Synthesis and study of transition metal oxides for supercapacitor applications

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Synthesis and Study of Transition Metal Oxides for Supercapacitor Applications

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Abstract

Supercapacitor which bridges conventional capacitor and battery in the energy storage field, is gaining increasing importance due to its higher power density, good energy density, fast charge/discharge rate, plus its excellent cyclic stability. In the present work, transition metal oxide based supercapacitors, such as MnO_2 , $\text{Co}(\text{OH})_2$, and surfactant CTAB modified MnO_2 ($\text{MnO}_{2\text{CTAB}}$), as well as multilayer hybrid films (graphene/ MnO_2 , and graphene/ $\text{MnO}_{2\text{CTAB}}$), have been deposited on stainless steel substrates by electrochemical deposition method. Their crystal structures, morphologies and supercapacitor performances have been systematically studied. The effects of synthesis approaches on the structures and morphologies of transition metal oxides, as well as the correlation between structure/morphology and the corresponding supercapacitor performances are explored. In addition, the enhancement mechanisms of transition metal oxides based supercapacitors are discussed.

Our results have shown that structural directing agent in the electrochemical deposition of transition metal oxides can significantly affect the nucleation formation and growth process, the resulted microstructure, morphology and supercapacitor performance have been systematically discussed. The CTAB modified MnO_2 shows 3-D porous network structure with very thin nanosheet, which is much smaller than that of MnO_2 prepared without the presence of CTAB, besides, the as obtained MnO_2 prepared in presence of CTAB shows larger pore size and more uniform surface morphology. It is also found that the concentration of CTAB may also affects the localized electrokinetic properties near deposition surface and eventually influences the morphology and supercapacitor performance of as prepared thin film electrode. Result shows that MnO_2 prepared in presence of 1wt. % CTAB has the best performance, a capacitance of 359 F g^{-1} at 1 A g^{-1} is obtained, which is larger than 297 F g^{-1} of MnO_2 . More remarkable is that MnO_2 prepared in presence of 1wt. % CTAB is able to remain 100% of the initial capacitance after 1000 cycles of charge/discharge test at a current density of 10 A g^{-1} . When the same idea of using structure directing agent to modify structure and morphology is applied to prepare $\text{Co}(\text{OH})_2$ for supercapacitor application, NMP modified $\text{Co}(\text{OH})_2$ electrode has shown similar positive result. With 20 V% addition of NMP in the pre-deposition solution, the resulted $\text{Co}(\text{OH})_2$ has much thinner nanosheet

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thickness and more uniform morphology, which leads to 37% increment in the capacitance of $\text{Co}(\text{OH})_2$.

Other than modification of the MnO_2 structure and morphology to enhance its supercapacitor performance, reducing the internal charge transfer resistance of MnO_2 to promote higher capacitance has also been studied. A simple layer-by-layer potentiostatic/electrophoretic deposition technique has been developed to prepare a multilayer hybrid film consisting of alternating MnO_2 and graphene layers. The as prepared multilayer hybrid film shows a capacitance as high as 396 F g^{-1} at 1 A g^{-1} , and better rate capability than individual MnO_2 and graphene electrode. Further characterization indicates that graphene/ MnO_2 multilayer hybrid structure effectively reduces internal charge transfer resistance and also has a synergetic effect on the supercapacitor performance of MnO_2 . The technique developed in this study to prepare graphene based multilayer hybrid structure is also readily generalized to many other graphene/transition metal oxide hybrid films.

Last but not least, the supercapacitor performance enhancement mechanism by modifying the morphology and reducing internal charge transfer resistance are combined to developed a graphene/CTAB modified MnO_2 multilayer hybrid film. The as prepared thin film exhibits a high capacitance of 403 F g^{-1} at 2 A g^{-1} . Further characterization by electrochemical impedance spectroscopy shows that it has smaller internal resistance than that of MnO_2 . Moreover, graphene/CTAB modified MnO_2 multilayer hybrid film remains 97% of the initial capacitances after 1250 cycles of charge/discharge test at a current density of 10 A g^{-1} . Meanwhile, it is also noticed that the two capacitance enhancement mechanism may interfered with each other and a better performance can be expected with further modification.

Chapter 1 Introduction

1.1 Background

In recent years, fast depletion of traditional energy sources such as fossil fuels and related environment pollution problems, have spurred the fast development of sustainable, environment friendly energy resources such as solar, wind and tide energy. However because of the non-continuous supply of these natural sources, energy storage devices such as batteries and electrochemical capacitors have received increasing attentions. For example, Batteries, especially lithium-ion batteries [1], have become a very important part of daily life. They offer a high energy density, flexible and lightweight design, and lifespan of tens to hundreds cycles [2]. However many new devices like electrical vehicles require higher power density and longer lifespan. As a result, supercapacitors which can provide ultra high power density, long cycle life, and moderate energy density, have found wide applications from portable equipment to electrical vehicles [3].

The operation mechanism of supercapacitor is to make use of either ultra high specific surface area to electrostatically absorb charges or fast reversible redox reactions at the electrode/electrolyte interface to store charges. Many materials have been investigated as supercapacitor electrodes; they can be generally classified into three categories: carbon-based material, conducting polymers and various transition metal oxide/nitride. Among them, transition metal oxides have shown outstanding capacitances and good lifespan (Table1.1). Ruthenium oxide, cobalt hydroxide and manganese dioxide, for example, have received wide attention. While ruthenium oxide has a very attractive capacitive performance, it is very worthy which limits its applications. Cobalt hydroxide, on the other hand, has very fascinating high capacitance at a moderate cost.

Table 1.1 Transition metal oxide based supercapacitor

Supercapacitor electrode	Specific capacitance	Lifespan	Preparation techniques
RuO_2	1.01 F cm^{-2}	2000 cycles (with 10.6% loss)	Surfactant assisted Solution method [4]
$\text{RuO}_2/\text{graphene}$	570 F g^{-1} with 38.3wt% RuO_2 loading	1000 cycles (with 2.1% loss)	combining sol–gel and low-temperature annealing processes[5]
Co(OH)_2	935 F g^{-1} at 2 Ag^{-1}	1500 cycles (with 17.4% loss)	Hydrothermal method[6]
$\text{MnO}_2/\text{graphene}$	310 F g^{-1} at 2 mvs^{-1}	15000 Cycles (with 4.6% loss)	microwave irradiation assisted self-limiting deposition[7]
$\text{V}_2\text{O}_5/\text{CNT}$	792 C g^{-1} at a charge/discharge time of 4 h	10000 (with 20% loss)	Hydrothermal method [8]

Last but not least, manganese dioxide delivers moderate capacitance, low cost and has an environment friendly nature. Although attractive capacitance (100 to 200 Fg^{-1} in alkali salt solution[9]) has been obtained for these materials, it is noted that what has been achieved is still much lower than their theoretical values (around 1380 Fg^{-1} [10]). This is because the main charge storage mechanism in transition metal oxides is based on redox reactions at the electrode/electrolyte interface, and in most practical situations, not all of the active materials are contributing. The transportation of electrolyte ions and electrons is affected by the surface properties, crystal structure, morphology and electrical conductivity of electrode materials [11-14]. Research efforts have focused on

the modification of the crystal structure and morphology so as to facilitate the redox reactions of transition metal oxide. These are carried out through various preparation approaches, as well as improving the intrinsic conductivity of electron/ion transportation which is often the rate determining step of redox reactions. As mentioned above, Cobalt hydroxide is an attractive supercapacitor electrode material due to its layered structure and large interlayer spacing, which promise high surface area and facilitate fast ion insertion/desertion rate. There are also reports on the modification of the structure or morphology to increase capacitance via inserting Al^{3+} ions to increase the interlayer spacing[15], or forming nanoporous structure by depositing Co-Cu composite first and then followed by dissolution of Cu [16] etc. However, very few reports [17-19] mentioned the facile preparation method of surfactants or organic solvents assisted synthesis of cobalt hydroxide and their supercapacitor performances.

Manganese dioxide has lower theoretical capacitance than that of cobalt hydroxide; however it has much higher potential window of 1 volt compared with that of only 0.5 volt for cobalt hydroxide, where potential window is a key parameter to assure high energy density according to $E = \frac{1}{2}CV^2$. In addition, manganese dioxide is more environmental friendly and with lower cost. Hence it is the material most intensively studied besides ruthenium oxide. It is noted that manganese dioxides with loose, porous and high surface area structure that could generate large quantity of electrochemically active sites for redox reactions as well as shortening the transport path length for both electrons and cations, are desired for supercapacitor electrode. While most of the researches have focused on modifying the experimental parameters or preparation techniques like hydrothermal, co-precipitation etc. [9, 20], very few attention has been paid to structure directing agent assisted method which is very easy and effective in preparing materials with controlled nanostructures and morphologies. It would be interesting to explore their applications in manganese dioxide synthesis for

supercapacitor application. On the other hand, to improve the intrinsic poor electrical conductivity of MnO_2 , researchers have been exploring incorporation of other metal elements into MnO_2 compounds [21, 22] or deposition of a thin MnO_2 layer on a porous and highly electronically conducting material which enhances electrical conductivity and charge storage capability of the whole composite [23]. These approaches have shown some improvements; however, the future improvements on effective material loading and homogenous distribution of conductive additives have always been difficult. Recently, graphene as a newly discovered material presents attractive properties as supercapacitor electrode material such as ultra high surface area, excellent electrical conductivity. Particularly, when graphene forms composites with other materials, they often show synergetic effects and result in remarkable electrochemical performances. Nevertheless most of the preparation of graphene involves a tedious and toxic chemical reduction process, not to mention the difficulty of making homogeneous graphene based composite, which is generally realized through physical mixing or ion absorption at graphene surface followed by precipitation [24]. A facile and easy control of the distribution and deposition of graphene/ MnO_2 nanocomposite is then highly desired for supercapacitor application.

To make active materials into supercapacitor electrode, If they are in powder form, polymer binders (such as Polyvinylidene fluoride) are needed to keep active materials attached to the conductive substrates, which will inevitably increase the intrinsic and contact resistance and also degrade the capacitive performance of the electrodes [25]. Therefore, techniques, which can apply active material directly onto substrates, are always preferred. Among the various preparation techniques such as sol-gel [26], sputtering [27], electrostatic spray deposition [28] and electrophoresis [29], electrochemical deposition shows the advantage of a wide selection of substrates, simple setup and easy control of experimental conditions. It is hence chosen as the electrode

preparation technique in the present work.

Hence, we aim to investigate the capacitive performances and improvements of manganese dioxide and cobalt hydroxide via modification of surface morphologies and electrical conductivity. Electrochemical deposition methods are adopted for the deposition of active materials onto conductive substrates and directly used as supercapacitor electrodes.

For MnO_2 , structural directing agent Cetyl trimethylammonium bromide (CTAB) which often shows a structural stabilization side effect is used to assist MnO_2 synthesis. The resulting morphology and electrochemical performances as well as cyclic stability are investigated. In addition, the brief mechanism of CTAB on MnO_2 growth is explored.

With the successes of modifying the morphology and supercapacitor performances of MnO_2 through surfactant, the same idea was applied for cobalt hydroxide. For cobalt hydroxide, morphology has been found to have tight relationship with capacitive performances, therefore the effect of introduction of different concentrations of organic solvent NMP into the cobalt hydroxide pre-deposition solution was investigated. The resulting morphologies and electrochemical performances were studied. Results showed that the surface morphology of cobalt hydroxide has a close relationship with the concentration of NMP in the pre-deposition electrolyte solution. When 20 vol.% NMP surfactant was added into the pre-deposition solution, the as obtained morphology had much narrower interlayer spacing, thinner layer thickness as well as more uniform pore distribution, which lead to 37% increment in capacitance.

As mentioned above, other than surface morphology and structure modification, the electrochemical performances of MnO_2 can also be improved by increasing the electronic conductivity of electrode; therefore a facile approach to incorporate conductive additive graphene into MnO_2 was also conducted. A graphene/ MnO_2 multilayer hybrid film was

obtained by sequential potentiostatic deposition of MnO_2 and electrophoretic deposition of graphene, the resulting microstructure and electrochemical performances were analyzed and compared. Significant improvement on the electrochemical performances was thought to be closely related to the synergetic effect of graphene/ MnO_2 hybrid structure. To further study and improve the electrochemical performances of MnO_2 , the capacitance enhancement mechanisms of morphology modification through surfactant assisted deposition and electronic conductivity improvement by adding conductive additives are combined, multilayer hybrid films consisting of MnO_2 prepared in presence of 1 wt.% CTAB and graphene layer were synthesized, and their resulting electrochemical performances were analyzed. It was found that the capacitance of the facile multilayer hybrid film was further improved with a capacitance of 403 F g^{-1} which is higher than those of $\text{MnO}_{2\text{CTAB}}$ and graphene/ MnO_2 , however the improvement is not simply adding up of the two capacitance enhancement mechanisms. The two mechanisms may interfere with each other by blocking effect and leads to capacitance less than expected.

1.2 Objectives and scope

The objectives of the present project are listed as follows: (1) To improve the supercapacitor performance of MnO_2 by using structural directing agent CTAB to control the crystal structure and morphology growth. (2) To synthesize cobalt hydroxide with optimal morphology desired for high capacitive performance by adjusting organic solvent NMP concentrations (3) To synthesis graphene/ MnO_2 multilayer hybrid films and investigate the electrochemical properties. (4) To combine the capacitance enhancement mechanisms of MnO_2 through morphology and electric conductivity modification and form CTAB modified MnO_2 /graphene multilayer film.

1.3 Organization of the thesis

The thesis contains 8 chapters, starting from the introduction as chapter 1.

Chapter 2 starts by giving a brief literature review on the history of supercapacitors. It is followed by the supercapacitor mechanism exploration, the similarities and differences between supercapacitor, battery and common capacitor. Finally, the performance and challenges of most commonly used supercapacitor electrode materials were introduced.

Chapter 3 covers the study of structural direction agent CTAB mediated synthesis of MnO_2 , the presence of CTAB in the electrolyte shows influences on the microstructure, surface morphology and cyclic stability, finally the supercapacitor performances of MnO_2 . The effect of CTAB on MnO_2 growth mechanism was also briefly proposed.

Chapter 4 presents the investigation of NMP assisted synthesis of cobalt hydroxide supercapacitor electrode, the variation of cobalt hydroxide morphologies with NMP concentrations as well as the effects of variations on the electrochemical performances were systematically studied.

In Chapter 5, a simple approach to produce graphene/ MnO_2 multilayer hybrid films via layer-by-layer deposition was proposed. The selection of substrates, detailed deposition procedures and advantages of proposed technique were presented. The crystal structure, morphology, and electrochemical performances of the as-obtained multilayer hybrid films were also systematically studied.

Chapter 6 combines the capacitance enhancement approaches developed from chapter 4 and chapter 5, a multilayer hybrid film consisting of MnO_2 layer synthesized in

presence of CTAB and graphene layer was developed, their capacitive performances and morphologies were studied and compared with MnO₂/ graphene prepared in chapter 5.

Chapter 7 presents the conclusions and Chapter 8 gives the recommendation for the future works to improve supercapacitor electrode performance.

