED as shown in Figure 7.2f.

Figure 7.2 (a) and (b) TEM images of sample NCA 7-1 at different magnifications; (c) SAED pattern of sample 7-1; (d) and (e) TEM images of sample NCA 7-1T at different magnifications; (f) SAED pattern of sample 7-1T.

X-ray photoelectron spectroscopy (XPS) was performed to monitor the change in the surface chemical states of metal cations in the LHs. Figure 7.3a shows the Al 2p scan of the sample NCA 7-1. The presence of Al element signal originates from the Al^{3+} in the layered hydroxides. On contrary, as shown in Figure 7.3b, the Al signal is negligible after chemical etching, which suggests the removal of near surface Al element from sample NCA 7-1.

Figure 7.3 High resolution XPS spectra of (a) sample NCA 7-1 Al 2p; (b) sample NCA 7-1T Al 2p; (c) sample NCA 7-1 Co 2p; (d) sample NCA 7-1T Co 2p; (e) sample NCA 7-1 Ni 2p; (f) sample NCA 7-1T Ni 2p.

It is common that there is spin-orbit splitting of $2p_{1/2}$ and $2p_{3/2}$ components in the high resolution Co 2p spectrum.^[162] Both $2p_{1/2}$ and $2p_{3/2}$ components carry the

same element state information. Hence, we select Co 2p_{3/2} bands only with higher intensity for curve fitting. In sample NCA 7-1, only Co II (781.0 eV, Co(OH)₂) state can be deconvoluted, as shown in Figure 7.3c. The deconvolution of Co 2p_{3/2} scan in Figure 7.3d reveals that both Co II (780.5 eV, Co(OH)₂) and Co III (782.7 eV, CoOOH) are present in the sample NCA 7-1T. These binding energy positions correspond well with previous studies.^[162] The additional existence of Co III state suggests the partial oxidation of Co II into Co III state during the chemical etching. On the other hand, for Ni element, the binding energy of sample NCA 7-1 and NCA 7-1T all locate around 855.8 eV, which corresponds to the binding energy of Ni(OH)₂.^[163] Therefore, the Ni element remains intact during the chemical etching process in NaOH.

AFM tests were carried out to further elucidate whether the defects in the LHs are in the surface or penetrate through the micro sheets. As shown in Figure 7.4, there is no obvious height change along the line scan of AFM tip in both samples. Therefore, the surface defects of sample NCA 7-1T observed under TEM only locate in the surface few nanometers. From the crystallography view, di- and trivalent transition metal cations are the building blocks in the positively charge metal hydroxide unilaminars.^[96] The removal of Al³⁺ after NaOH treatment will be compensated by Co³⁺ transformed from Co²⁺. This will help to maintain the crystal structure of LHs.

Figure 7.4 (a) AFM image of sample NCA 7-1, blue line indicates the scan direction for surface height profile; (b) surface height profile of sample NCA 7-1; (c) AFM image of sample NCA 7-1T, blue line indicates the scan direction for surface height profile; (d) surface height profile of sample NCA 7-1T.

7.3 Electrochemical characterization

Cyclic voltammetry (CV) was first performed to investigate the influence of NaOH treatment on the electrochemical behavior of different samples. As shown in Figure 7.5a, the CV curves show two redox peaks from -0.1~0.55 V. The redox reactions originate from the faradic reaction between nickel/cobalt hydroxides with alkaline electrolyte.^[98, 99] The possible faradic reactions are listed in equation 7.1~7.3:

In Figure 7.5a, a smaller voltage difference of cathodic and anodic peaks in sample NCA 7-1T can be observed comparing with NCA 7-1. As for most pseudocapacitive reactions, the redox reaction is quasi-reversible. Therefore, chemically etched LH sample exhibits a faster reaction kinetic than pristine sample.^[53]

Galvanostatic charge-discharge tests were performed from 0~0.5 V vs Ag/AgCl to determine the specific capacitances of different samples. Equation 3.1 is used to calculate the specific capacitances of different samples. As shown in Figure 7.5b, all the samples after NaOH treatment show elevated specific capacitances at 20 A g⁻¹ compared with the pristine samples. The capacitance retention can be defined by the ratio between C_{sp} @ 20 A g⁻¹ and C_{sp} @ 1 A g⁻¹. Sample NCA 3-1T, NCA 5-1T and NCA 7-1T show the capacitance retention ratio of are 54.7 %, 64.9 % and 69 %, respectively. Meanwhile, the specific capacitances of pristine samples at 20 A g⁻¹ are far below 200 F g⁻¹, which indicates the poor rate performance due to the low intrinsic electric conductivity.

Figure 7.5 (a) CV curves of sample NCA 7-1 and sample NCA 7-1T tested in 2 M NaOH at a scan rate of 5 mV s⁻¹; (b) relationships between specific capacitances and current densities of different samples; (c) Nyquist plots of sample NCA 7-1 and NCA 7-1T, inset is the enlarged Nyquist plots at high frequency region; (d) relationships between equivalent series resistances (ESRs) and different samples.

From Figure 7.5b, it can be also observed that the specific capacitances increase with the decrease of Al content in the starting solution (Thus, C_{sp} : NCA 7-1(T) > NCA 5-1(T) > NCA 3-1(T)). Due to the inert nature of Al within the test potential window, lowering the ratio of Al in the LHs will increase the effective mass of

active material. Therefore, it will lead to a higher specific capacitance. However, the addition of Al during the synthesis is necessary. As shown in Appendix Figure 3a, the crystal phase of material synthesized without $\text{Al}(\text{NO}_3)_3$ does not belong to layered hydroxides. Meanwhile, nanowires can be observed to form on the surface of micro sheets as shown in Appendix Figure 3b. Hence, the addition of $\text{Al}(\text{NO}_3)_3$ is essential to preserve the phase of layered hydroxide.