1.4 References

1. Arico, A.S., et al., *Nanostructured materials for advanced energy conversion and storage devices*. Nature Materials, 2005. **4**(5): p. 366-377.
2. Tarascon, J.M. and M. Armand, *Issues and challenges facing rechargeable lithium batteries*. Nature, 2001. **414**(6861): p. 359-367.
3. Arbizzani, C., M. Mastragostino, and F. Soavi, *New trends in electrochemical supercapacitors*. Journal of Power Sources, 2001. **100**(1-2): p. 164-170.
4. Zhang, G.Q., et al., *Single-crystalline NiCo₂O₄ nanoneedle arrays grown on conductive substrates as binder-free electrodes for high-performance supercapacitors*. Energy & Environmental Science, 2012. **5**(11): p. 9453-9456.
5. Wu, Z.-S., et al., *Anchoring Hydrous RuO₂ on Graphene Sheets for High-Performance Electrochemical Capacitors*. Advanced Functional Materials, 2010. **20**(20): p. 3595-3602.
6. Zhang, Y., et al., *Hydrothermal synthesized porous Co(OH)₂ nanoflake film for supercapacitor application*. Chinese Science Bulletin, 2012. **57**(32): p. 4215-4219.
7. Yan, J., et al., *Fast and reversible surface redox reaction of graphene-MnO₂ composites as supercapacitor electrodes*. Carbon, 2010. **48**(13): p. 3825-3833.
8. Chen, Z., et al., *High-Performance Supercapacitors Based on Intertwined CNT/V₂O₅ Nanowire Nanocomposites*. Advanced Materials, 2011. **23**(6): p. 791-795.
9. Wei, W.F., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. Chemical Society Reviews, 2011. **40**(3): p. 1697-1721.
10. Bao, L., J. Zang, and X. Li, *Flexible Zn₂SnO₄/MnO₂ Core/Shell Nanocable–Carbon Microfiber Hybrid Composites for High-Performance Supercapacitor Electrodes*. Nano Letters, 2011. **11**(3): p. 1215-1220.

11. Xie, X.W., et al., *Synthesis of Nanorod-Shaped Cobalt Hydroxycarbonate and Oxide with the Mediation of Ethylene Glycol*. Journal of Physical Chemistry C, 2010. **114**(5): p. 2116-2123.
12. Conway, B.E., *TRANSITION FROM SUPERCAPACITOR TO BATTERY BEHAVIOR IN ELECTROCHEMICAL ENERGY-STORAGE*. Journal of The Electrochemical Society, 1991. **138**(6): p. 1539-1548.
13. Wu, N.L., *Nanocrystalline oxide supercapacitors*. Materials Chemistry and Physics, 2002. **75**(1-3): p. 6-11.
14. Cottineau, T., et al., *Nanostructured transition metal oxides for aqueous hybrid electrochemical supercapacitors*. Applied Physics a-Materials Science & Processing, 2006. **82**(4): p. 599-606.
15. Gupta, V., S. Gupta, and N. Miura, *Al-substituted alpha-cobalt hydroxide synthesized by potentiostatic deposition method as an electrode material for redox-supercapacitors*. Journal of Power Sources, 2008. **177**(2): p. 685-689.
16. Chang, J.K., C.M. Wu, and I.W. Sun, *Nano-architected Co(OH)(2) electrodes constructed using an easily-manipulated electrochemical protocol for high-performance energy storage applications*. Journal of Materials Chemistry, 2010. **20**(18): p. 3729-3735.
17. Zhou, W.J., et al., *Electrodeposition of ordered mesoporous cobalt hydroxide film from lyotropic liquid crystal media for electrochemical capacitors*. Journal of Materials Chemistry, 2008. **18**(8): p. 905-910.
18. Wang, G.X., et al., *Highly Ordered Mesoporous Cobalt Oxide Nanostructures: Synthesis, Characterisation, Magnetic Properties, and Applications for Electrochemical Energy Devices*. Chemistry-a European Journal, 2010. **16**(36): p. 11020-11027.
19. Al-Bishri, H.M., I.S. El-Hallag, and E.H. El-Mossalamy, *Preparation and Characterization of Ordered Nanostructured Cobalt Films via Lyotropic Liquid Crystal Templated Electrodeposition Method*. Bulletin of the Korean Chemical Society, 2010. **31**(12): p. 3730-3734.

20. Subramanian, V., et al., *Hydrothermal synthesis and pseudocapacitance properties of MnO₂ nanostructures*. Journal of Physical Chemistry B, 2005. **109**(43): p. 20207-20214.
21. Rajendra Prasad, K. and N. Miura, *Electrochemically synthesized MnO₂-based mixed oxides for high performance redox supercapacitors*. Electrochemistry Communications, 2004. **6**(10): p. 1004-1008.
22. Nakayama, M., et al., *Electrodeposition of Manganese and Molybdenum Mixed Oxide Thin Films and Their Charge Storage Properties*. Langmuir, 2005. **21**(13): p. 5907-5913.
23. Fischer, A.E., et al., *Incorporation of Homogeneous, Nanoscale MnO₂ within Ultraporous Carbon Structures via Self-Limiting Electroless Deposition: Implications for Electrochemical Capacitors*. Nano Letters, 2007. **7**(2): p. 281-286.
24. Park, K.W. and J.H. Jung, *Spectroscopic and electrochemical characteristics of a carboxylated graphene-ZnO composites*. Journal of Power Sources, 2012. **199**: p. 379-385.
25. Ruiz, V., et al., *Influence of electrode preparation on the electrochemical behaviour of carbon-based supercapacitors*. Journal of Applied Electrochemistry, 2007. **37**(6): p. 717-721.
26. Reddy, R.N. and R.G. Reddy, *Sol-gel MnO₂ as an electrode material for electrochemical capacitors*. Journal of Power Sources, 2003. **124**(1): p. 330-337.
27. Lim, J.H., et al., *Thin Film Supercapacitors Using a Sputtered RuO₂ Electrode*. Journal of The Electrochemical Society, 2001. **148**(3): p. A275-A278.
28. Kim, I.-H. and K.-B. Kim, *Ruthenium Oxide Thin Film Electrodes for Supercapacitors*. Electrochemical and Solid-State Letters, 2001. **4**(5): p. A62-A64.
29. Lee, C.Y., et al., *Characteristics and electrochemical performance of supercapacitors with manganese oxide-carbon nanotube nanocomposite electrodes*. Journal of The Electrochemical Society, 2005. **152**(4): p. A716-A720.

Chapter 2 Literature Review

From large scale energy storage units used for solar, wind and tide energy to light and small energy sources used for portable electronic devices, energy storage devices have shown increasingly importance in modern society. Recently the supercapacitor, which has good energy density and power density as well as long cycle life, has received increasing interests as it fills up the gap between battery and conventional capacitor. It has found wide applications in various fields by providing versatile, clean, and efficient energy. In this chapter, a brief history of supercapacitor will be presented, followed by the exploration of the supercapacitor mechanism, the similarities and differences between supercapacitor, battery and conventional capacitor will be listed. Finally, the most popular supercapacitor electrode materials, current collectors, electrolytes and their challenges will be introduced.

2.1 History of supercapacitors

The Capacitor effect was discovered in 1745 and the prototype of modern capacitor, which consists of two foil conductors separated by a dielectric region, came around 1900. This type of capacitor provides very limited energy which is less than 360 joules per kilogram in energy density and with unit of only μFg^{-1} or few Fg^{-1} . In 1957 Becker [1] first described the concept of electrochemical capacitor (also called supercapacitor later) when he used porous carbon coated metallic current collector in sulphuric acid solution and found it has much higher capacitance than conventional capacitor. Becker believed the “exceptionally high capacitance” came from mass carbon pores, which provided high specific surface area. In 1966, researchers from Standard Oil of Ohio (SOHIO) also discovered this exceptionally high capacitance effect during experimental fuel cell

designs, and they developed the modern version of the devices, later SOHIO sold the technology to NEC (Japan) and finally marketed it as “supercapacitors” in 1978, which was used as backup power for maintaining computer memory [2]. The market of supercapacitor was quite small at first, but since the mid-1990s, various advances in material science and optimization of the existing supercapacitor design led to the rapid development of supercapacitor and reduction in cost. Nowadays supercapacitors can reach capacitance of few thousands Faradic per gram and deliver energy density more than 5 Wh kg^{-1} , power density as high as 10 Kw kg^{-1} and quick charging process, plus ultra long cycle life up to 10k cycles [2]. These properties make supercapacitors very attractive in complementing or replacing batteries in energy storage field, especially when very large output energy is needed in short time, such as regenerative braking applications in tanks, submarines, diesel trucks and railroad locomotives. A detailed overview of the opportunities for supercapacitor can be found in recent reviews from Miller et al [3] and Kotz et al [4]. Supercapacitors with small capacitance (a few farads) have been extensively used as power buffers or memory back up for portable electronic devices like cameras, mobile phones and so on. Supercapacitors of a few tens of farads can be used as energy source for applications where fast charging/ discharging and superior cycle life are needed. Electric screwdrivers and cutters using supercapacitor as energy source are very popular, another exciting example is to use supercapacitor on an Airbus 380 to provide safe and reliable power supply for emergency door system. However what supercapacitor can do is more than above examples, their more exciting and brighter future actually lies in the transportation market, such as hybrid electric vehicles, metro trains and tramways which required further improvement of supercapacitors on capacitance and energy density. However, the success of supercapacitor doesn't mean it is going to replace batteries completely. The two energy storage devices have their own merits. Li-ion battery can provide much higher energy

density as indicated in Figure 2.1, but if it is used to provide repeated high power density supply within a short duration (10s or short), the system will be damaged and its cycle life will quickly degrade [3]. To solve this problem, the battery must be oversized, which inevitably increases the cost and volume; similarly, if we use a supercapacitor for power supply for more than 10s, it requires oversize. The best relationship for battery and supercapacitor is to complement each other, which will extend the cycle life and maximize the performances of battery. However, it should be noted that some situation, which requires fast charge/discharge capacity as well as outstanding cycle life, supercapacitor is the best choice as the main power and energy sources.

2.2 Battery, conventional capacitor and supercapacitor

2.2.1 Battery and conventional capacitor

In the energy storage field, the properties of supercapacitors lie between battery and conventional capacitor (see the Ragone plot which plots the specific power against specific energy in Figure 2.1). It stores hundreds to thousands of times more energy (tens to hundreds of Fg^{-1}) than a conventional capacitor, has a much quicker charging process and longer cycle life than battery, however it has a much lower energy density than a battery, and its optimal discharge time is usually limited to less than a minute. Although these three types of energy storage devices: capacitor, supercapacitor and battery, look quite different, there are also many similarities among their energy storage mechanisms. Basically electrical energy can be stored in two different ways: (1) in-directly in batteries as chemical energy which release charges through Faradaic oxidation and reduction of the electrochemically active reagents and (2) directly as negative and positive electric charges on the plates of a capacitor through electrostatic force, which is known as non-Faradaic electrical energy storage. The efficiency of these two electrical energy storage modes is usually substantial [5]. Although battery and pseudo-capacitor both store energy

through Faradaic reactions, there are significant kinetic differences between them. One of them is that the electrodes of the batteries usually undergo substantial phase changes during charge and discharge (although the intercalation system seldom does), which causes kinetic and thermodynamic irreversibility. Despite that the overall charge/discharge process is done in a relatively reversible thermodynamic way and keep most of the energy, some of the electrode reagents are still irreversible, so that the cycle life of battery cells is usually restricted to a thousand to few thousands charge/discharge cycles. On the other hand, conventional capacitors carry on only electrostatic charge accumulation without any chemical reactions of electrode material, despite that electrolyte may have some small but significant reversible electrostriction during charging/discharge process [5], therefore theoretically a capacitor has an almost unlimited cycle life. However, it should be noted that although battery has much shorter cycle life, it stores much more energy than conventional capacitor due to the Faradaic process, which involves usually one or two valence electron charges per atom (sometimes 3 for Al or Bi) or molecule of electro-active reactant. By contrast, conventional capacitor stores charges at electrode plate surface through electrostatic force, its capacitance depends on the insulator between the two electrode plates, plate surface area and separation distance between plates according to equation 2.1, where ϵ is the dielectric constant of an insulator, A is the surface area of plates and d is the separation distance between the two plates.

$$C = \epsilon A / d \quad (2.1)$$

Due to the limited charge storage surface area and geometric constraints of the separation distance between plates, a conventional capacitor is destined to store very limited energy.

Figure 2.1 Ragone plot for various electrical energy storage devices [6]

2.2.2 Electrochemical double layer capacitor

Electrochemical double layer capacitor (EDLC) also called supercapacitor was first marketed in 1978 with greatly enhanced capacitance. The EDLC makes use of electrochemical double layer (EDL) which means ultra large interfacial area and atomic range of charge separation distances for a capacitor. As a result, very high capacitance can be obtained according to equation 2.1. The concept of EDL was first described and modeled by von Helmholtz in the 19th century when he investigated the distribution of opposite charges at the interface of colloid particles [6]. As schematically illustrated in Fig 2.2a, the Helmholtz double layer model states that two layers of opposite charges form at the electrode/electrolyte interface, separated by an atomic distance. The model is similar to that of two-plate conventional capacitors, and it was further modified by Gouy and Chapman [7, 8], adding consideration of a continuous distribution of electrolyte ions (both cations and anions) in the electrolyte solution, driven by thermal motion, which is referred to as the diffuse layer (Figure 2.2b). However, the Gouy-Chapman model leads to an overestimation of the EDL capacitance. The capacitance of two separated arrays of charges increase inversely with their separation distance, hence a very large capacitance value would arise in the case of point charge ions close to electrode surface. Later, Stern

[9] combined the Helmholtz model with the Gouy-Chapman model and proposed that there are two regions of ion distribution: the inner region called the compact layer or stern layer and the diffuse layer, (Figure 2.2c). In the compact layer, ions (very often hydrated) are strongly absorbed by the electrode, consisting both of specifically absorbed ions (in most cases they are anions irrespective of the charge nature of the electrode) and non-specifically absorbed counter-ions. Based on the types of absorbed ions, the compact layer is further divided into the inner Helmholtz plane and outer Helmholtz plane. Beyond the inner region; there is the diffusion layer as what the Gouy-Chapman model defines. Thus the capacitance in EDL (C_{dl}) can be considered as integral capacitances from the two regions (1) the Stern type of compact double layer capacitance C_H and the diffusion region capacitance C_{diff} .

Figure 2.2 Models of the electrical double layer at a positively charged surface: (a) the Helmholtz mode, (b) the Gouy-Chapman model, and (c) the stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) [10]

Their relationship can be expressed as follow:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (2.2)$$

The EDL behavior at a planar electrode surface is determined by a few factors including the electrical field across the electrode, the type of electrolyte ions, the solvent in which

the electrolyte ions are dissolved in, and the chemical affinity between the adsorbed ions and the electrode surface. As for EDL behavior at the surface of pores in a porous electrode, situation is more complex as ion transportation in a confined system are greatly affected by a number of parameters, such as tortuous mass transfer path, space constraint inside the pores, ohmic resistance associated with the electrolyte, and the wetting behavior at the pore surface by the electrolyte. Figure 2.3 represents the EDLC configuration based on porous electrode materials.

Figure 2.3 Schematic representation of an EDLC based on porous electrode materials

The capacitance of an EDLC is generally calculated using the same equation (Equation 2.1) for conventional capacitor, however with a different definition of parameters. For EDLC, ϵ_r is the electrolyte dielectric constant, ϵ_0 is the permittivity of vacuum, A is the accessible specific surface area of the electrode for electrolyte ions, and d is the effective thickness of the EDLC (the Debye length). According to this equation, the specific capacitance should increase linearly with specific surface area. However, a few experiments have shown that the linear relationship doesn't hold [10, 11]. This non-linear relationship between capacitance and specific surface area may be caused by a long accepted idea that the sub-micropores are not participating in the formation of EDL due to inaccessibility of the submicropore surface to the large solvated ions, however, recent

studies [10, 12] revealed that pores smaller than the solvated ion size can still contribute to the capacitance. Huang and co-workers [13] proposed that pore curvature should be taken into account and capacitive behavior varies with different pore size. Although there have been many experimental and theoretical advances in EDLC charges storage mechanism in the nano-confined spaces recent years, an in-depth understanding is still lacked. More efforts are needed for EDLC mechanism development.

2.2.3 Pseudocapacitor

Pseudocapacitor is actually a batter-type capacitor. Unlike the conventional capacitor and Electric double layer capacitor, where no electron transfer takes place at the electrode interface and the electric charge is stored by electrostatic force. Pseudocapacitor involves Faradaic reactions during electric charge and energy storage process, where electron transfer takes place across the double layer with a consequent change of oxidation state of the electrode. As a result, due to special thermodynamic conditions, the chemistry of the electro-active materials appears that the potential V of the electrode is some continuous function of the quantity of charge Q passed through. From this relationship, a derivative $\Delta Q/\Delta V$ arises and is equivalent to and measurable as a capacitance, which is also called pseudocapacitance [5]. This energy storage mechanism is very different from that of EDLC. Due to the electrochemical redox reactions involved, a pseudocapacitor generally has much higher capacitance and energy density than EDLC, but at the cost of shorter cycle life, which is caused by structure degradation during electrochemical redox reactions. A good example of Pseudocapacitor electrode material is ruthenium oxide, which has been extensively studied in the past 30 years [5, 14] due to its intrinsic ability of fast, reversible electron transfer as well as electro-adsorption of protons on the surface of RuO_2 particles. A high capacitance of 720 Fg⁻¹ has been reported for $\text{RuO}_2 \cdot \text{H}_2\text{O}$ involving proton and electron double injection/expulsion at the electrode interface according to the following equation [5, 15]:

Where $\text{RuO}_x(\text{OH})_y$ and $\text{RuO}_{x-\delta}(\text{OH})_{y+\delta}$ represent the interfacial oxy-ruthenium species at higher and lower oxidation states. In a proton rich electrolyte environment, the faradic charges can be reversibly stored and delivered through the redox transitions of the oxy-ruthenium groups. It is interesting to note that although ruthenium oxide undergoes redox reactions instead of electrostatic repulsion force to store electric charges, it performs like an ideal capacitor with fast charge/discharge rate, long cycle life (thousands of cycles) and at the same time stores much more energy than EDLC. It also should be noted that even though a pseudocapacitor stores charges and energy through Faradaic reactions like battery, there are fundamental thermodynamic differences between them. For battery, it has a unique and specific free energy ΔG of the electro-active phases involved in the charge and discharge process; while pseudocapacitor has a continuously changing free energy of electro-active material with the extent of charge and discharge.

$$G=1/2CV^2$$

$$\Delta G = \Delta G^0 + RT \ln[X/(1-X)] \quad (2.4)$$

Their electrical characteristic differences are scheduled in table 2.1 shown below:

Table 2.1 Electrical characteristic differences between battery and pseudocapacitor[2]

Battery	Pseudocapacitor
Ideally has single valued free energy of component	Has continuous variation of free energy with degree of conversion of materials or extent of charge held
Electromotive force (emf) is ideally constant with degree of charge and discharge, except for non-thermodynamic incidental effects, or phase changes	Potential is thermodynamically related to state of charge through $\log [X/1-X]$ factor, in a continuous manner

during discharge	
Irreversibility is an usual behavior (materials irreversibility and kinetic irreversibility)	High degree of reversibility is common (10^4 - 10^6 cycles with RuO_2)
Response to linear modulation of potential gives irreversible i vs. V profile with non-constant current	Response to linear modulation of potential gives nearly constant charging current profile but with some dependence on materials
Discharge at constant current arises at a nearly constant potential except for intercalation Li batteries	Discharge at constant current usually gives linear decline of potential with time, which is characteristic of a capacitor

In summary, there are two types of energy storage mechanisms in a supercapacitor. One uses pure physical electrostatic force to accumulate charges at the electrode/electrolyte interface, while the other type stores energy through fast and reversible surface faradic reactions at characteristic potentials. The corresponding supercapacitors are named as Electric double layer capacitor and pseudocapacitor. However, it should be kept in mind that although we roughly distinguish supercapacitor into EDLC and pseudocapacitor based on whether charge storage is achieved through electrostatic force or faradic reactions, the two mechanisms usually function together in a single supercapacitor.

2.3 Essential parameters of supercapacitor

The operation of supercapacitor consisting of two electrodes can be viewed as two individual capacitors that are connected in series as shown in Figure 2.4. C_a and C_c are the capacitance of the anode and cathode, respectively. R_s is the equivalent series

resistance (ESR) of the whole cell and R_F is the resistance responsible for the self-discharge of a single electrode.

Figure 2.4 A simple RC equivalent circuit representation illustrates the basic operation of a single cell supercapacitor

The total C_T of the supercapacitor electrode is calculated according to:

$$\frac{1}{C_T} = \frac{1}{C_a} + \frac{1}{C_c} \quad (2.5)$$

In a resistor-capacitor (RC) circuit, the time constant (τ) expressed as resistance (r) x capacitance (c) gives important information on the characteristic of a capacitor. The Larger the value of τ is, the smaller the leakage of electrode will be. The maximum energy density (E) and power density (P) in a single cell supercapacitor are defined as follows:

$$E = \frac{1}{2} C_T V^2 \quad (2.6)$$

$$P = \frac{V^2}{4R_s}$$

Where V is the cell voltage, C_T is the total capacitance and R_s is the ESR. Every element shown in the equation is essential to the supercapacitor performance. The capacitance greatly relies on the electrode material and the cell voltage (operation voltage window) which is determined by the thermodynamic stability of the electrolyte solution. While for ESR, it could come from various types of resistances such as the intrinsic electric resistance of the electrode and the electrolyte solution, mass transfer resistance of the ions in the matrix, contact resistance between the current collector and the electrode and

so on. Hence to produce a high performance supercapacitor, it must simultaneously have large capacitance, high operating voltage and minimum ESR. The future enhancement of supercapacitor performance relies on in depth research of electrode material, electrolyte selection as well as electrode preparation technique.

2.4 Supercapacitor electrode materials

As already known, the properties of the electrode material is very important to enhance overall supercapacitor performances. Over the past few decades, many materials have been studied as supercapacitor electrode. They can be generally classified into three categories: (1) carbon based materials (2) conducting polymers and (3) various transition metal oxides and nitrides[16].

2.4.1 Carbon based material for supercapacitor

The very first EDLC was made of porous carbon in 1978, since then carbon based material, including active carbon, carbon aerogel/xerogel, carbon nanotube, carbon fiber, carbon fabric, template carbon, graphene and many other carbon based composite have been widely studied. The attractive of carbon as supercapacitor material arise from a unique combination of physical and chemical properties, including: high conductivity, high surface area range (~ 1 to $> 2000 \text{ m}^2 \text{ g}^{-1}$), excellent corrosion resistance, high temperature stability, controllable pore structure, easy processability, good compatibility with other materials and also relatively low cost. All of these factors make carbon-based material ideal for electrochemical double layer capacitor application.

Active carbon

Active carbons (ACs) are the most widely used supercapacitor electrode materials today because of their unique combination of properties like large surface area, high conductivity and moderate cost. ACs can be derived from carbon-rich organic precursors by physical (thermal) or chemical carbonization of various carbonaceous materials (e.g.

wood, coal, nutshell, etc.). After activation, micro-pores ($< 2\text{nm}$ in size), mesopores ($2\text{-}50\text{ nm}$) and macro-pores ($>50\text{nm}$) can be created in carbon grains, depending on the activation methods as well as the carbon precursors used. By doing so, ACs with various physical-chemical properties and well developed surface area as high as $3000\text{m}^2\text{ g}^{-1}$ can be produced [11, 12, 17]. The corresponding EDL capacitances are $100\text{-}120\text{ Fg}^{-1}$ in organic electrolytes and $150\text{-}300\text{ Fg}^{-1}$ in aqueous electrolyte at a lower cell voltage [10]. However discrepancy between the capacitance and specific surface area is observed, although the surface area can reach up to $3000\text{m}^2\text{ g}^{-1}$, the corresponding specific capacitance is less than $10\text{ }\mu\text{F cm}^{-2}$, which is much smaller than the theoretical electrochemical double layer capacitance ($15\text{-}25\mu\text{F cm}^{-2}$) [5], therefore it is reckoned that although high specific surface area is important for active carbon to obtain high capacitance, some other factors like the size distribution, shape and structure of pores, electrical conductivity and surface functionality can also influence the electrochemical performance to a great extent. In recent studies by Largeot et al [18], they observed that an EDLC made of carbide-derived carbons achieved the maximum capacitance when the pore size matches the ion size. The pore size –dependent capacitive behavior is shown in Figure 2.5.

Figure 2.5 Normalized capacitance change as a function of pore size for CDC samples prepared at different temperatures [19].

Surface functional groups are also very important. It not only provides additional pseudocapacitance but also affects the wettability, performance stability and cycle life of electrode. An activated carbon with low porosity can still show a high energy density of 10 Wh kg^{-1} at a high power density of 10 kW kg^{-1} in acid electrolyte when it has high concentration of oxygen-functional group. However these functional groups are also responsible for capacitance fading, increment of series resistance and electrode aging according to Azais et al [19] and Pandolfo et al [20], so most commercial supercapacitors based on active carbon are pre-treated to remove moisture and a majority of functional groups. In conclusion, supercapacitors made of active carbon provide quick and reliable performances and take over majority of the commercial supercapacitor market. However their limited energy storage and rate capability have restricted their usage to a niche market. Future enhancement in supercapacitor performances requires active carbons to have narrow pore size distribution (comparable with the electrolyte ion size), interconnected pore structure and short pore lengths as well as controlled surface chemistry.

CNT

Carbon nanotubes (CNTs) have also attracted considerable interest as supercapacitor electrode [21, 22]. Their unique nano-scale tubular morphology that combines low electrical resistivity and high porosity, which are beneficial to provide high power density and high surface area. Their high electrical conductivity, good mechanical, thermal and chemical stability have also made them ideal as support matrix for other active materials. CNTs can be categorized into single walled (SWCNT) and multi-walled carbon nanotube (MWCNT), both of which have been studied as supercapacitor electrode materials in aqueous and non-aqueous electrolytes. Their specific capacitances are found to be tightly related to the morphology and purity [23]. CNT with high purity (i.e., without residual catalyst or amorphous carbon) and moderate surface area which range from 120 to 400 m² can deliver specific capacitance ranging from 15 to 80 Fg⁻¹ [24]. It can be observed that the surface area is much smaller than that of active carbons. The surface area of CNTs can come from the internal tubes and exterior voids arising from the entangled nanotubes and sometimes even from the accessible central canal. Research efforts have been dedicated to increase the specific surface area of CNTs through chemical activation process such as KOH activation. However, the porosity and conductivity must be properly balanced in order to have both high capacitance and stable supercapacitor performance. Recently, a CNT-aerogel composite has been developed. it was synthesized by dispersing a carbon aerogel uniformly throughout the CNTs host matrix, which maintained the integrity of composite and also reduced the aspect ratio of the CNTs [25]. A surface area as high as 1059 m² g⁻¹ and very high capacitance of 524 Fg⁻¹ were obtained, but with shortcoming of tedious preparation process. Higher specific capacitances can also be obtained through subsequent oxidative treatment that modifies the surface texture of the CNTs and introduces additional surface functional groups that contribute to pseudocapacitance[26]. Besides surface area, the alignment of CNTs also

affects their supercapacitor performance. Entangled CNTs are less efficient in facilitating fast ionic transportation when compared with aligned CNT due to their irregular pore structures and high entanglement of the CNTs. In summary, CNTs have excellent properties as supercapacitor electrodes, but the limited surface area, limited availability, difficulty in purification and high cost restrict its commercial utilization.

Graphene

Recently, a unique type of carbon material called graphene has caused some interests in supercapacitor application. Graphene was isolated in 2004 for the first time[27], is a two-dimensional single atomic planar sheet of sp^2 bonded carbon atoms that are densely packed into a honeycomb lattice structure [28-30]. A conceptual depiction as well as SEM image of graphene is shown in Figure 2.6 below. There have been many reports about graphene-based supercapacitor either by itself or in composite format [31, 32], and graphene has shown superior supercapacitor performances with specific capacitance as high as 205 Fg^{-1} [32]. Besides that, via the help of ionic electrolyte, the operating voltage window can be extended up to 3.5V [31], which greatly enhances its energy density. However, it is also evident that the full potential of the supercapacitor performance of graphene is not achieved, its reported capacitance remains low (less than 150 in aqueous electrolyte); their performances are found directly related to the numbers of graphene layers and the inherent surface area.

Figure 2.6 A conceptual schematic model of the structure of graphene [35] and SEM image of a single atomic layer of graphite, known as graphene [32]

Another important application of graphene in supercapacitor is to make a graphene-based hybrid material, which make usage of the outstanding high surface area and high conductivity of graphene. In these studies [33-35], graphene showed a potential to outperform its counterparts as supercapacitor electrode material. The improvement in capacitance are believed not only come from enhanced surface area but also due to the increment of lattice defect density and interlayer spacing of graphene [36]. Besides, how the graphene is mixed with other material [37] also matters. These findings indicated that graphene has a great potential as supercapacitor electrode. Although it has limitations like high cost, poor reproducibility and difficult scalability, as a new discovered material, further advancements in characterization and mechanism exploration are likely widen its properties and application.

2.4.2 Conducting polymers

Since the first application of Conducting polymers as supercapacitor electrodes in 1990s [38], various conducting polymers such as polyaniline, polypyrrole and polythiophene have been studied and tested for supercapacitor application. Conducting polymers have very attractive characteristics such as: flexibility, high intrinsic conductivity (a few Scm^{-1} to 500 Scm^{-1} in the doped state), easy processability and low cost. These properties are beneficial to develop supercapacitor with low equivalent series resistance, high power and energy density. There are two ways to synthesize conducting polymer: either chemically or electrochemically, and the as-prepared polymer can exist in two or three general states: p-doped, undoped and n-doped. Most of the as prepared polymers can be oxidized into the “p-doped” state, in which the polymer backbone is positively charged and therefore has high electronic conductivity. The p-doped polymer can also be reduced into the “undoped” state, by varying the degree of reduction process; the polymer can be transferred into insulating or semi-insulating state. For a limited number of polymers, such as polyacetylene, they can be electrochemically reduced into the “n-doped” state, which is also has high electronic conductivity; they can also be oxidized back to insulating “undoped” state. The corresponding equations for these two types of charging process are as follows:

From the above equations, it is clearly seen that conducting polymer undergo Faradaic reactions during charging/discharging process, which enable them to store much more charges than carbon based supercapacitors. Its capacitance is mainly pseudo-capacitance and ranges from tens of Fg^{-1} to over one thousand Fg^{-1} depending on the synthesis

methods and polymer types [38-40]. However, one big problem associated with conducting polymers is degradation. With increasing doping level, higher specific capacitance can be obtained, but the large number of counter ion insertion and de-insertion into the polymer matrix as indicated in equation 2.7 will cause intense volume change and swelling, eventually changes the physical structure of the conducting polymer and leads to mechanical failure of electrode [41]. Therefore many efforts have been made to improve the structure stability of conducting polymer during cycling. Such as using ionic liquid electrolytes which are found to promote better conducting polymer performances with greater life time [42], other approaches like forming composites of conducting polymer and other materials such as carbon, inorganic oxides and hydroxides, as well as metal compounds have been tested. The supercapacitor performances of conducting polymers have been greatly enhanced due to improved structure stability [38]. In summary, conducting polymer is a very promising supercapacitor material; it can provide higher capacitance and energy density than carbon based EDLC. However it also suffers from poor cyclic stability due to redox reactions.