Electrochemical impedance spectroscopy (EIS) tests were carried out to study the detailed electrochemical behavior of different samples. Nyquist plots of sample NCA 7-1 and sample NCA 7-1T are presented in Figure 7.5c. The first inset with real axis of sample NCA 7-1T is much smaller than that of sample NCA 7-1, which indicates a lower equivalent series resistance (ESR) of the electrode.^[100] Based on this evidence, we can conclude that the conductivity of LHs is promoted by the chemical treatment by NaOH. Hence, the improved conductivity of electrode material results in faster electrode kinetics as shown in Figure 7.5a. On the other hand, comparing the Nyquist plots at the low frequency region, the plot from sample NCA 7-1T is more parallel with the imaginary axis. It suggests that the chemical treatment helps to enhance the capacitive behavior and create better electrolyte diffusion.^[100] Based on the EIS test and previous structural information, it can be concluded that the chemically induced defects on LH sheets are beneficial for electrolyte diffusion. In addition, all the treated samples show greatly reduced

ESRs as shown in Figure 7.5d. It shows that NaOH treatment is universal to Co-Al LHs with various ratios.

Previous studies in nickel alkaline batteries have shown that the electrochemical performance can be improved by cobalt metal/cobalt hydroxide additives.^{[159, 160,}

^{164]} At the first test cycle, cobalt additives are oxidized into CoOOH, while after oxidation most CoOOH remains at the Co III state. Though the Co species could not be further reduced back to Co II, the Co III will act as a conductive wrapping for nickel material. Moreover, it is found by Pralong et al. that the chemical oxidized CoOOH would have a certain amount of Co IV state, which has higher conductivity than electrochemically oxidized CoOOH.^[159, 165] It is also found that the electric conductivity of chemically oxidized CoOOH (10^{-2} S cm⁻¹) was 3 orders higher than electrochemically oxidized CoOOH (10^{-5} S cm⁻¹).²⁵ Moreover, in our case, the sheet resistance of NaOH treated LHs pullet is measured to be 4.42×10^5 Ω sq⁻¹, which is one order higher than that of pristine NCA 7-1 pellet 1.64×10^6 Ω sq⁻¹. Thus, we propose the following explanation for the enhancement of conductivity of the samples after NaOH treatment. The NaOH chemical treatment introduces chemically oxidized CoOOH species in Ni-Co-Al LHs. Due to the higher conductivity of Co IV in the CoOOH, it helps to decrease the resistance of LHs. As a result, the chemically treated LHs are able to achieve lower ESRs with enhanced rater performances.

Figure 7.6 (a) relationships between specific capacitances and current densities of different samples; (b) discharge curves of sample NCA 7-1Tb at different current densities; (c) specific capacitances of sample NCA 7-1Tb at different current densities; (d) long term cycling test of sample NCA 7-1Tb at 5.0 A g⁻¹.

As Ni/Co ratio is found to be of great effect in the specific capacitance of LHs,^[166, 167] we use the sample NCA 7-1Tb (Ni/Co=1:1) and sample NCA 7-1Tc (Ni/Co=2:1) for further investigation. As shown in Figure 7.6a, sample with Ni/Co=1:1 ratio exhibits a high capacitance over 1200 F g⁻¹, showing the best value in the three samples. Hence, detailed electrochemical study of sample NCA 7-1Tb

is carried out. As shown in Figure 7.6b, the discharge curves from galvanostatic charge-discharge tests are used to calculate the specific capacitances of the sample NCA 7-1Tb. The specific capacitances of sample NCA 7-1 at different current densities are shown in Figure 7.6c. The specific capacitance can reach 1289 F g^{-1} at 1 A g^{-1} , while it maintains 738 F g^{-1} at 30 A g^{-1} . The capacitance retention is 57.3 % at 30 A g^{-1} , indicating a good rate performance. The long term cycling stability of sample NCA 7-1Tb is further examined by 2000 consecutive charge-discharge cycles at 5.0 A g^{-1} . The specific capacitance could maintain 82.2 % after the test. It suggests that the chemically treated layered hydroxide shows a good stability under high current density cycling. A thorough comparison of our results with previous literatures is shown in Table S1. It is obvious that NaOH treatment method provides a new route to elevate the electrochemical performance of layered hydroxides.

7.4 Summary

In this chapter, we propose a simple method to enhance the electrochemical performance of cobalt and aluminum containing layered hydroxides using NaOH as chemical treatment. The chemically treated samples are carefully characterized. It is found that the chemical etching would create defective LHs by dissolving the surface Al from original materials. This will be beneficial for the electrolyte diffusion during the electrochemical process. On the other hand, a certain amount

of Al is necessary for maintaining the phase of layered hydroxides.

It is also found that the chemical treatment also oxidizes Co II into Co III, which enhances the overall conductivity of the layered hydroxides. It can be observed that the ESRs of all the chemically treated samples are greatly reduced. As a result, the rate performances of LHs are greatly improved. Ni/Co=1:1 is the best ratio for achieving the best specific capacitance for Ni-Co-Al LHs. The specific capacitance can reach 1289 F g^{-1} at 1 A g^{-1} and 738 F g^{-1} at 30 A g^{-1} .

Chapter 8 Micro electrode design for enhanced supercapacitor performance

8.1 Motivation

In previous chapters, we focus on the strategies of enhancing the electron conduction during the electrochemical energy storage process. Apart from the electron conduction process, electrolyte diffusion from the bulk solution to the electrode surface (mass transfer process) is also an important process during electrochemical energy storage. Facilitating the mass transfer process will no doubt be helpful for achieving enhanced supercapacitor performance. Micro-supercapacitors, which have in-plane interdigitated finger electrode design with micro scale gap, are attracting increasing attention.^[82-84] Such design is believed to efficiently minimize the overall area, thickness and maximize the electrode utilization for the power sources.^[82, 168, 169] Nearly all the efforts to date are focusing on the fabrication of micro-supercapacitor on rigid SiO₂/Si substrate. The interdigitated finger electrode pattern can be fabricated through consecutive patterning and metallization processes. Nevertheless, silicon wafer based process limits the possibility in future flexible/wearable electronics applications. Meanwhile, there is no systematic study on the interdigitated electrode design on the electrochemical performance. Apart from device processing, the electrode material selection in current micro-supercapacitor mainly focuses on carbon materials, which usually have low device energy density^[82, 83, 168] and trade off the advantage of small area in micro-supercapacitor. Pseudocapacitive materials,

which store energy through Faradic redox reaction, are promising to elevate the energy density. Unfortunately, from the principle of electrochemistry view, the nickel-cobalt based metal oxide/hydroxides are not suitable for this symmetric micro-supercapacitor design. As discussed in the Chapter 2.2.1, the operation of a supercapacitor device requires the electrochemical reaction happened simultaneously at both cathode and anode. More specifically, as shown in Figure 8.1, when charging the device, the positive electrode will take in anion to get oxidized, while the negative electrode will consume cation to be reduced. Overall, the supercapacitor device is charged to higher voltage. If it comes to Ni/Co metal oxide/hydroxide based symmetric supercapacitor device, it is not the case. When one electrode is charge, consuming OH^- , the other side doesn't consume any counter cation to be reduced, which will inevitably causing irreversible side reaction such as the reduction of dissolved oxygen or else. Thus, it is not feasible to apply Ni/Co based oxide/hydroxide materials for the investigation of micro-supercapacitor.

Figure 8.1 Illustration of the supercapacitor device voltage during charge and discharge process.

There are limited reports using MnO_2 ,^[170] polypyrrole,^[171] and polyaniline^[84] have been investigated as electrode materials in micro-supercapacitors. However, previous works encounter different problems, such as poor rate performance,^[170] poor stability^[171] and low areal energy density.^[84, 170, 171] A flexible micro-supercapacitor with high performance is of great importance to meet the requirements for future application in flexible or wearable electronics.

Recent trend to develop functional miniaturized/portable electronic devices in flexible/wearable electronics^[172, 173] requires high performance, compact, lightweight and integratable energy storage/supply module to ensure functionality. Paper is a traditional fabric material which was invented thousands of years ago. This low cost, flexible and environmentally friendly material is the ideal substrate

for the development of flexible micro-supercapacitor. On the other hand, paper generally has large surface roughness, which is not favorable for the metallic interconnection and functional device fabrication.^[174] This makes it difficult for future integration of functional electronic counterparts on paper substrate. Parylene is a kind of commercially available polymer, which is widely used for insulation and moisture/chemical resistant coating.^[174, 175] Meanwhile, it is also demonstrated that parylene is helpful to reduce the surface roughness of paper substrate.^[174]

In this chapter, we present the design and fabrication of high performance all solid state flexible micro-supercapacitor on the parylene passivated paper. Three dimensional interconnected polyaniline-manganese oxide composite materials are electrochemically deposited on the interdigitated finger electrodes. The parameters of interdigitated electrode, such as aspect ratio and inter electrode gap, are investigated. With appropriate hard mask design, it is feasible to print micro-supercapacitor units repeatedly in large scale. It also makes it possible for future integration with functional electronics units on paper.

8.2 Structural characterization

The electrochemically deposited PANI-MnO_x composite materials on different interdigitated finger electrodes (refer to Table 3.1 in Chapter 3 for details) all show similar morphologies. Typical morphologies of sample on MC-6 (electrode length 5000 μm , electrode width 100 μm , inter electrode gap 100 μm , total area 0.08 cm^2)

prepared with 150 CV cycles (sample MC-6-150) are shown in Figure 8.2. Under low magnification in Figure 8.2a, the Au electrodes are fully covered with fluffy materials, while a clean area is observed between the electrode gaps. Closer examination in Figure 8.2b~d shows that the electrode material has a three dimensional interconnected porous structure which resembles the structure of coral. This composite material consists of dendritic PANI-MnO_x structures with random branches. The diameter of individual dendrite is over 100 nm. Coral like porous structure will be more accessible to electrolyte and will be more beneficial for electrolyte diffusion and material utilization. Meanwhile, the highly conductive PANI-MnO_x matrix is also beneficial for electrons conduction. In contrast, the absence of Mn²⁺ in the deposition precursor results in a dense PANI film with much less open structure, which is not favorable for fast electrolyte diffusion.

Figure 8.2 SEM images of PANI-MnO_x composite material on interdigitated finger electrodes, sample MC-6-150.^[176] Reproduced from Ref. 171 with permission from The Royal Society of Chemistry.

To further examine the structural information of the composite material, TEM image is shown in Figure 8.3a. Echoing the observation in SEM in Figure 8.2, the composite material also shows an interconnected dendritic structure under TEM. The chemical composition of the composite material is determined by TEM based EDX. The presence of Mn comes from the MnO_x in composite material, while S originates from the sulfate anion doping in PANI.^[177] C comes from both PANI and

TEM grid. Cu signal comes from the TEM grid and Si is from the TEM background signal, which is also detected at sample free location. To elucidate the crystallinity of the composite material, selected area electron diffraction (SAED) was performed in the area shown in Figure 8.3c. As shown in Figure 8.3d, there is no diffraction ring detected, which suggests that the PANI-MnO_x composite material is amorphous in nature.

Figure 8.3 (a) TEM image of PANI-MnO_x composite material, sample MC-6-150; (b) EDX spectrum of PANI-MnO_x composite material, sample MC-6-150; (c) TEM image of SAED area; (d) SAED image of PANI-MnO_x composite material.^[176] Reproduced from Ref. 171 with permission from The Royal Society of Chemistry.