2.4.3 Transition metal oxides

Transition metal oxides are considered as very promising candidate materials for supercapacitor due to their high specific capacitance and high energy density coupled with very low resistance that result in a high specific power density. There are generally several oxidation states in transition metal oxides and therefore plenty of charges can be stored during through redox reactions during charge/discharge process. Their reported specific capacitance valued between 50 to 1100 F g⁻¹ [16]. Metal oxides including ruthenium oxide, manganese oxide, cobalt oxide, nickel oxide, indium oxide, tin oxide, iron oxide etc. have been studied as supercapacitor electrode. Among them, RuO₂ is the most ideal supercapacitor electrode material due to its high specific capacitance, good conductivity, long cycle life and excellent electrochemical reversibility [43]. However,

its high cost limits its application to very limited area, exploration of cheaper transition metal oxides candidates with good capacitance and cyclic stability is very necessary.

Ruthenium oxide

As mentioned above, ruthenium oxide is the most promising supercapacitor electrode material; it has been the focus of Pseudocapacitor research in the past 30 years. There are two forms of RuO_2 used for supercapacitor: amorphous hydrous and crystalline form. Generally, amorphous hydrous RuO_2 performs better than crystalline form, a specific capacitance of 768 F g^{-1} has been reported [44], which is higher than that of crystalline ruthenium oxide. Moreover, amorphous ruthenium oxides also have higher maximum potential window of 1.35 V compared with 1.05V for crystalline ruthenium oxide in aqueous electrolytes [16]. The specific capacitance of RuO_2 can reach $150\text{-}250 \text{ F cm}^{-2}$, which is about ten times higher than that of carbon [20], plus a potential window of 1.35V in H_2SO_4 electrolyte, which is also higher than that of 1V for carbon material. All these properties make RuO_2 very attractive as supercapacitor material, however its high cost is the biggest obstacle of its application. To reduce the cost of RuO_2 based supercapacitor and increase material utilization ratio, RuO_2 has been mixed with other relative cheaper supercapacitor materials such as carbon nanotube, carbon aerogel, SnO_2 , IrO_2 , V_2O_5 etc, or loaded on highly porous substrates. Sato et al.[45] first reported RuO_x /active carbon composite with low Ru content of 7.1 wt%. Miller and Dunn [46] made RuO_x /carbon aerogel nanocomposites with various Ru content, they observed that as Ru content increases, the material utilization of RuO_2 decreased gradually, when the high loading of Ru is over 62.81%, the use of ruthenium oxide decreases due to aggregation of RuO_2 particles [47]. There is also report about $\text{Ru}_{1-y}\text{Cr}_y\text{O}_2$ loaded on TiO_2 [48] which gave a specific capacitance of 1272.5 F g^{-1} , such a high capacitance was attributed to the three-dimensional nanotube network of TiO_2 which not only offered a solid support structure for active materials but also increased the accessible surface area

of active material for electrochemical reactions, which means higher the utilization of active material.

Manganese dioxide

Manganese dioxide can also be used in supercapacitor electrode; it has high specific capacitance, low cost, large availability, various crystallite forms, and very attractive environment friendly nature. By choosing from a wide diversity of crystal forms, defect chemistry, morphology, porosity and texture, manganese dioxide can exhibit many distinct electrochemical properties, which make it the most widely studied supercapacitor material besides ruthenium oxide. The pioneer work on the pseudo-capacitive behavior of manganese dioxide in aqueous solution was done by Lee and Goodenough in 1999 [49], followed by several studies on the energy storage mechanism of manganese dioxide. It is believed that the major charge storage mechanism is due to pseudo-capacitive reaction that occurs on the surface and in the bulk of manganese dioxide electrode [50]. Equation 2.8 shows the surface Faradaic reaction that is related to the adsorption of electrolyte cations such as C^+ , H^+ , Li^+ , Na^+ , K^+ on the manganese dioxide surface.

While Equation 2.9 shows the bulk faradaic reaction that involves the intercalation and de-intercalation process of electrolyte cations in the bulk of the manganese dioxide:

Although the theoretical specific capacitance for manganese dioxide is around 1300 F g^{-1} , most of the reported hydrated manganese dioxides show a specific capacitance of $100\text{--}200 \text{ F g}^{-1}$ in alkali salt solutions. The limited capacitance is believed to be due to low electronic conductivity and poor electrolyte ion penetration. Besides that, manganese dioxide also suffers from structural instability due to phase transformation during charge/discharge process, unsatisfying long term cyclic stability and low rate-capacity

(e.g. when the cyclic voltammetry scan rate increase 4 times, 74% of the initial capacitance remained[51]). Thus extensive efforts have been dedicated to adjust synthesis conditions or compositions of electrodes so as to obtain manganese dioxide with large capacitance, high structural flexibility and cyclic stability, as well as fast ion diffusion rate. The approaches can be characterized into three categories: (1) introducing more electrochemically active sites for the redox reactions through chemical and structural modification; (2) increasing electronic conductivity by adding other conducting additives or shortening of the transport path length for both electrons and cations by using porous, high surface area, and electrical conducting carbon architectures; (3) addressing of the low structural stability and flexibility and electrochemical dissolution of active materials by forming manganese dioxide/conductive polymers in manganese oxide.

In the first type of approach, MnO_2 has been prepared via many synthesis routes such as co-precipitation, sol-gel, hydrothermal, molten salt route, thermal decomposition, solid state reaction, sol-gel dip coating, anodic/cathodic electrodeposition, electrophoresis, sputtering-electrochemical oxidation and so on. By varying the preparation techniques and conditions, MnO_2 with various morphologies and electrochemical performances have been reported. As for approach 2 to improve the poor electrical conductivity and electrochemical cyclability of MnO_2 , attempts like incorporation of other conductive additives and structure stabilizers have also been intensively studied. It was reported that by introducing 20% NiO into MnO_2 , the specific capacitance of MnO_2 increased from 166 Fg^{-1} to 210 Fg^{-1} with higher rate capacity in this Mn/Ni mixed oxide due to formation of micropores and increment of surface area [52]. Chang et al [53] observed an effective electrochemical cyclic stability improvement when a high Co content (>15 wt%) was added into manganese dioxide. In Sun et al [54]'s report, a co-deposited MnO_2 -PANI composite electrode exhibited a specific capacitance of 532 Fg^{-1} at 2.4

mAcm^{-2} discharging current plus a columbic efficiency of 97.5% and 76% capacitance retention over 1200 cycles. Nevertheless, it should be noted although conducting additives or structure stabilizer improves the electrochemical performances of MnO_2 as supercapacitor electrode effectively, the relative low mass loading of MnO_2 and low volumetric or gravimetric energy density remains problem. The loading of MnO_2 has to be optimized to achieve high specific capacitance without increasing the charge-transfer resistance or blocking the electrolyte transport within the composite electrodes.

Other transition metal oxides studied for supercapacitor application include cobalt oxide, Nickel oxide; Tin oxide, Indium oxide and vanadium oxide etc. Cobalt oxide are reported with wide range of capacitances, from 165 Fg^{-1} to 2104 Fg^{-1} (cobalt-nickel layered double hydroxides [55]), which is also the highest value for transition oxide materials reported so far. Nickel oxide performs quite similar with cobalt oxide and can be prepared by many methods like thermal treatment, sol-gel and electrostatic spray deposition. Their Specific capacitance (Sc) was from 200 to 278 Fg^{-1} in 1 M KOH within 0.5V potential windows. Tin oxide is a widely used material in lithium battery. Wu et al. deposited tin oxide onto graphite by cathodical electrodeposition method, which resulted in a rough, porous and nano-structured morphology which was composed of small nanowires. The as prepared electrode showed a Sc of 298 Fg^{-1} at a scan rate of 10 mVs^{-1} . Recently, amorphous vanadium oxide (V_2O_5) has received a lot of attention as supercapacitor electrode material in aqueous and organic electrolyte. Lee and Goodenough synthesized amorphous V_2O_5 by quenching V_2O_5 powders that were heated at 1183K, and obtained a Sc of 350 Fg^{-1} [56]. An even higher capacitance of 910 Fg^{-1} was reported for a $\text{V}_2\text{O}_5/\text{CNT}$ nanocomposite at 10 mVs^{-1} .

In conclusion, transition metal oxides show a wide range of specific capacitance values and energy density, which generally are higher than those of carbon based or conducting polymer based supercapacitors. Their vast diversity in type, structure, morphology,

preparation methods and corresponding properties make them very promising supercapacitor materials. Current studies have not fully realized their full potentials. Future evolution of transition metal oxide based supercapacitor electrode material relies on advances in nanostructure design and better understanding of energy storage mechanisms.

2.5 Current collectors and electrolyte

As stated before, the electrochemical performance of supercapacitors is closely related to the internal resistance. Low contact resistance between active material and current collector is a benefit for better supercapacitor performance. Many approaches have been adopted to decrease the contact resistance. Surface treatment has been shown to be able to decrease the ohmic drop at the interface and improve electrochemical stability at high load condition [57]. Using a nanostructured current collector is another approach; it could not only provide increased contact area but also control the interfacial property between current collector and active electrode material. By coating porous carbon or carbon nanotubes on current collector before further active material deposition, the pseudo-capacitive material would be restricted into a thin film with high specific surface area. As a result, the as obtained nano-architected electrode could outperform the composite electrode and reach higher specific capacitance due to the increased active material utilization ratio.

The electrolyte is another important factor affecting the electrochemical performance of the supercapacitor electrode. There are few types of electrolyte: aqueous, organic and ionic liquid electrolyte; they have different decomposition voltage which determines the potential range that electrode material can be charged and discharged in. For Aqueous electrolyte like KOH and Na₂SO₄, their maximum operation voltage is around 0.9 V. While for an organic electrolyte, the voltage can reach to 2.5-2.7 V. As for ionic liquid

electrolytes, they are liquid solvent-free electrolytes at room temperature, therefore their decomposition voltage is only limited by the electrochemical stability of the ions, thus by careful design, it can withstand very high voltage the potential window [58]. From Equation 2.6, we know that the energy density is proportional to the voltage squared, thus stable electrolytes with wide potential window and high conductivity are strongly desired in order to obtain high energy density. Currently, although electrode materials usually exhibit higher capacitance in aqueous electrolyte due to better ionic conductivity, in practical applications, organic electrolyte solutions in acetonitrile or propylene carbonate are commonly used because they can provide larger potential window, higher energy density as well as more stable performances. As for ionic liquid electrolytes, since they have very low ionic conductivity at room temperature, they are mainly used in situations when high operation temperature is needed.

2.6 References

1. US 2800616, B., H.I., "Low voltage electrolytic capacitor", issued 1957-07-23.
2. Conway, B.E., *Electrochemical Supercapacitors*. 1999.
3. Miller, J.R. and P. Simon, *Materials science - Electrochemical capacitors for energy management*. Science, 2008. **321**(5889): p. 651-652.
4. K √ ∂tz, R. and M. Carlen, *Principles and applications of electrochemical capacitors*. Electrochimica Acta, 2000. **45**(15-16): p. 2483-2498.
5. Conway, B.E., *Electrochemical supercapacitors: sientific fundamentals and technological applications*. 1999: Springer. 698.
6. H. V. Helmholtz, A.P.L., 1853, 89, 21.
7. G. Gouy, J.P., 1910, 4, 457.
8. D. L. Chapman, P.M., 1913, 6, 475.
9. O. Stern, Z.E., 1924, 30, 508.
10. Simon, P. and Y. Gogotsi, *Materials for electrochemical capacitors*. Nature Materials, 2008. **7**(11): p. 845-854.
11. Qu, D. and H. Shi, *Studies of activated carbons used in double-layer capacitors*. Journal of Power Sources, 1998. **74**(1): p. 99-107.
12. Raymundo-Pi √ ± ero, E., et al., *Relationship between the nanoporous texture of activated carbons and their capacitance properties in different electrolytes*. Carbon, 2006. **44**(12): p. 2498-2507.
13. Huang, J., B.G. Sumpter, and V. Meunier, *A Universal Model for Nanoporous Carbon Supercapacitors Applicable to Diverse Pore Regimes, Carbon Materials, and Electrolytes*. Chemistry – A European Journal, 2008. **14**(22): p. 6614-6626.
14. Wen, T.-C. and C.-C. Hu, *Hydrogen and Oxygen Evolutions on Ru-Ir Binary Oxides*. Journal of The Electrochemical Society, 1992. **139**(8): p. 2158-2163.
15. Hu, C.-C., et al., *Design and Tailoring of the Nanotubular Arrayed Architecture of Hydrous RuO₂ for Next Generation Supercapacitors*. Nano Letters, 2006. **6**(12): p. 2690-2695.
16. Lokhande, C.D., D.P. Dubal, and O.-S. Joo, *Metal oxide thin film based supercapacitors*. Current Applied Physics, 2011. **11**(3): p. 255-270.
17. Barbieri, O., et al., *Capacitance limits of high surface area activated carbons for double layer capacitors*. Carbon, 2005. **43**(6): p. 1303-1310.
18. Largeot, C., et al., *Relation between the Ion Size and Pore Size for an Electric Double-Layer Capacitor*. Journal of the American Chemical Society, 2008. **130**(9): p. 2730-2731.
19. Azais, P., et al., *Causes of supercapacitors ageing in organic electrolyte*. Journal of Power Sources, 2007. **171**(2): p. 1046-1053.