Detailed investigation of the element chemical states in the amorphous PANI-

MnO_x composite material is carried out using XPS. The deconvolution of C 1s scan is shown in Figure 8.4a. The peaks at 284.7 eV and 286.3 eV can be attributed to are C=C and C-N from PANI,^[178] while C-O bonds (288.3 eV) may come from the impurities in aniline monomer. The fitting of N 1s scan in Figure 8.4b shows three peaks at 401.9 eV, 399.7 eV and 398.3 eV respectively, corresponding to nitrogen cationic radical (N⁺), benzenoid amine (-NH-) and quinoid amine (-N=).^[178-180] It is found that the PANI-MnO_x composite material mainly consists of nitrogen cationic radical and benzenoid amine, which indicates a high doping level of PANI and ensures a good electric conductivity.^[181] The binding energy of Mn 2p_{3/2} is 641.9 eV as shown in Figure 8.4c is between that of Mn³⁺ and Mn⁴⁺.^[182] Thus, we suggest that the PANI-MnO_x composite material consists of highly doped PANI with mixed manganese oxide with both +3 and +4 oxidation states. Meanwhile, the atomic ratio of Mn/N is 1:15 as calculated from the XPS study.

Figure 8.4 (a) C 1s scan and fitting of PANI-MnO_x composite material; (b) N 1s scan and fitting of PANI-MnO_x composite material; (c) Mn 2p scan and fitting of PANI-MnO_x composite material.^[176] Reproduced from Ref. 171 with permission from The Royal Society of Chemistry.

8.3 Electrochemical characterization

8.3.1 Interdigital finger electrode design optimization

Despite the previous reports on micro-supercapacitor, the influences of interdigitated finger electrode design on device performance are seldom addressed specifically.^[82, 83] Here, we first investigate the optimum design of the aspect ratio of interdigitated finger electrode and inter-electrode gap distance before further electrochemical deposition optimization. Micro-electrode patterns MC-1, MC-2

and MC-3 (refer to Table 3.1 in Chapter 3) were deposited with PANI-MnO_x from -0.2 V ~0.9 V for 100 cycles, and the samples after deposition were labelled as sample MC-1-100 (electrode length 5000 μm, electrode width 500 μm, inter electrode gap 300 μm, total area 0.15 cm²), MC-2-100 (electrode length 5000 μm, electrode width 300 μm, inter electrode gap 300 μm, total area 0.15 cm²), and MC-3-100 (electrode length 5000 μm, electrode width 100 μm, inter electrode gap 300 μm, total area 0.15 cm²) respectively. The optimum operation window for the symmetric devices is determined to be 0~0.7 V as shown in Figure 8.5. Higher operation window shows distinct distortion of CV curves in Figure 8.5a and decrease in coulombic efficiency in Figure 8.5b.

Figure 8.5 (a) CV curves of sample MC-1-100 from 0~0.7 V and 0~0.8 V respectively; (b) charge-discharge curves of sample MC-1-100 from 0~0.7 V and 0~0.8 V respectively.

The specific areal capacitances (C_{area}) of sample MC-1-100, MC-2-100 and MC-3-

100 at various current densities are determined by galvanostatic charge-discharge test and are shown in Figure 8.6a. They can be calculated from the discharge curve after IR drop as in Equation 8.1.

$$C_{area} = I\Delta t / A\Delta V \text{ (eq. 8.1)}$$

Where I is the current, Δt is the discharge time after IR drop, A is the total area of the interdigitated finger electrode array and ΔV is the potential window of symmetric capacitor. Sample MC-3-100 shows the highest $C_{area} = 32.79 \text{ mF cm}^{-2}$ at 0.1 mA cm^{-2} with 82.9% retention of capacity at 10 mA cm^{-2} . Sample MC-1-100 shows nearly no degradation of capacity at high current density. Such high rate performance of micro-supercapacitor is due to the short diffusion paths using the interdigitated finger electrode design.^[82-84] As the total areal and electrode gap of pattern MC-1, MC-2 and MC-3 are the same, the increase of C_{area} may be due to the difference in the deposited active material masses caused by the different aspect ratios of individual finger electrode.

It is widely accepted that during electrochemical experiments, the electrode geometry will influence the flux of mass diffusion of electrolyte.^[183-185] Our results suggest that different design of finger electrodes would have varying mass diffusion around the patterned gold electrodes during electrochemical deposition. The high aspect ratio interdigitated finger electrodes with higher pattern density lead to a higher mass loading at the same electrochemical deposition condition.

To further elucidate the electrochemical behavior caused by electrode design, the electrochemical impedance (EIS) studies of sample MC-1-100, MC-2-100 and MC-3-100 are. In Figure 8.6c, it can be clearly observed that sample MC-1-100 has the smallest intercept with the real axis, which means the lowest equivalent series resistance (ESR) among all three samples.^[54] The difference in ESR may attribute to the increase in ohmic resistance induced by the decrease in electrode width ($R=\rho l/A$). Thus, sample MC-1-100 presents the best rate performance (Figure 8.6a). On the other hand, all samples show nearly 90° linear curves at low frequency regions, which indicate an ideal capacitor behavior.^[186, 187] Considering both specific areal capacitance and rate performance, we decide to use 100 μm electrode width for further structure optimization.

Figure 8.6 (a) relationships between specific areal capacitances and current densities of sample MC-1-100, MC-2-100 and MC-3-100; (b) relationships between specific areal capacitances and current densities of sample MC-4-100, MC-5-100; (c) Nyquist plots of sample MC-1-100, MC-2-100 and MC-3-100; (d) Nyquist plots of sample MC-4-100 and MC-5-100; (e) Bode plots of sample MC-

1-100 and MC-5-100. ^[176] Reproduced from Ref. 171 with permission from The Royal Society of Chemistry.

Interdigitated electrode patterns MC-4 (electrode length 5000 μm , electrode width 100 μm , inter electrode gap 500 μm , total area 0.08 cm^2), MC-5 (electrode length 5000 μm , electrode width 100 μm , inter electrode gap 300 μm , total area 0.08 cm^2) and MC-6 (electrode length 5000 μm , electrode width 100 μm , inter electrode gap 100 μm , total area 0.08 cm^2) are used for electrochemical deposition at the same condition described above. The samples are labelled as MC-4-500, MC-5-300 and MC-6-100, respectively. The sample MC-6-100 shows short circuit for the two electrode test, which indicates the connection between two adjacent electrodes. It also suggests that the mass diffusion during deposition is influenced by the geometry design of interdigitated finger electrode. Samples MC-4-500 and MC-5-300 work well and the electrochemical performances are shown in Figure 8.6b. MC-4-500 and MC-5-300 present specific areal capacitances of 36.4 mF cm^{-2} and 33.5 mF cm^{-2} at 0.1 mA cm^{-2} respectively, while sample MC-5-300 shows much better rate performance. As shown in Figure 8.6d, sample MC-4-500 shows more obvious 45° Warburg resistance curve comparing with sample MC-5-300.^[188, 189] The improved rate performance is realized by reduced electrode gap in pattern MC-5. The smaller electrode gap leads to shortened diffusion length for electrolyte ions. It will facilitate the electrolyte diffusion during the electrochemical test.

Bode plots of sample MC-1-100 and MC-5-100 are shown in Figure 8.6e to further understand the response characteristic of micro supercapacitor. The frequency response of a supercapacitor can be compared using characteristic frequency f_0 where the frequency corresponds to the phase angle at -45° .^[83, 190] The relaxation time constant ($\tau_0=1/f_0$) of the device is defined as the minimum time for fully discharging the device with above 50 % efficiency. The corresponding frequency f_0 is where the resistive and capacitive impedance are equal.^[83, 190] As shown in Figure 8.6e, sample MC-5-100 ($f_0=10.16$ Hz, $\tau_0=98$ ms) shows the better frequency response compare to sample MC-1-100 ($f_0=6.46$ Hz, $\tau_0=154.7$ ms). This indicates a better frequency response of micro-supercapacitor can be achieved by using high aspect ratio and small inter-electrode gap design.

In summary, the optimum strategy for interdigitated electrode design for micro-supercapacitor is to fabricate high aspect ratio electrode with small inter-electrode gap. 300 μm electrode gap with 100 μm electrode width (pattern MC-5) is the optimum electrode design for PANI-MnO_x composite material micro-supercapacitor. Such design is able to ensure a high specific areal capacitance, high rate performance as well as high frequency response.

8.3.2 High performance flexible PANI-MnO_x symmetric micro-supercapacitor

Knowing the optimum interdigitated finger electrode design, the electrochemical deposition is further optimized based on pattern MC-5. It is found that 200 cycles

CV deposition shows the best specific areal capacitance. The sample is labelled as MC-5-200 and it is tested in PVA-H₃PO₄ gel electrolyte. The corresponding electrochemical test results are shown in Figure 8.6. The CV curves of sample MC-5-200 in Figure 8.7a all show typical rectangular shapes at different scan rates, which indicate a typical capacitor performance with good rate capability.^[189] In Figure 8.7b, the charge-discharge curves of sample MC-5-200 all show well symmetric triangular shapes indicating good capacitor behavior.^[54, 167] The specific areal capacitances calculated from charge-discharge tests are 94.73 mF cm⁻² at 0.1 mA cm⁻², while maintain as high as 71.43 mF cm⁻² at 1.0 mA cm⁻² (73.1 % retention). The capacitance loss at high current density is much higher than tested in aqueous electrolyte. This may be due to the slower ion diffusion in gel electrolyte as demonstrated in Figure Appendix 4. As shown in the Nyquist plots, sample tested in gel electrolyte shows obvious Warburg resistance in the high frequency region.^{28, 29} Despite the relatively slow electrolyte diffusion in gel electrolyte, the devices still present a high areal capacitance compared with previous reports.^[84] We also want to highlight the importance of MnO_x in enhancing the areal capacitance of micro-supercapacitor device. As shown in Figure Appendix 5, symmetric device using PANI only has a specific areal capacitance of 34.1 mF cm⁻², which is 36 % that of composite electrode material. The pseudocapacitive behaviors of both MnO_x and PANI within the same potential

window ensure the elevated areal capacitance of symmetric device.^[191, 192]

Meanwhile, the capacitive response of micro device is much better than that of conventional PANI-MnO_x device fabricated using carbon cloth.^[192]

Long time cycling is another important parameter in practical application. The cycling test for our device is performed at a current density of 0.5 mA cm⁻², as shown in Figure 8.7c. The sample MC-5-200 only experiences 7.5 % capacitance loss after 1000 cycles, showing a good cycling stability. The energy and power densities are further calculated based on Equation 8.2 and Equation 8.3:^[55, 188]

$$E_{area} = C_{area} V^2 / 2 \text{ (eq.8.2)}$$

$$P_{area} = E_{area} / t \text{ (eq.8.3)}$$

where C_{area} is the specific areal capacitance, V is the working potential, t is the discharge time. The Ragone plot of sample MC-5-200 is shown in Figure 8.7d. Our device shows a high energy density of 12.7 mWh cm⁻² at a power density of 69.8 mW cm⁻², while the energy density maintains as high as 9.7 mWh cm⁻² at a power density of 6980 mW cm⁻². Such values are the best reported for micro-supercapacitor so far, which are much higher than the reports by Pech et al. (carbon onion, 5 mWh cm⁻² at 500 mW cm⁻²),^[82] Wang et al. (PANI, 7.46 mWh cm⁻² at 144 mW cm⁻²)^[84] and Beidaghi et al. (CNT-rGO, 0.708 mWh cm⁻² at 3614.8 mW cm⁻²).^[83] Our device hereby is suitable for high energy and power storage and delivery in microscale systems, such as active radiofrequency identification (RFID) tags,

wireless sensors, and self-powered devices.