20. Pandolfo, A.G. and A.F. Hollenkamp, *Carbon properties and their role in supercapacitors*. Journal of Power Sources, 2006. **157**(1): p. 11-27.
21. Zhang, H., et al., *Growth of Manganese Oxide Nanoflowers on Vertically-Aligned Carbon Nanotube Arrays for High-Rate Electrochemical Capacitive Energy Storage*. Nano Letters, 2008. **8**(9): p. 2664-2668.
22. Niu, C., et al., *High power electrochemical capacitors based on carbon nanotube electrodes*. Applied Physics Letters, 1997. **70**(11): p. 1480-1482.
23. Frackowiak, E., et al., *Nanotubular materials for supercapacitors*. Journal of Power Sources, 2001. **97-98**(0): p. 822-825.
24. Frackowiak, E. and F.B. B. √ ©guin, *Carbon materials for the electrochemical storage of energy in capacitors*. Carbon, 2001. **39**(6): p. 937-950.
25. Bordjiba, T., M. Mohamedi, and L.H. Dao, *New Class of Carbon-Nanotube Aerogel Electrodes for Electrochemical Power Sources*. Advanced Materials, 2008. **20**(4): p. 815-819.
26. Frackowiak, E., et al., *Enhanced capacitance of carbon nanotubes through chemical activation*. Chemical Physics Letters, 2002. **361**(1-2): p. 35-41.
27. Brownson, D.A.C. and C.E. Banks, *Graphene electrochemistry: an overview of potential applications*. Analyst, 2010. **135**(11): p. 2768-2778.
28. Pumera, M., *Electrochemistry of graphene: new horizons for sensing and energy storage*. The Chemical Record, 2009. **9**(4): p. 211-223.
29. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nat Mater, 2007. **6**(3): p. 183-191.
30. McCreery, R.L., *Advanced Carbon Electrode Materials for Molecular Electrochemistry*. Chemical Reviews, 2008. **108**(7): p. 2646-2687.
31. S.R.C. Vivekchand, C.S.R., K.S. Subrahmanyam, A. Govindaraj and C.N.R. Rao. J. Chem. Sci., 120 (2008), p. 9.
32. Wang, Y., et al., *Supercapacitor Devices Based on Graphene Materials*. The Journal of Physical Chemistry C, 2009. **113**(30): p. 13103-13107.
33. Wang, H., et al., *Graphene oxide doped polyaniline for supercapacitors*. Electrochemistry Communications, 2009. **11**(6): p. 1158-1161.
34. Lu, T., et al., *Electrochemical behaviors of graphene, ZnO and graphene, ZnO composite films for supercapacitors*. Electrochimica Acta, 2010. **55**(13): p. 4170-4173.
35. Zhang, Y., et al., *Capacitive behavior of graphene, ZnO composite film for supercapacitors*. Journal of Electroanalytical Chemistry, 2009. **634**(1): p. 68-71.
36. Du, X., et al., *Graphene nanosheets as electrode material for electric double-layer capacitors*. Electrochimica Acta, 2010. **55**(16): p. 4812-4819.
37. Pan, D., et al., *Li Storage Properties of Disordered Graphene Nanosheets*. Chemistry of Materials, 2009. **21**(14): p. 3136-3142.
38. Snook, G.A., P. Kao, and A.S. Best, *Conducting-polymer-based supercapacitor devices and electrodes*. Journal of Power Sources, 2011. **196**(1): p. 1-12.

39. Huang, L.-M., T.-C. Wen, and A. Gopalan, *Electrochemical and spectroelectrochemical monitoring of supercapacitance and electrochromic properties of hydrous ruthenium oxide embedded poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid) composite*. *Electrochimica Acta*, 2006. **51**(17): p. 3469-3476.
40. Li, W., et al., *Application of ultrasonic irradiation in preparing conducting polymer as active materials for supercapacitor*. *Materials Letters*, 2005. **59**(7): p. 800-803.
41. Sivaraman, P., et al., *All-solid supercapacitor based on polyaniline and sulfonated poly(ether ether ketone)*. *Journal of Power Sources*, 2003. **124**(1): p. 351-354.
42. Vaillant, J., et al., *Chemical synthesis of hybrid materials based on PANi and PEDOT with polyoxometalates for electrochemical supercapacitors*. *Progress in Solid State Chemistry*, 2006. **34**(2-4): p. 147-159.
43. Kim, I.-H. and K.-B. Kim, *Electrochemical Characterization of Hydrous Ruthenium Oxide Thin-Film Electrodes for Electrochemical Capacitor Applications*. *Journal of The Electrochemical Society*, 2006. **153**(2): p. A383-A389.
44. Zheng, J.P., P.J. Cygan, and T.R. Jow, *Hydrous ruthenium oxide as an electrode material for electrochemical capacitors*. *Journal of The Electrochemical Society*, 1995. **142**(8): p. 2699-2703.
45. Sato, Y., et al., *Electrochemical behavior of activated-carbon capacitor materials loaded with ruthenium oxide*. *Electrochemical and Solid-State Letters*, 2000. **3**(3): p. 113-116.
46. Miller, J.M. and B. Dunn, *Morphology and Electrochemistry of Ruthenium/Carbon Aerogel Nanostructures*. *Langmuir*, 1999. **15**(3): p. 799-806.
47. Kim, H. and B.N. Popov, *Characterization of hydrous ruthenium oxide/carbon nanocomposite supercapacitors prepared by a colloidal method*. *Journal of Power Sources*, 2002. **104**(1): p. 52-61.
48. Bo, G., et al., *Amorphous RuI-yCryO2 loaded on TiO2 nanotubes for electrochemical capacitors*. *Electrochimica Acta*, 2006. **52**(3): p. 1028-1032.
49. Lee, H.Y. and J.B. Goodenough, *Supercapacitor Behavior with KCl Electrolyte*. *Journal of Solid State Chemistry*, 1999. **144**(1): p. 220-223.
50. Wei, W.F., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. *Chemical Society Reviews*, 2011. **40**(3): p. 1697-1721.
51. Xu, M., et al., *Hydrothermal Synthesis and Pseudocapacitance Properties of α -MnO₂ Hollow Spheres and Hollow Urchins*. *The Journal of Physical Chemistry C*, 2007. **111**(51): p. 19141-19147.
52. Kim, H. and B.N. Popov, *Synthesis and Characterization of MnO₂-Based Mixed Oxides as Supercapacitors*. *Journal of The Electrochemical Society*, 2003. **150**(3): p. D56-D62.
53. Chang, J.-K., W.-C. Hsieh, and W.-T. Tsai, *Effects of the Co content in the material characteristics and supercapacitive performance of binary Mn-Co oxide electrodes*. *Journal of Alloys and Compounds*, 2008. **461**(1-2): p. 667-674.

54. Sun, L.-J. and X.-X. Liu, *Electrodepositions and capacitive properties of hybrid films of polyaniline and manganese dioxide with fibrous morphologies*. European Polymer Journal, 2008. **44**(1): p. 219-224.
55. Gupta, V., S. Gupta, and N. Miura, *Potentiostatically deposited nanostructured $\text{Co}_x\text{Ni}_{1-x}$ layered double hydroxides as electrode materials for redox-supercapacitors*. Journal of Power Sources, 2008. **175**(1): p. 680-685.
56. Lee, H.Y. and J.B. Goodenough, *Ideal Supercapacitor Behavior of Amorphous $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in Potassium Chloride (KCl) Aqueous Solution*. Journal of Solid State Chemistry, 1999. **148**(1): p. 81-84.
57. Portet, C., et al., *Modification of Al current collector surface by sol-gel deposit for carbon-carbon supercapacitor applications*. Electrochimica Acta, 2004. **49**(6): p. 905-912.
58. Kim, T.Y., et al., *High-Performance Supercapacitors Based on Poly(ionic liquid)-Modified Graphene Electrodes*. ACS Nano, 2010. **5**(1): p. 436-442.

Chapter 3 CTAB modified MnO₂ for supercapacitor application

3.1 Introduction

As mentioned in last chapter, there are three types of supercapacitor electrode materials: carbon-based material, conducting polymers and transition metal oxides. Among them, transition metal oxide delivers the highest capacitance and energy density; however it also has limitations like short cycle life and poor rate performances. There is plenty room for the development of transition metal oxide based supercapacitors. Ruthenium oxide is a very good supercapacitor material because of its ideal pseudo-capacitor behavior, high capacitance and stable cyclic stability, however its high cost and toxicity limit its application to only a very few fields, and not suitable for mass applications. In this situation, Manganese dioxide, which also provides high capacitance but has much lower cost and environment friendly nature has caused great interests of researchers. Moreover, manganese dioxide has multiple oxidation states, wide diversity of crystal forms, defect chemistry, morphology, porosity and texture, which makes it capable of exhibiting a variety of distinct electrochemical properties by carefully control of these crystal structure and morphology properties. In 1999, Lee and Goodenough firstly reported the use of amorphous MnO₂ as supercapacitor electrode, which delivered a specific capacitance of about 200 F/g. Since then, MnO₂ has been actively studied. In 2002, a carbon/MnO₂ based aqueous asymmetric capacitor with 2 V operating voltage, which was two times of that of symmetric aqueous capacitor, was reported and even widened the application of MnO₂ as supercapacitor electrode material.

To get a better understanding of electrochemical performances of MnO₂ as supercapacitor material, it is necessary to look at the crystal structures of MnO₂.

MnO_2 represents a general class of materials exhibiting rich chemistry; it is diverse in crystalline structure and valence state. Normally, MnO_2 is a complex, non-stoichiometric oxide and often contains foreign cations, structural vacancies; physisorbed and structure water molecular. Therefore the average valence of Mn in MnO_2 usually locates between 3 and 4. It also should be noted that although MnO_2 has multiple crystalline structures, only one basic structure unit builds it up: MnO_6 octahedron. By sharing can share vertices and edges, MnO_6 octahedral can form endless chains of octahedral subunits, which can then be linked to neighboring octahedral chains by sharing corners or edges. The building up of MnO_6 units is able to create one dimensional (1D), two dimensional (2D) or three dimensional (3D) tunnels, as shown in Figure 3.1 below [1].

Figure 3-1 Crystallographic structures of MnO_2

Table3.1 Crystal structure of manganese dioxides

Type	Crystal structure	Description
$\alpha\text{--MnO}_2$ (psilomelane)[2]	Monoclinic, $A2/m$ $A=b=9.7876 \text{ \AA}$ $C=2.8650 \text{ \AA}$	Cross-linking of double or triple chains of the [3] octahedral resulting in two-dimensional tunnels within the lattice
$B\text{--MnO}_2$ (pyrolusite)[4]	Rutile structure, $P4_2/mmm$ $A=4.428 \text{ \AA}$ $B=2.878 \text{ \AA}$	Rutile structure with an infinite chain of [3] octahedral sharing opposite edges; each chain is corner linked with four similar chains
$B\text{--MnO}_2$ (ramsdellite)[5]	$Pbnm$ $A=4.513 \text{ \AA}$ $B=9.264 \text{ \AA}$ $C=2.859 \text{ \AA}$	Similar to rutile that the single chains of edge-sharing octahedral are double chains instead
$\gamma\text{--MnO}_2$ (nsutite)[6]	Orthorhombic $A=4.45 \text{ \AA}$ $B=9.305 \text{ \AA}$ $C=2.85 \text{ \AA}$	Irregular intergrowth of pyrolusite and ramsdellite
$\lambda\text{--MnO}_2$ [7]	Spinel structure, $Fd3m$ $A=B=C=8.0974 \text{ \AA}$	Mn ions occupy the 16d sites in the $Fd3m$ and form a 3D structure with corner-sharing tetrahedral
$\delta\text{--MnO}_2$ (phyllosilicate)[8]	Birnessite, $R3m$ $C=7.2 \text{ \AA}$	Layer structure, containing infinite two-dimensional sheets of edge-shared [3] octahedral

These structures could also be characterized by the number of octahedral subunits $T (n * m)$ that compose the tunnels. The representative 1D tunnel structures include pyrolusite ($T_{1,1}$), ramsdellite ($T_{1,2}$), and hollandite ($T_{2,2}$); famous 2D structure is birnessite $\delta\text{-MO}_2$ ($T_{1,\infty}$) which has a lamellar structure with space distance between the two layers ranges from 0.55 to 1.00 nm depending on the presence of foreign cations or water molecules; for 3D tunnel structure, the characteristic one is spinel $\lambda\text{-MnO}_2$. All of the tunnels in MnO_2 are ready for foreign cations or water molecules intercalation. In nature, there exist many natural forms of MnO_2 composites intercalated with various univalent or bivalent cations. The presence of foreign cations in the tunnels will force Mn^{4+} ions transform into Mn^{3+} ion to balance the charge, therefore the cation-containing feature coupled with the reversible transition between Mn^{4+} and Mn^{3+} make MnO_2 a relatively ideal

supercapacitor electrode material. By proper combination of tunnel structures and selection of optimal foreign cations intercalated in the tunnels, MnO₂ with specific electrochemical properties could be designed.

3.1.1 Energy storage mechanism of MnO₂

MnO₂ has been used in energy storage field for more than 100 years since the application of Zn/MnO₂ cell, which dominated in primary battery chemistry for a long time. In Zn/MnO₂ cell, MnO₂ stores charges by so called double injection process, which involves the insertion of protons from the aqueous solutions and the reduction of Mn in oxides by electrons from external circuit. Later, lithium battery based on spinel Li_{1-x}MnO₂ has been commercialized for mass application, where MnO₂ stores charges by absorbing lithium cations from the electrolyte into the tunnels and meanwhile transferring electrons to neighboring Mn(IV) state to balance the charge. As soon as the capacitive behavior of MnO₂ in aqueous electrolyte has been discovered, intensive research are dedicated to study the energy storage mechanism of MnO₂. Some researchers [9] proposed that the capacitive charge storage mechanism of MnO₂ is similar to that of RuO₂ and Zn/MnO₂. The charging/discharging process can be expressed as:

This process involves the reversible insertion/desertion of protons and change of Mn valence states between Mn(IV) and Mn(III). It was also observed that the specific capacitance of MnO₂ was directly related to the type of species and concentrations of the alkaline metal cations with the same PH value. Therefore it is proposed that the chemisorption of alkaline metal cations on the surface of MnO₂ as well as hydrated cations also play important roles. The corresponding process is expressed as follows, where M⁺ is the alkaline metal cations:

Subsequent researches on the role of electrolyte cations species and concentration indicated a logarithmic dependence of the capacitance on alkaline metal cation activity [10], which confirmed the alkaline metal cations play an important role in the charge storage process. Later, Belanger et al. calculated a theoretical specific surface capacitance of 110 $\mu\text{F cm}^{-2}$ by assuming that a pure faradic charge transfer storage mechanism happens on the surface of MnO₂ [1]. However, most published reports showed higher specific surface capacitances than the theoretical value, which leads to the suggestion that alkaline metal cations will intercalate/de-intercalate within the oxide lattice during charging/discharging process as expressed in equation 3.3, where M⁺ is the alkaline metal cations:

In 2004, Toupin et al.[11] verified this alkaline metal cations intercalate/de-intercalate theory by using ex situ x-ray photoelectron spectroscopy (XPS) to determine the valence state of Mn during charging/discharging process and an in-situ synchrotron x-ray diffraction to monitor the expansion and shrinkage in lattice spacing. The apparent lattice expansion and shrinkage during redox process indicated that the insertion of cations in the electrolytes is the main charge storage process of MnO₂ [12].

After a brief review of the different forms of crystal structure and charge storage mechanism of MnO₂, it is easy to see how the proper choose of tunnel structures and insertion ions would affect the supercapacitor performances of MnO₂. The first systematic study comparing the capacitive properties of MnO₂ powders in various crystal structures was reported by Brousse et al in 2006 [13]. The MnO₂ powders in α -, β -, δ -, γ - and λ - crystal structures were prepared through co-precipitation and sol-gel methods

under different synthesis conditions. A list of their crystal structure, BET surface area and corresponding specific capacitances were shown in table 3.2.