Figure 8.7 (a) CV curves of sample MC-5-200 tested in gel electrolyte at different scan rates; (b) charge-discharge curves of sample MC-5-200 tested in gel electrolyte at different current densities; (c) cycling test of sample MC-5-200 tested at 0.5 mA cm⁻² in gel electrolyte; (d) Ragone plot of sample MC-5-200 in gel electrolyte. ^[176] Reproduced from Ref. 171 with permission from The Royal Society of Chemistry.

Flexibility is a crucial problem for the application in future flexible and wearable electronics. One advantage in our device is that paper substrate widely available and naturally flexible. To demonstrate the flexibility of paper based micro-

supercapacitor, the sample MC-5-200 is bent onto a quartz tube with a diameter of 1.55 cm. The electrochemical tests are further carried out and the results are shown in Figure 8.8. The CV curves of sample MC-5-200 exhibits well defined rectangular shapes at bent state in Figure 8.8a, indicating a negligible influence of bending on the supercapacitor behavior. Meanwhile, the area of CV curve at a bent radius of 0.75 cm is slightly smaller than that of normal states, which suggests a slight capacitance decrease at bent state. The specific capacitances at bent state are calculated from charge-discharge tests as shown in Figure 8.8b and c. In Figure 8.8b, the capacitance at bent state is 98.7 % that of normal state. While in Figure 8.8c, the nearly similar rate capabilities suggest that the fast electrochemical reaction and electrolyte diffusion are not significantly affected by bending. These results strongly prove a good flexibility of our paper based micro-supercapacitor.

Figure 8.8 (a) CV curves of sample MC-5-200 at normal and bent states at a scan rate of 10 mV s^{-1} ; (b) charge-discharge curves of MC-5-200 at normal and bent states at a current density of 0.1 mA cm^{-2} ; (c) relationships between specific areal capacitance and current densities sample of MC-5-200 at normal and bent states.

8.4 Summary

In summary, we design a flexible micro-supercapacitor device and study the effects of interdigitated electrode design on the electrochemical performance. Based on in-depth electrochemical studies, we suggest that high aspect ratio interdigitated finger electrode with small inter-electrode gap is favorable design for high performance micro-supercapacitor. Flexible micro-supercapacitor is successfully fabricated using 3D PANI-MnO_x as electrode material on parylene passivated

paper substrate.

The outstanding electrochemical performance of flexible PANI-MnO_x symmetric micro-supercapacitor can be attributed to the following few points: 1) paper substrate is naturally flexible; 2) in plane micro-supercapacitor design ensures good mechanical properties by eliminating the conventional sandwich device structure; 3) interdigitated finger electrode design ensures fast electrolyte diffusion and provides a high rate performance; 4) 3D interconnected PANI-MnO_x coral like electrode material ensures high electrochemical energy storage.

Based on the optimum design, symmetric device is able to achieve a high energy density of 12.7 mW cm⁻² at a power density of 69.8 mW cm⁻², while the energy density maintains as high as 9.7 mWh cm⁻² at a power density of 6980 mW cm⁻². The excellent flexibility of our device is demonstrated as well. Such flexible micro-supercapacitor on a paper is promising for future flexible and wearable electronics application. Such values are the best reported for micro-supercapacitor so far, which are much higher than the symmetric micro supercapacitors reported, such as carbon onion (5 mWh cm⁻² at 500 mW cm⁻²), CNT-rGO (0.708 mWh cm⁻² at 3614.8 mW cm⁻²) and PANI (7.46 mWh cm⁻² at 144 mW cm⁻²). Our device hereby is suitable for high energy and power storage and delivery in microscale systems, such as active radiofrequency identification (RFID) tags, wireless sensors, and self-powered devices.

Chapter 9 Conclusion and Future Recommendations

9.1 Conclusion

In this dissertation, we focused on the investigation of different strategies to enhance the electrochemical performance of pseudocapacitive supercapacitor electrodes/devices. The core philosophy is to facilitate the main factors that restrict the electrochemical kinetic process, such as electrode conductivity and mass transfer. The corresponding strategies are: 1) constructing one dimensional electrode nanostructure of active material; 2) hybridization of active material with conducting additives; 3) enhancing the electric conductivity of pristine active material; 4) creating facile mass transfer by novel device configuration. Based on these strategies, several physical/electrochemical factors are found to be crucial in achieving high electrochemical performance, such as high aspect ratio nanowire structure, the effective electrochemical active area, fast surface faradic reaction, and high aspect ratio design of interdigitated electrodes.

In Chapter 4, a new method to prepare high-aspect ratio porous polycrystalline $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowires grown on the current collector was proposed. It is found that the growth of nanowire structure was governed by crystallization-dissolution-recrystallization process. Benefited from the intrinsic high electric conductivity ($10^{-2} \text{ S cm}^{-1}$), the one dimensional nanostructure not only offers high electron conduction channels for the redox reaction, but also creates abundant spacing for

electrolyte transport. Meanwhile, the small nanocrystals (~ 10 nm) ensure small ion diffusion length. As a result, specific capacitance as well as rate capability of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ electrode material are greatly enhanced comparing with the previous studies. Meanwhile, the prototype asymmetric supercapacitor device shows high energy density with high power density.