Table 3.2 Relationship between the crystal structure, BET surface area, and specific capacitance[14]

Compound	Structure	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$C/F \text{ g}^{-1}$	Scan rate/ mV s^{-1}	Electrolyte
co-MnO ₂	α -MnO ₂	200	150	5	0.1 M K ₂ SO ₄
Ambigel H ₂ SO ₄	α -MnO ₂	208	150	5	0.1 M K ₂ SO ₄
Ambigel H ₂ O	α -MnO ₂	8	125	5	0.1 M K ₂ SO ₄
λ -MnO ₂	λ -MnO ₂	35	70	5	0.1 M K ₂ SO ₄
γ -MnO ₂	γ -MnO ₂	41	30	5	0.1 M K ₂ SO ₄
β -MnO ₂	β -MnO ₂	1	5	5	0.1 M K ₂ SO ₄
Birnessite H ₂ O	Birnessite δ -MnO ₂	17	110	5	0.1 M K ₂ SO ₄
Birnessite H ₂ SO ₄	Birnessite δ -MnO ₂	89	105	5	0.1 M K ₂ SO ₄
Birnessite	Birnessite δ -MnO ₂	3	80	5	0.1 M K ₂ SO ₄

From these data, it is revealed that the capacitance depends not only on specific surface area but also on the crystalline structure of MnO₂, because the size of the tunnels would affect the intercalation of cations. Birnessite δ -MO₂ with a 2-D tunnel structure doped with potassium has relatively high capacitance 110 F/g even with moderate BET surface area (17m²/g). A more recent work by Ghodbane et al [15] discovered that 3-D type λ -spinel showed the highest capacitance, followed by the 2D layer birnessite sample, for the 1D tunnel group, a larger cavity corresponded to a larger capacity [15]. Besides that the presence of other pre-existed metal cations in the tunnel would hinder the diffusion and storage of the electrolyte cations and result in smaller capacitance[15]. In addition, other research showed that aprotic ionic liquid anions with far bigger diameters than that

of alkaline metal ion such as DCA^- in butylmethylpyrrolidinium-dicyanamide could also be stored in the MnO_2 tunnels. In this aprotic ionic liquid electrolyte, the potential window could be enlarged to 3 V, three times higher than in the mild aqueous electrolytes, which significantly increased the energy density of MnO_2 . Lately, a multivalent cation storage mechanism is proposed [16], which is expected to increase the redox level that is determined by the number of intercalated ion concurrent with the charge transfer of the required number of electrons[1], and as a result, gravimetric capacity and energy density will increase.

It should be noted that although the intercalation redox process of the electrolyte cations is the main charge storage mechanism of MnO_2 , other factors also play an important role in determining the overall supercapacitor performances. Comparison study of some of the reported MnO_2 performances showed that there is a big divergence between the results reported on the specific surface area and capacitance of nanocrystalline MnO_2 , which means that there are other factors affecting the supercapacitor performance such as the pH value of electrolyte, morphology, defect chemistry (cation distributions and oxidation states) and residual water content. There is no best uniform structure and morphology for MnO_2 electrode. Surface and bulk (crystal structure and microstructure) properties simultaneously determine the overall electrochemical performances of MnO_2 . A rational design to maximize the electrochemical active sites for electrochemical redox reactions through increasing BET surface area and modification of electrode/electrolyte interfacial property are essential to enhance the supercapacitor performance of MnO_2 .

3.1.2 Various preparation techniques of MnO_2

Manganese dioxides are generally used in two forms in supercapacitor, one is in powder form and the other is in thin film architecture. Most of the MnO_2 powders are prepared through simple co-precipitation method according to the following equation:

The first reported MnO₂ supercapacitor electrode in amorphous powder form was synthesized by reacting KMnO₄ with Mn(CH₃COO)₂ in water. Later many other reducing agents like MnSO₄, sodium dithionite [11], and ethylene glycol [17] have been reacted with KMnO₄ to produce MnO₂ using co-precipitation method. The as prepared MnO₂ powders without further process except baking at a low temperature (lower than 100°C) are usually in amorphous α- MnO₂ form with nearly 20% water content, their specific surface area could reach more than 200 m²/g [1]. Upon heating, structure water is removed and crystallinity increases. At very high temperature, MnO₂ can be completely transformed into Mn₃O₄, with significant change of morphology and chemistry. At the same time, a decrease of surface area and specific capacitance is observed as heating temperature increases, indicating the tight relationship between the microstructure and capacitance. Figure 3.2 shows the SEM images of the MnO₂ annealed at different temperatures [18].

Figure 3.2 SEM images of MnO_2 samples. (a) Dried in air and annealed at 50°C, (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C, (f) 600°C, for 3 h in air [19]

The co-precipitation method also allows to prepare MnO_2 with various morphologies and crystalline structures through modifying electrolyte pH values [20], temperature [21], additives [22], Mn sources [22] and reaction environment (such as ultrasonic assistant [23]). Other preparation techniques like hydrothermal or solvothermal method are also used to prepare MnO_2 with different nano-architectures including nanoparticles, nanorods, nanowires and nanotubes by choosing properly reaction temperature, time, active fill level and solvent used for the reaction [24]. Subramanian et al reported a hydrothermal route to prepare MnO_2 through reaction of MnSO_4 and KMnO_4 . By varying reaction time, morphologies from plate like to nanorods could be obtained and they found that nanostructure with combination of plate like and nanorod morphology showed the moderate surface area and highest capacitance of 168F/g at 20mA/g [25]. Xu et al reported another simple hydrothermal process using KMnO_4 , sulfuric acid and Cu scraps. α - MnO_2 hollow spheres and hollow urchins with a highly loose, mesoporous cluster

structure consisting of thin plates of nanowires were obtained [26] (Figure 3.3 c), which exhibited enhanced rate capacity and cyclic stability. Besides the two techniques: co-precipitation and hydrothermal mentioned above, low temperature reduction, microwave sources assisted or template-assisted sol gel method [27] as well as solution combustion technique[28] were also developed to prepare MnO₂ of various morphologies as shown in Figure 3.3. A brief comparison of MnO₂ prepared using different methods and their corresponding electrochemical performances are listed in Table 3.3.

Figure 3.3 crystalline MnO₂ with plate like (a) nanorod (b), hollow sphere, urchin (c), cubic (d), nanowires, (e) lamellar, (f) morphologies prepared by hydrothermal method

Table 3.3 Synthesis conditions, physicochemical features, and subsequent specific capacitance of crystalline MnO₂ [29]

Technique	Synthesis conditions	Morphology	Structure	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$C/F \text{ g}^{-1}$
Hydrothermal	$\text{MnSO}_4 \cdot \text{H}_2\text{O} + \text{KMnO}_4$, 140 °C[25]	Plate-like, nanorods	$\alpha\text{-MnO}_2$	100–150	72 to –168 (200 mA g^{-1})
Hydrothermal	$\text{KMnO}_4 + \text{nitric acid}$, 110 °C[30]	Urchin-like	$\alpha\text{-MnO}_2$	80–119	86–152 (5 mV s^{-1})
Hydrothermal	$\alpha\text{-NaMnO}_2 + \text{nitric acid}$, 120 °C[31]	Lamellar	$\delta\text{-MnO}_2$	—	241 (2 mA cm^{-2})
Low temperature reduction	$\text{KMnO}_4 + \text{formamide}$, 40 °C[32]	Nanoflower	Cubic MnO_2 ($Fd3m$)	225.9	121.5 (1000 mA g^{-1})
Microwave-assisted emulsion	$\text{KMnO}_4 + \text{oleic acid} +$ microwave[33]	Belt-like	$\delta\text{-MnO}_2$	—	277 (0.2 mA cm^{-2})
Sol–gel process	Manganese acetate + citric acid, 80 °C[34]	Nanorods	$\gamma\text{-MnO}_2$	—	317 (100 mA g^{-1})
Solution combustion	$\text{Mn}(\text{NO}_3)_2 + \text{C}_2\text{H}_5\text{NO}_2$ [35]	Plate-like	$\varepsilon\text{-MnO}_2$	23–43	71–123 (1000 mA g^{-1})

Despite MnO₂ powders perform well as supercapacitor electrode, it also has limitations like low electronic conductivity, which restricts high rate charge/discharge process and large contact resistance between MnO₂ powder and conductive substrate that deteriorates the supercapacitor performances of MnO₂. As a result, in a typical MnO₂ powder electrode, it needs to be mixed with other electronic conductive enhancer (usually a high surface area graphite carbon) and a polymeric binder. The total amount of carbon and

polymeric binder ranges from 15 to 35% in weight and up to 70% in volume, which inevitably reduces gravimetric and volumetric energy densities.

Therefore from fundamental mechanism studies and potential application in micro-scale energy storage systems point of view, supercapacitor electrode based on MnO_2 thin film has caused wide interest. MnO_2 thin film based supercapacitor electrode doesn't need any binders or conductive enhancers and thus usually delivers higher capacitance due to higher material utilization ratio. In a typical application, a manganese oxide thin layer with desirable physical features is directly applied on a current collector through a variety of techniques, including sol-gel dip coating [36], anodic/cathodic electrodeposition, electrophoresis deposition [37], electrochemical formation of manganese dioxide and followed by sputtering-electrochemical oxidation [38]. Sol-gel deposition of thin MnO_2 involves preparing stable MnO_2 colloidal solution, then dip-coating or drop coating colloidal MnO_2 solution onto conductive substrate followed by calcination at various temperatures. During synthesis, calcination temperature plays an important role in determining surface morphology, specific surface area, and capacitance. The highest surface areas and specific capacitances were normally achieved at temperatures ranging from 200 to 300°C, which is believed to generate high porosity and well defined pore size distribution through evaporation of absorbed water, solvent, and organic molecules. However, calcination at high temperature limits the type of material that can be used as substrate and also the phase structure of deposited MnO_2 . By contrast, electrophoretic deposition and anodic/cathodic electrodeposition are two room temperature techniques, which open up wide selection of substrates. Electrophoretic deposition is achieved through the movement of charged small particles towards conductive substrate surface in stable suspensions. In this technique, the MnO_2 particles are formed before electrophoretic deposition and remain unchanged during deposition.

While for anodic/cathodic electrodeposition, it starts with electrolyte solution containing Mn ions followed by series of redox reactions, and finally MnO₂ precipitates are deposited on conductive substrate. This technique allows wide selection of substrates and is able to produce uniform MnO₂ thin films with great variety of morphologies and structures by varying pH value, concentrations and types of electrolyte, as well as deposition voltage, current density and time etc. Therefore it is extensively used to prepare MnO₂ thin films. In anodic electrodeposition, when an electric field is applied, charged reactive species will diffuse through the electrolyte with specific direction, followed by oxidation of the charged species on a deposition substrate, which also serves as an electrode [24]. This process can be expressed as follows:

Since Pang et al. prepared the first electrodeposited MnO₂ thin film for supercapacitor in 2000 [24], intensive studies have been dedicated to prepare MnO₂ thin film electrode using anodic electrodeposition. Most of them focused on varying the deposition parameters such as voltage, electrolyte concentration etc. to obtain MnO₂ thin films with various water contents, oxidation states and specific surface area, the purpose it to obtain MnO₂ thin film electrode with high capacitance, good cyclic stability and fast charge/discharge rate. Among these efforts, morphology controlled growth has attracted much attention, as proper morphology is able to provide more accessible electroactive sites and shorter cation diffusion length. Morphology controlled growth is usually achieved by controlling the deposition parameters, filling template membranes or using etched, nanoporous substrates. By modifying the deposition parameters, various morphologies like continuous coating with equiaxed and fibrous feature, petal- and flower like morphology, discrete oxide cluster, columnar structure, interconnected

nanosheets, and micro/nano-scale fiber, rod morphology have been obtained as shown in Figure 3.4 [39].

Figure 3.4 Typical surface morphologies for MnO_2 electrodes prepared through template free anodic electrodeposition processes [40]

Wei et al.[39] synthesized a series of MnO_2 with different morphologies by controlling of nucleation and growth process. They concluded that anodic electrodeposition prepared MnO_2 from aqueous solutions will most likely form sheet-like morphology. By controlling the nucleation and growth kinetics, thin nanosheets with different width and height can be obtained and finally result in different morphologies. Noteworthy, the

nucleation and growth kinetics are principally determined by the supersaturation ratio of the electrolyte. Suppose there are active ions of type $I = 1, 2, \dots, j$ exist in the electrolyte solution, then the supersaturation ratio (S) is defined as:

$$S = \frac{\alpha_1^{n_1} \alpha_2^{n_2} \dots \alpha_j^{n_j}}{\alpha_{1,e}^{n_1} \alpha_{2,e}^{n_2} \dots \alpha_{j,e}^{n_j}} \quad (3.6)$$

Where a_i and $a_{i,e}$, are the actual and equilibrium activities of the i th ions and n_i is the number of electrons needed for the i th ion to form a molecule of the compound. At equilibrium condition, $S = 1$; when $S > 1$, nucleation and growth of deposition material will start. According to Rastogi et al.'s research, the frequency of nucleation increases with an increase in the supersaturation ratio is lowered than 10^3 [41]. For template-free anodic deposition of MnO₂, two active species Mn(II) and OH⁻, are involved, therefore by modifying the experiment parameters like electrolyte concentration, deposition voltage (current density), electrolyte pH and temperature, the activities of Mn(II) and OH⁻ will changed accordingly, and the supersaturation ratio will also change. At a specific supersaturation ratio, a high nucleation rate will suppress the epitaxial growth of thin nanosheets, resulting in a continuous coating composed of equiaxed particles; on the other hand, a low nucleation rate will lead to less oxide nuclei sites on the electrode surface in the early stage of electrodeposition, subsequently thin nanosheet will epitaxial grow preferentially on the small nanoparticles [42], resulting the fibrous and petal shaped morphologies; at very low nucleation rate, ridges, columnar, interconnected nanosheet architectures will be obtained. A schematic diagram correlates the variation of deposition parameters and supersaturation ratio with evolution of physicochemical features of manganese dioxide during anodic electrodeposition is shown in Figure 3.5 below:

Figure 3.5 Schematic diagram correlating manganese dioxide morphology evolution with supersaturation ratio changes (thin sheets, rods, aggregated rods and non-uniform continuous coatings are formed as the current density, solution concentration, pH and temperature are increased [43])

Among these various MnO_2 morphologies, MnO_2 with oriented nanostructures such as columnar structure and interconnected nanosheet architecture often have higher specific capacitance and better rate capability than others due to higher specific surface area and improved manganese dioxide utilization[44].

Structure directing agent assisted method is another very effective way to prepare material with controlled nanostructures and morphologies. It can either use hard template like mesoporous silica, Anodic aluminum oxide (AAO), polystyrene sphere or soft template like surfactant, to guide the growth of the reactants and control the morphology and nanostructure of MnO_2 . The AAO template, which has ordered hexagonal nanochannels, offers a promising route to synthesize a high surface area, ordered nanowire electrode. Xu et al [45] deposited MnO_2 on AAO/Ti/Si substrate followed by dissolution of AAO. The unique mechanical and conductive properties of Ti/Si substrate helped to retain the nanostructure after AAO was removed and MnO_2 with ordered nanowire structure on Ti/Si substrate was obtained, which exhibited an average pore diameter of 40 nm and specific capacitance of 254 F/g at 10 mV/s. However, in the application of hard template, it needs to be removed after the formation of MnO_2 by chemical dissolution or combustion, which leads to a complex preparation procedure; while for soft template, it is more versatile, easier to be removed by dissolution and therefore it is more popular

than hard template. In a typical microemulsion method which uses surfactant to assist MnO₂ preparation, micro/nano droplets of water phase containing reactants are dispersed and stabilized by a surfactant in an organic medium to form microemulsion. When the water droplets of two reactants collide, the reactants could diffuse through surfactant layer between the two droplets and reactions take place at the interphase to produce nanoparticles. The surfactant also acts to restrict the growth of nanoparticles when the particle size approaches that of water droplets. As a result, MnO₂ powders in nanosphere, nanotube, nanowire and nanoporous morphologies could be obtained with capacitances ranging from 240 F/g to 297 F/g [1]. Typical surfactants used for MnO₂ powder preparation include sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in iso-octane solution [46], CCL₄ [47] and ferrocene/chloroform solution [48] etc.. Surfactant can also be used to prepare MnO₂ thin films using surfactant assisted co-precipitation method. However, compared with powder MnO₂ there are only few papers about structural directing agent assisted MnO₂ thin film synthesis. One typical example is EO₂₀PO₇₀EO₂₀ triblock copolymer Pluronic P123 [49], which was able to coordinate with MnO₂ precursors and form certain complex to direct the structure of MnO₂ precipitate. After filtration and washing with water and ethanol, P123 was removed and the as prepared MnO₂ showed a loose and clew-like shape, consisting of nanowires of 8-20 nm in diameter and 200-400 in length, the maximum capacitance is 176 F/g compared with 77 F/g for MnO₂ prepared without 123. Another good example of soft template is lyotropic liquid crystal (LLC) that has unique principle and flexibility in controlling the structure of meso-structured materials. The LLC template is formed by dissolution of LLC phase surfactant (>40 wt %) in plating solution, and subsequently served like “hard template” to determine the electrodeposited microstructure. Dong et al. [50] prepared a binary system of 60 wt% Brij56 (polyoxyethylene (10) cetyl ether, C₁₆EO₁₀) surfactant and 40 wt% 0.5 M MnAc₂ as electrolyte for anodic electrodeposition of MnO₂, followed by calcinations at 200 °C

to remove the Brij56 template. Finally MnO_2 with amorphous nature and small size of crystalline grain was obtained, exhibiting a copy of Brij56 template with a vine-like morphology. A high capacitance of 460 F/g was observed at 10mv/s. Xu and his co-workers combined the AAO template with LLC template together to obtain an array of mesoporous MnO_2 nanowires, the specific capacitance of which can reach 493 F/g at 4 A/g, the only disadvantage is that it has much lower capacitance (only 84F/g) at high charge/discharge rate of 12A/g. Besides high concentration surfactant such as LLC can act as template, very dilute ionic surfactant solution (surfactant solution < 10 wt %) can also act as meso-structure template during electrochemical deposition. In these approaches, surfactant interacts with inorganic ions through electrostatic force and arranges the inorganic ions into certain order. The surfactant concentration is usually set to a minimum value just enough to form a desired array on the electrode surface [51]. Devaraj et al.[52] reported MnO_2 synthesized with 0.1 mole anionic surfactant sodium lauryl sulfate (SLS) during potentio-dynamically deposition. The as obtained MnO_2 showed smaller particle size, greater porosity and higher MnO_2 utilization efficiency with a specific capacitance of 310 F/g. Non-ionic surfactant can also be used to direct the growth of MnO_2 thin film electrode, Devaraj et al.[53] published that $\delta\text{-MnO}_2$ thin film prepared by electrodeposited method in the presence of triton X-100 showed greater porosity and hence greater surface area compared with film prepared in the absence of the surfactant, the maximum capacitance was 355F/a at 5mV/s.

Cetyltrimethyl-ammonium bromide (CTAB) is a very common cationic surfactant used to synthesis nano-oxides with controlled structure and morphology. It has wide applications in electroplating, corrosion, batteries and fuel cells, electrometallurgy, electrocatalysis, electroanalysis, electroorganic chemistry and photo-electrochemistry [54]. There are reports about formation of gold nano-rods [55], enhancement of oxidation

of estradiol for nano- Al_2O_3 [56], increment of organic compound yield [57] and improved solar energy conversion efficiency when CTAB was added during synthesis[58]. One of the remarkable properties of films synthesized in presence of CTAB is inhibition of corrosion. In Khamis's study of the adsorption effects of CTAB on steel corrosion inhibition[59]; they found that the presence of CTAB during synthesis could affect the dissolution of metal and the cathodic reaction of hydrogen evolution. Moreover, with concentrations above the critical micelle concentration (cmc), the inhibitive effect of the surfactant increases with the alkyl chain length. However, the applications and effects of CTAB on manganese dioxide synthesis were rarely mentioned. In a CTAB-mediated electrochemical synthesis of MnO_2 for alkaline batteries, manganese sulfate with 0.1 wt.% CTAB was deposited onto titanium cylinder by anodic electrochemical deposition method [60]. Impedance data showed that CTAB modified MnO_2 had a lower charge transfer resistance due to enhanced interfacial phenomena and as a result faster kinetics and higher electrochemical reversibility; moreover, the resulted film had shorter diffusion path length with enhanced proton diffusion kinetics. Sun et al. [61] successfully used CTAB in their work to synthesis magnetite fibers ascribing to the structure directing effect by interacting the polar heads of CTAB (CTA^+) with the inorganic ions (e.g. O_2^-). However, so far to the best knowledge of author, there has been no report about the CTAB-mediated synthesis of MnO_2 for supercapacitor application. Therefore, as we have already know how important the crystal structure and morphologies can determine the supercapacitor performances of manganese dioxide, for the first time, CTAB is adopted during anodic electrochemical deposition of MnO_2 for supercapacitor application. The advantages of this approach include: (1) electrochemical deposition of MnO_2 directly onto conducting substrate without requirement of mixing with other conducting additives (like carbon black) and polymer binders which would increase the internal resistance and deteriorate electrochemical performances; (2)

electrochemical deposition allows to deposit very thin layer of active material which could maximize the material utilization ratio and therefore provides higher capacitance (3) CTAB surfactant assisted electrochemical deposition of MnO_2 provides an easy way to control the crystal structure and morphology growth of MnO_2 by simply adjusting the experiment conditions and the surfactant concentration; (4) last but not least, the corrosion resistance or cyclic stability promoted property of CTAB may help to improve the cyclic stability of MnO_2 , which is a major drawback of MnO_2 in supercapacitor application.

3.2 Experimental procedure

Selection of substrates

In this study, active materials were deposited on substrate and subsequently used as electrode for supercapacitor performance analysis, therefore a substrate with high conductivity and strong affiliation to the deposited active material are preferred. Three types of substrates were selected for study: conducting glass coded with indium tin oxide (ITO), graphite paper as well as stainless steel. It was observed that there was weak tendency for active material to “sit on” the substrate, very little manganese dioxide active material were deposited on the ITO substrate and the as-deposited material might peel off during subsequent electrochemical measurement. For both of graphite paper and stainless steel, manganese dioxide could firmly attached to the substrate, and manganese dioxide deposited on stainless steel showed slightly better electrochemical performances than manganese dioxide deposited on graphite paper, this could be due to difference in interfacial energy and texture orientation. Therefore, in this study, stainless steel was selected as the substrate for deposition of active materials.

Materials and electrochemical deposition setup

Analytical grade Manganese nitrite ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cetyltrimethylammonium bromide (CTAB) and sodium sulfate (Na_2SO_4) were purchased from Sigma-Aldrich and used without further purification. All other chemicals and solvents were of analytical grade. Ultra pure water from a Milli-Q reagent water system at a resistivity $> 18\text{M}\Omega\text{ cm}$ was used throughout the experiment. A three-electrode electrochemical cell was set up for electrochemical deposition and electrochemical characterization purpose, with a platinum foil ($2\text{cm} \times 2\text{cm}$), Ag/AgCl (KCl-saturated) and Stainless steel (SS) as counter electrode, reference electrode and working electrode respectively, and the distance between working electrode and counter electrode is fixed at 2 cm. Before the deposition, stainless steel plates (size $2\text{cm} \times 1\text{cm} \times 0.9\text{ mm}$) were polished with emery paper to a rough finish, then washed with ethanol and distilled water, followed by drying in oven at 60°C , after that back side of the SS film is covered with parafilm to prevent deposition of MnO_2 . A photo of the experiment setup is shown in figure 3.6 below

Figure 3.6 Experiment setup of three-electrode cell for anodic electrochemical deposition of MnO_2

Synthesis of MnO_2 film in presence of CTAB

To prepare the precursor solution for MnO₂ deposition, 1wt. %, 5 wt. % CTAB were separately added into 0.1 M manganese nitrate solution; while a 0.1 mol manganese nitrate solution was used for comparison. In a typical synthesis process, porous MnO₂ thin films were potentiostatically deposited onto SS substrates from 0.1 M manganese nitrate solutions containing 0 wt.%, 1 wt.%, and 5 wt.% CTAB at 1 V respectively. The total charge passed was controlled to be around 0.4 C. After that, the as obtained electrodes were washed in 70°C ethanol for 1 hour and then in distilled water for 1 hour, the washing cycle was repeated for three times, followed by drying in oven overnight at 60°C. The obtained electrodes were denoted as MnO₂, MnO₂CTAB1 and MnO₂CTAB5. The loading of the active materials of the as-prepared electrodes was measured as the weight difference of the electrode before and after coating of active materials by using a microbalance with an accuracy of 10 µg (Mettler Toledo, MT5).

Characterization of graphene/ MnO₂ multilayer hybrid film

The morphology and microstructure of the as-obtained MnO₂ electrodes were characterized via field emission scanning electron microscopy (FE-SEM, JOEL, JSM-6340F) and X-ray sequence spectrometer (Bruker AXS, Germany) with Cu K α radiation ($\lambda = 1.5406\text{\AA}$) operating at 40kv and 40 M α .

Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge experiment as well as electrochemical impedance spectra measurement were performed to evaluate the electrochemical performances of MnO₂ electrodes. All of the above electrochemical measurements were carried out in 1 M Na₂SO₄ aqueous electrolyte solution using the same three-electrode electrochemical setup described above for electrochemical

deposition. Voltage supply and electrochemical performance data were provided and recorded by AUTOLAB® machine (Eco Chemie, PGSTAT 30).

3.3 Results and discussion

3.3.1 Crystal structure and morphology of MnO_2 synthesized in presence of CTAB

Fig. 3.7 shows the X-ray diffraction (XRD) patterns of the as-prepared MnO_2 with 0wt.%, 1wt.%, and 5 wt.% CTAB. All three samples exhibited poor crystalline nature, which is common for anodically deposited MnO_2 , and they all matched with $\alpha\text{-MnO}_2$ (JCPDS NO.44-0141) XRD diffraction pattern. However, slightly structure evolution was observed with increasing CTAB concentration in the electrolyte. For MnO_2 , only diffraction peaks at (211) (411) and (002) were observed; while for $\text{MnO}_{2\text{CTAB}1}$, diffraction peaks at (110), (211), (411) and (002) were visible and for $\text{MnO}_{2\text{CTAB}5}$, one more peak at (310) was observed. Peak marked with (*) can be assigned to stainless steel substrate. These results showed that as the concentration of CTAB in pre-deposition solution increases, the crystallinity of MnO_2 also slightly increases. Moreover, it is noticed that there were 0.2 to 0.8 deviations between the peaks of as prepared $\alpha\text{-MnO}_2$ samples and standard JCPDS NO.44-0141 sample, the (110), (310), (211) and (002) peaks of $\alpha\text{-MnO}_2$ samples tended to shift to the left side. According the $2d\sin\theta=\lambda$, it means the as prepared $\alpha\text{-MnO}_2$ had larger interlayer spacing and slightly distortion structure, this could be probably caused by intercalated foreign ions like NO_3^+ and structural water during synthesis.

Figure 3.7 XRD patterns of MnO_2 , $\text{MnO}_{2\text{CTAB1}}$ and $\text{MnO}_{2\text{CTAB5}}$

Further microstructure and morphology characterizations of as-prepared MnO_2 films synthesized with different CTAB concentrations were measured by FESEM, results are presented in Figure 3.8 as shown below.

Figure 3.8 FESEM images of MnO_2 synthesized in presence of (a) 0wt.% CTAB, (b) and (d) 1wt.% CTAB, (c) and 5 wt.% CTAB

It can be seen from Figure 3.8 (a) that MnO_2 film prepared without CTAB exhibited a 3D fibrous network structure which is the most common surface morphology in MnO_2 electrodes prepared through galvanostatic or potentiostatic method [24]; while for MnO_2 prepared in presence of 1wt.% CTAB (b) and 5 wt.% CTAB (c), they both presented a uniform pore structure that were created by extremely thin interconnected nanosheets, their unique morphologies undoubtedly increased the accessible surface area. As mentioned before, open porous structure with high surface area is desirable for supercapacitor electrode, which not only promotes easy access of the solvated ions to the electrode/electrolyte interface but also increases accessible surface area for interface electrochemical reactions and therefore higher specific capacitance is expected. It was also interesting to note that in $\text{MnO}_{2\text{CTAB1}}$ as shown in figure 3.8 (d), some of the interconnected nanosheets even contained several sub-layers which were near transparent

and had thickness as thin as 1.5 nm. Moreover, it was noted that MnO_{2CTAB1} had more uniform and ordered pore structure than MnO_{2CTAB5} where some randomly grown nanosheet existed in the open spaces between interconnected nanosheets.

3.3.2 Influence of surfactant CTAB on the synthesis of MnO₂ electrode

As indicated in Figure 3.8, the morphologies of surfactant CTAB mediated synthesized MnO₂ have shown a relationship with the concentrations of surfactant in the pre-deposition electrolyte. It is important to explore the possible mechanism involved. The electrodeposition of MnO₂ in acidic solution is mainly the following two steps:

In the first step, Mn²⁺ is oxidized at the growing surface to form MnO₂ and some related solid intermediates (such as MnOOH, Mn₂O₃, etc). Since Mn³⁺ is unstable in hot acidic solution, it will slowly and disproportionately transform into Mn²⁺ and Mn⁴⁺. Mn²⁺ remains in the solution while Mn⁴⁺ converts to MnO₂ solid deposit with Mn³⁺ trapped through a rather fast hydrolysis reaction [22]. The reaction rate of the two steps could be affected by experiment parameters like temperature, electrolyte pH value, current density and surfactant concentrations. In the presence of surfactant CTAB, the absorbed CTAB on the interface may slow down the reaction rate of equation 3.7 as compared with equation 3.8. Besides, the absorbed surfactants located at the active growth sites or on surface high point leads to less adsorption in the rest areas where preferential deposition of materials occurs[62]. Moreover, the presence of surfactants on the electrode/electrolyte interface, micropores and interparticle channels in the already formed active material will make it harder for external electroactive species to pass through, thus an inhibition phenomena and lower growth rate are observed. That is to say

surfactant influence the kinetics of electron/ion transfer mainly by covering the electrode surface through mechanical blocking and/or electrostatic effects [63, 64]. These factors could also change the characteristic of the electric double layer and their related interface properties such as interfacial energy, dielectric constant, potential and current distribution that are vital to the crystal growth.

It is noteworthy that the specific reactivity and interactions of surfactants are related to their structures and orientations in the solution. Since surfactants are long chain molecules which contain ionic or neutral polar head groups and also non-polar regions. With proper applied potential range, surfactant with amphiphilic molecules can be absorb/desorb at solid/solution interfaces. The surfactant concentration also plays an important role, when its concentration is smaller than the critical micelle concentrations (cmc) and the head groups had a very strong columbic interaction with the surfaces, the hydrocarbon chains of surfactant will face the water and form a layer, which is named as hemimicelles as shown in Figure 3.9 below. When the surfactant concentration further increases, other structural patterns could emerged in the double layer of the electrode, for example the formation of admicelle (Figure 3.9), in which the first molecular layer attach their head groups to the electrode surface and the second layer spread their head groups into the solution.