In Chapter 5, to fully exploit the merit of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$, we further enhanced the rate performance of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ by hybridizing with reduced graphene oxide. It is found that the unique decomposition of intercalated anion in the layered hydroxide precursor leads to ~ 5 nm $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals as well as porous structure. As a result, faster surface faradic reaction is $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is achieved. Meanwhile, the reduced graphene oxide also provides a conductive matrix for $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanocrystals. Overall, the pseudocapacitive behavior of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ is greatly enhanced due to readily available faradic charge storage.

In Chapter 6, we enhanced the electrochemical performance of Ni-Co layered hydroxides by making Ni-Co LDH- Zn_2SnO_4 nanowire 1D hybrid materials. The impact of hybrid nanostructure on electrochemically active area is discovered. The electrochemically active area of Ni-Co layered hydroxides is found to be greatly enhanced using one dimensional nanowire as current collector. Meanwhile, the electrochemically active area per mass will be reduced by long term electrochemical deposition. The uniform thin coating of layered hydroxides on the

Zn_2SnO_4 nanowire facilitates the material utilization, while the conducting Zn_2SnO_4 nanowire offers low electrode resistance. Overall, the Ni-Co layered hydroxides- Zn_2SnO_4 nanowire hybrid material achieves a superior specific capacitance and rate performance with excellent cycling stability.

In Chapter 7, we provided a simple chemical treatment approach for Ni-Co-Al layered hydroxides to enhance the electric conductivity of layered hydroxides for the first time. The intrinsic low electric conductivity is overcome by introducing higher conductive Co III into the layered hydroxides without any phase change. In addition, surface defects are created by Al etching from the pristine layered hydroxides, which promotes better electrolyte diffusion. As a result, enhanced rate performances of layered hydroxides materials are obtained over all the pristine samples.

In Chapter 8, we proposed planar supercapacitor device architecture based on interdigitated finger electrodes to promote the overall rate performance of supercapacitor device. In addition, a flexible micro-supercapacitor device on paper was fabricated for the first time. We also carried out systematically investigation on the influence of electrode design on micro-supercapacitor device performance. MnO_x -PANI composite material was selected for the proof of concept. The high aspect ratio design of individual finger electrodes and small inter-electrode gap are critical for obtaining higher rate performance, due to faster mass transfer process.

Additionally, the flexibility of the micro device was also demonstrated.

Overall, in our study, the Ni-Co based hydroxide/oxide materials could provide high specific capacitances over 1000 F g^{-1} with superior rate capability. As a result, in Figure 9.1a, the asymmetric devices in our study all shows superior energy densities at high power densities (over 1 kW kg^{-1}) comparing with those Ni-Co oxide//AC,^[107] $\text{Co}_3\text{O}_4\text{@Ni(OH)}_2\text{//rGO}$,^[108] $\text{Co(OH)}_2\text{//USY//AC}$,^[156] $\text{Ni(OH)}_2\text{//GNs/NF//AC}$ ^[157] and Ni-Co LDH//rGO.^[158] Until recently, a significant improvement of energy density was made by Wang et al. in their Ni-Co oxide//PANI derived carbon asymmetric supercapacitor (2014).^[109] The advantage of PANI derived carbon is to provide addition redox reaction originating from N group. Such improvement of charge storage ability in carbon will help to enhance the overall energy density in device.

On the other hand, when assembled into asymmetric supercapacitor device, the energy density and power density of Ni-Co based hydroxide/oxide//activated carbon systems are among the best few in the current available literatures (shown in Figure 9.1b),^[193-205] especially for our $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire material. The higher device operation window of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire//AC device leads to higher energy density. Meanwhile, the super high rate capability of Ni-Co LDH/ZTO hybrid material is beneficial for the high experimental power density. Thus, we are optimistic to predict that future Ni-Co based asymmetric supercapacitor device will

be able to reach an energy density higher than 80 Wh kg^{-1} with optimized material selection and design.

Figure 9.1 (a) Ragone plot of the Ni-Co based asymmetric supercapacitor devices (line plots are our works); (b) Ragone plot of the aqueous electrolyte based asymmetric supercapacitor devices (line plots are our works).

9.2 Future Recommendations

Based on the studies in present research, the future work for high performance supercapacitor/energy storage devices may focus on the following several directions:

- 1) Design and fabrication of three dimensional current collectors for micro-device (3D energy storage).
- 2) Developing new energy storage chemistry for enhanced energy density.

3) Developing flexible and stretchable supercapacitor electrode.

The extensive studies of electrode materials based on nanotechnology have shown greatly potential for achieving high electrochemical performance in the future practical applications. As demonstrated in Chapter 8, the micro-device configuration with effective mass transfer and high aspect ratio current collector is of great significance in the revolution of next generation energy storage device. The philosophy can be illustrated in Figure 9.2^[206] 3D electrode design breaks down the conventional planar current collector into much higher surface area current collectors. The combination of interdigitated electrode design with 3D electrode will greatly enhance the mass transfer during the electrochemical process. The additional one dimensional concentric tube will facilitate the electron conduction as well as support higher active material mass. Such design will be beneficial to achieve superior rate performance of the device. Specifically, future work may be focused on developing aligned nanowire arrays of electrodes, such as gold, nickel, or ITO. Additionally, the 3D positive and negative electrodes need to be concisely aligned to form a 3D cross-finger configuration.

Figure 9.2 Schematic of concentric tube structured 3D energy storage device. T. S. Arthur, D. J. Bates, N. Cirigliano, D. C. Johnson, P. Malati, J. M. Mosby, E. Perre, M. T. Rawls, A. L. Prieto, B. Dunn, Three-dimensional electrodes and battery architectures, MRS Bulletin 2011, 36, 523. Reproduced with permission.

Apart from achieving high rate performance of the device, another important aspect is to achieve higher energy density. Currently, most energy storage device uses single phase electrolyte, such as organic and aqueous electrolyte. Though promising performance and cycling stability have been demonstrated for various materials in either electrolyte, the limitation of single phase electrolyte is obvious. As shown in Figure 9.3 though Li-ion battery systems offer high operation voltage, the safety and energy density are inferior to that of the Ni-MH battery. However, Ni-MH battery in aqueous electrolyte has low working voltage. Recently, a new strategy involving the utilization of both organic and aqueous electrolyte have evolved using LISICON as Li^+ conductor as well as separator in the binary electrolyte system.^[207] This new device configuration uses both Li^+ battery and Ni-

MH battery chemistry, which provides both high energy density and device voltage. It offers an alternative direction for developing next generation energy storage device. The utilization of electrochemistry in different electrolyte systems will be advantageous. The possible research directions would be: 1) developing high performance ionic conducting solid to be used in the junction of organic and aqueous electrolyte; 2) developing high capacity and high rate capability pseudocapacitive materials suitable for organic electrolyte systems, such as TiO_2 , V_2O_5 , polyaniline and so on.

Figure 9.3 Schematic illustrations of energy storage systems in different electrolytes. Reprinted (adapted) with permission from (Rechargeable Ni-Li Battery Integrated Aqueous/Nonaqueous System). Copyright (2009) American Chemical Society.

Flexible and wearable devices markets are big growing markets with great potential. Pioneering devices, such as google glasses, Samsung gear, and Nike⁺

bracelet, have attracted a lot of attentions. The power sources right now are still based on traditional design. There are several on-going research of prototype intrinsic flexible/stretchable electronics devices.^[172, 173, 208, 209] Powering future flexible and wearable devices require advanced design and development of current energy storage device with specific features, such as light weight, flexible, compact design and highly integratable. The possible research directions would be: 1) developing flexible supercapacitor electrodes based on graphene, carbon nanotube or metallic nanowires; 2) developing supercapacitor electrodes on elastomers, such as polydimethylsiloxane.

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Appendix

Cyclic voltammetry

Cyclic voltammetry (CV) is a type of potentiodynamic electrochemical measurement. In a CV test, the working electrode potential is changed linearly versus time. Generally, CV test is used to study the electrochemical properties of an analyte in solution. When the working electrode potential is increasing, the electrode is oxidized, this process is called anodic process. The CV peaks during this process are called anodic peaks. While, the working electrode potential is reducing, it is called cathodic process. The CV peaks occur during this process are cathodic peaks.

Principle of scan rate dependant analysis:

1. Experiment setup

The experiments were carried out using cyclic voltammetry at various scan rates. Electrochemical working station (Autolab PGSTAT 30 potentiostat) was utilized for providing electrical signals and recording data. The electrochemical tests of various samples were conducted using a three electrode system in appropriate electrolyte using Ag/AgCl in 3 M KCl as the reference electrode and Pt plate as counter electrode.

2. Data manipulation

a. Trasatti procedure

The total charge stored during cathodic or anodic CV process could be divided into two portions: $Q_{\text{total}} = Q_{\text{inner}} + Q_{\text{outer}}$. The inner charge is diffusion controlled $Q_{\text{inner}} \sim \nu^{-1/2}$, which is more difficult as scan rate increases. Whereas, the outer charge storage Q_{outer} is assumed not dependent on scan rate. Thus there gives the relationship of charge stored with scan rate:

$$Q_{\text{total}} = k\nu^{-1/2} + Q_{\text{outer}}$$

When scan rate $\nu \rightarrow \infty$, Q_{outer} is the charge stored instantly at the outer and easily accessible surface, which equals with Q_{outer} . On the other hand, when scan rate $\nu \rightarrow 0$, the access to all electrochemically active sites is fully available and Q_{total} includes both inner and outer charge. To calculate Q_{outer} , a set of CV experiments have been conducted. The Q_{outer} can be derived from the extrapolated value of Q_{total} (either cathodic/reduction or anodic/oxidation process) vs $\nu^{-1/2}$.

b. Randles-Sevcik equation

For a reversible electrochemical reaction, the anodic or cathodic peak current value conforms to the linear relationship: $i_p = 2.69 \times 10^5 n^{3/2} ACD^{1/2} \nu^{1/2}$ at 25 °C, where n is the number of electrons transferred in the redox reaction, A is the electrochemically active area in cm^2 , D is the diffusion coefficient of electrolyte in $\text{cm}^2 \text{s}^{-1}$, C is the concentration of electrolyte in mol cm^{-3} and ν is the scan rate of the CV test. By plotting the peak anodic/cathodic currents and CV scan rates, it is able to uncover the following kinetics factors: number of electron transfer, electrochemically active area or ion diffusion coefficient. Specifically in Chapter 6, the ratio between different samples regarding electrochemically active surface area can be deduced from the slope of i_p vs ν .

Figure 1. SEM images of (a) low magnification and (b) high magnification $\text{NiCo}_2\text{O}_4/\text{rGO}$ composite material prepared without SDS in starting solution.

Figure 2. SEM images of (a) sample NCA 3-1; (b) sample NCA 5-1; (c) sample 7-1; (d) sample 3-1T; (e) sample 5-1T; (f) sample 7-1T. The micro structure of layered hydroxides are persevered after NaOH treatment as shown in Figure 3d~e.

Figure 3. (a) XRD pattern of sample prepared with $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ as metal source only (the labeled peaks belong to LDH, while the star labeled peaks belong to the Ni-Co carbonate hydroxides); (b) SEM image of sample prepared with $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ as metal source only.

Figure 4. Nyquist plots of sample MC-5-200 tested in aqueous electrolyte and gel electrolyte.

Figure 5. (a) CV curve of pure PANI symmetric device prepared using the same condition with sample MC-5-200, tested in 1 M H_2SO_4 ; (b) relationships between specific areal capacitance and current density of pure PANI device, tested in 1 M H_2SO_4 .

Publication list

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