Figure 3.9 Different arrangement of surfactants at the electrode/electrolyte interface

When the surfactant concentration is even higher than cmc and/or certain specific values, various conformations of surfactant could be generated, such as the interweaving of hydrophobic chains of adjacent molecules and the admicelles. Since the cmc value for CTAB is about 3×10^{-3} M (0.1 wt. %), CTAB concentrations used in this study (1 wt. % and 5 wt. %) both exceeded the cmc value. Despite the cationic nature of CTAB, which may repel itself from the anode surface, the high concentration CTAB may form admicelle near the electrode surface in the solution, which therefore may lead to inversion of the ion charge at the inner boundary of the diffuse layer, and subsequently cause changes to the double layer properties and electro-kinetics. The presence of CTAB in the solution may also facilitate the surface diffusion of adatoms and as a result suppress the nuclei formation rate (higher rate of Eq. (3.8) compared to Eq. (3.7)), combined with the preference of CTAB to retain the interfacial surface tension over the growing electrode surface, adatoms will preferentially locate on the specific site on the electrode in an ordered way, as a result a compact deposit would formed with thin layer thickness, large surface areas and narrow pore size distribution, which was exactly what we observed in MnO₂ electrode prepared in presence of 1 wt.% CTAB. It is also noticed that the presence of CTAB reduces surface tension, as a result less activation energy or

surface temperature are needed for the initiation of gas/vapour bubble nucleation process. That is to say abundance of small gas bubbles could be nucleated and generated uniformly on the substrate surface even at low surfactant concentration. However, higher concentration of surfactant would increase the interfacial viscosity and bubbles could not easily escape; as a result, the limiting current reduces and electrode over potential occurs and finally leads to an irregular morphology. This could be the reason for the irregular morphology observed in MnO_2 electrode prepared in presence of 5 wt. % CTAB.

3.3.3 Supercapacitor performance of MnO_2 synthesized in presence of CTAB

To further explore the supercapacitor performances of MnO_2 prepared in different CTAB concentrations, cyclic voltammetry (CV) test was conducted. It is a type of potentiodynamic electrochemical measurement, where the working electrode potential is ramped linearly with time like linear sweep voltammetry. In cyclic voltammetry test, a voltage is applied between the reference electrode and the working electrode at certain ramping rate, when the working electrode potential reaches a preset value; the ramp will be inverted until the working electrode potential reaches another pre-set value. During this process, the corresponding current between the counter electrode and the working electrode will be measured. It should be noted that the voltage inversion can happen multiple times in one test and the voltage ramping rate is called scan rate. The as obtained data of current (i) and potential (E) is plotted and known as CV curve. As shown in figure 3.10, the forward (upper) scan corresponds to oxidation of any analyte through the range of the potential scanned. The current increases as the potential reaches the highest oxidation potential of the analyte and then reduces when the analyte near the electrode/electrolyte interface is depleted. If the oxidation reaction is reversible, when the scan rate is reversed, materials formed during the first oxidation reaction will be reduced and produce a reverse current of same magnitude and similar shape to the forward scan.

Therefore, information about the redox potential and electrochemical reaction of the electrode can be read from the curve. For example, if the electric transfer at the surface is fast and the redox reaction is only limited by the diffusion of species to the electrode surface, then the peak current will have a linear relationship with the square root of the scan rate, which can be described by the Cottrell equation. In this study, cyclic voltammetry (CV) measurements were performed at a scan rate of 100 mVs^{-1} in $1 \text{ M Na}_2\text{SO}_4$ aqueous solution with a potential window of $-0.1 - 0.9 \text{ V}$, as shown in Figure 3.10.

Figure 3.10 CV curves of MnO_2 , $\text{MnO}_{2\text{CTAB1}}$ and $\text{MnO}_{2\text{CTAB5}}$ at scan rate of 100 mV/s

It is observed that CV curves for all of the three samples (MnO_2 prepared in presence of $0 \text{ wt. \% CTAB}$, $1 \text{ wt. \% CTAB}$ and $5 \text{ wt. \% CTAB}$) exhibited a symmetric but slightly distorted rectangular shape, which is the characteristic shape of CV curve for MnO_2 . The symmetry of CV shape indicated highly reversible redox reactions and good cyclic stability of as prepared MnO_2 films. In theory, if the electrochemical reactions in MnO_2

are fast and efficient enough, when a voltage is applied, the current would increase immediately like conventional capacitor and starts charging process, however in practical application, the CV curves are often distorted due to the following reasons: (1) Faradaic reactions take place during the sweep process [65] (2) internal resistance arises from electrode material and (3) the diffusion limitation of electrolyte ions in the electrode [66]. If we can reduce either the internal resistance of electrode material or improve the charge transfer in the electrode, the MnO₂ electrode will perform more close to its ideal state and therefore higher specific capacitance. Therefore in figure 3.10, when MnO₂ prepared with surfactant CTAB was observed to have CV curves more close to rectangular shape than that of MnO₂ prepared without surfactant, it is suggesting improved capacitive performances. In addition, since at the same scan rate, the average areas of CV curve is proportional to the specific capacitance of electrodes [67], it is clearly observed that the specific capacitance of the three electrodes increase in this order: MnO₂ < MnO₂ (5 wt.% CTAB) < MnO₂ (1wt.% CTAB). With information obtained FESEM images as shown in Figure 3.8, it is therefore reckoned that MnO₂ synthesized in presence of CTAB have improved supercapacitor performance due to the formation of ultra thin nanosheets and much more uniform and open porous morphology.

Figure 3.11 CV curves of $\text{MnO}_2\text{CTAB1}$ at scan rate of 100mv/s, 50mv/s, 20mv/s and 10mv/s (a) i_p vs. V plots of $\text{MnO}_2\text{CTAB1}$

Typical cyclic voltammetry curves of MnO_2 electrode prepared in presence of 1 wt. % CTAB at different scan rates (10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s) are shown in figure 3.11 (a). Note that the shape of these voltammetric curves was not significantly influenced by the change in scan rate of CV, indicating fast redox reaction rate. To further study the CV characteristics of MnO_2 electrode prepared in presence of 1 wt. % CTAB, the anodic peak current i_p (measured at 0.4 V) vs. V (voltage scan rate) is plotted in figure 3.11 (b). It is known that in an absorption process, i_p vs. V is expected to give a linear relationship regardless of the scan rates [68]. In figure 3.11(b), i_p vs. V shows a reasonably linear plot, indicating an ideally capacitive behavior of MnO_2 electrode.

Galvanostatic charge/discharge method is another useful method to study the electrochemical performances of electrode, where a constant current is applied to the working electrode, when the voltage at the working electrode reaches a pre-set potential, the current of working electrode is inverted until it reaches the next pre-set potential. The inversion can be repeated many times depending on the design of experiment. The potential is applied between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. The data is then plotted as potential (V) vs. time (s). As shown in figure 3.12, the forward (positive slope) scan indicates a reduction process while the downward (negative slope) scan indicates an oxidation process. The information of redox potential and capacitance can also be obtained from the galvanostatic charge/discharge curve, when the charge storage mechanism is EDLC, the charge/discharge curve would be a straight line, while when the charge storage mechanism is dominated by redox reactions, humps would appear on the charge/discharge curve at corresponding redox potential. In this study, galvanostatic charge/discharge measurements of MnO_2 electrode were carried out in 1 M Na_2SO_4 solution between -0.1 and 0.9 V at different current densities. Figure 3.12(a) presents the respective charge/discharge curve of MnO_2 prepared in presence of 0wt.% CTAB, 1wt.% CTAB and 5 wt.% CTAB at 1 A/g, all of them exhibited an symmetric and slightly curving shape, indicating the good reversibility of electrochemical reactions and the presence of pseudo-capacitance along with double layer capacitance. The negligible voltage drop at the tip of charge/discharge curves reveals small equivalent series resistance (ESR) and good electrical conductivity. Their specific capacitances C_s are calculated based on the discharge curves according to $C_s = I * \Delta t / (\Delta V * m)$ [69], where I is the constant discharge current, Δt is the discharge time, and ΔV is the potential drop during discharge stage [70]; The calculated C_s for MnO_2 prepared in presence of 0wt.% CTAB, 1wt.% CTAB and 5 wt.% CTAB at 1A g^{-1} are 297, 309 and 359 F g^{-1}

¹ respectively. Those results are in agreement of data obtained from CV curves. The CD curves for MnO_2 prepared in presence of 1 wt.% CTAB at different current densities (1, 2, 5, 10 and 20 A g^{-1}) are also shown in figure 3.12(b) and their corresponding capacitances are calculated to be 359, 286, 228, 195 and 168 F g^{-1}

Figure 3.12 (A) Charge/discharge curves of MnO_2 , $\text{MnO}_{2\text{CTAB}1}$ and $\text{MnO}_{2\text{CTAB}5}$ at current density of 1 Ag^{-1} (B) Charge/discharge curves of $\text{MnO}_{2\text{CTAB}1}$ at current densities of 20 Ag^{-1} , 10 Ag^{-1} , 5 Ag^{-1} , 2 Ag^{-1} , 1 Ag^{-1}

One great advantages of supercapacitor over batteries is cyclic stability, In order to evaluate the cyclic stability of the as-prepared MnO_2 prepared in presence of 1 wt.% CTAB at high load condition as in practical application, 1000 galvanostatic charge-discharge cycles were performed at a current density as high as 10 A g^{-1} between 0 and 0.8 V in 1 M Na_2SO_4 electrolyte solution. The result is shown in Fig. 3.13 with the charge/discharge curves of the first 24 cycles and the last 23 cycles displayed. It is noted that the total charge/discharge time for first 24 cycles and the last 23 cycles were the

same, which means after 1000 cycles, 104% of the initial capacitance was retained; While for MnO_2 prepared without the presence of CTAB, only about 70% of the initial capacitance remains after 1000 cycles, considering the cruel charge/discharge current density, this result shows the significant improvement of cyclicity for MnO_2 electrode prepared in presence of 1 wt.% CTAB. Following factors may be the reason for the enhancement of cycle-life: (1) electrolyte needs some time to fully penetrate through the thin film electrode, thus over time, the material utilization ration increases and specific capacitance increase accordingly (2) the presence of residual CTAB could strengthen the skeleton of MnO_2 electrode and prevent the dissolution of active materials; (3) large surface area of the mesoporous structure reduces the solid state diffusion path length of protons and electrons into and out the MnO_2 electrode [60]. As a result, higher structural tolerability of the electrode during charge/discharge cycling and better coulomb efficiency could be expected.

Figure 3.13 The charge/discharge curves of first 24 cycles and the last 23 cycles in a 1000 cyclic test

3.4 Conclusion

In this chapter, the effects of surfactant CTAB on the morphology and electrochemical performances of MnO₂ electrode have been studied. MnO₂ electrodes prepared in presence of 0 wt. % CTAB, 1 wt. % CTAB and 5 wt. % CTAB were systematically investigated through XRD, FESEM, Cyclic Voltammetry and Charge/Discharge techniques. The role of surfactant CTAB during synthesis has also been explored. The results can be concluded as follows:

- (1) The presence of CTAB in the pre-deposition electrolyte causes changes in the inner boundary of the diffuse layer as well as double layer characteristics and electrokinetics. As a result, MnO₂ electrodes with a uniform mesoporous structure formed by interconnected extremely thin nanosheets when 1 wt. % CTAB is added. Even higher concentration of CTAB (5 wt. %), however causes localized electrode overvoltage and leads to an irregular morphology.
- (2) The capacitive performances of as-prepared MnO₂ electrodes prepared with different CTAB concentrations were investigated using various techniques. It is observed that MnO₂ electrodes prepared with 1 wt. % CTAB shows the highest capacitance of 359 F g⁻¹ at 1 A g⁻¹, which is higher than those of MnO₂ and MnO₂ (5 wt. % CTAB) with capacitances of 297 F g⁻¹ and 309 F g⁻¹, respectively. The improved capacitive performances may be attributed to thinner layer thickness which means larger surface area
- (3) More importantly, the cyclic stability of MnO₂ electrodes prepared with 1 wt. % CTAB is significantly improved, with no capacitance loss after 1000 cycles. This improvement may come from the structure strengthen effects of CTAB which prevents active material loss and mesoporous structure which facilitates the charge transfer and increases structure tolerability.

Reference

1. Xu, C.J., et al., *Recent progress on manganese dioxide based supercapacitors*. Journal of Materials Research, 2010. **25**(8): p. 1421-1432.
2. Fernandes, J.B., B.D. Desai, and V.N.K. Dalal, *Manganese dioxide — a review of a battery chemical part I. Chemical syntheses and x-ray diffraction studies of manganese dioxides*. Journal of Power Sources, 1985. **15**(4): p. 209-237.
3. Devaraj, S. and N. Munichandraiah, *Effect of crystallographic structure of MnO₂ on its electrochemical capacitance properties*. Journal of Physical Chemistry C, 2008. **112**(11): p. 4406-4417.
4. Baur, W., *Rutile-type compounds. V. Refinement of MnO₂ and MgF₂*. Acta Crystallographica Section B, 1976. **32**(7): p. 2200-2204.
5. Poinسیون, C., J.M. Amarilla, and F. Tedjar, *Electrochemical reduction of β MnO₂, ramsdellite, γ - and ϵ MnO₂*. Solid State Ionics, 1994. **70–71, Part 1**(0): p. 649-653.
6. Turner, S. and P.R. Buseck, *Defects in nsutite ([gamma]-MnO₂) and dry-cell battery efficiency*. Nature, 1983. **304**(5922): p. 143-146.
7. Devaraj, S. and N. Munichandraiah, *Effect of Crystallographic Structure of MnO₂ on Its Electrochemical Capacitance Properties*. The Journal of Physical Chemistry C, 2008. **112**(11): p. 4406-4417.
8. Preisler, E., *Electrodeposited manganese dioxide with preferred crystal growth*. Journal of Applied Electrochemistry, 1976. **6**(4): p. 301-310.
9. Hu, C.-C. and T.-W. Tsou, *Ideal capacitive behavior of hydrous manganese oxide prepared by anodic deposition*. Electrochemistry Communications, 2002. **4**(2): p. 105-109.
10. Wen, S., et al., *The role of cations of the electrolyte for the pseudocapacitive behavior of metal oxide electrodes, MnO₂ and RuO₂*. Electrochimica Acta, 2004. **50**(2-3): p. 849-855.
11. Toupin, M., T. Brousse, and D. B. √ ©langer, *Charge Storage Mechanism of MnO₂ Electrode Used in Aqueous Electrochemical Capacitor*. Chemistry of Materials, 2004. **16**(16): p. 3184-3190.
12. Hu, C.-C., Y.-T. Wu, and K.-H. Chang, *Low-Temperature Hydrothermal Synthesis of Mn₃O₄ and MnOOH Single Crystals: Determinant Influence of Oxidants*. Chemistry of Materials, 2008. **20**(9): p. 2890-2894.
13. Brousse, T., et al., *Crystalline MnO₂ as Possible Alternatives to Amorphous Compounds in Electrochemical Supercapacitors*. Journal of The Electrochemical Society, 2006. **153**(12): p. A2171-A2180.

14. Wei, W., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. Chemical Society Reviews, 2011. **40**(3): p. 1697-1721.
15. Ghodbane, O., J.-L. Pascal, and F. Favier, *Microstructural Effects on Charge-Storage Properties in MnO₂-Based Electrochemical Supercapacitors*. ACS Applied Materials & Interfaces, 2009. **1**(5): p. 1130-1139.
16. Xu, C., et al., *Reversible Insertion Properties of Zinc Ion into Manganese Dioxide and Its Application for Energy Storage*. Electrochemical and Solid-State Letters, 2009. **12**(4): p. A61-A65.
17. Ragupathy, P., et al., *Remarkable Capacity Retention of Nanostructured Manganese Oxide upon Cycling as an Electrode Material for Supercapacitor*. The Journal of Physical Chemistry C, 2009. **113**(15): p. 6303-6309.
18. Ragupathy, P., H.N. Vasan, and N. Munichandraiah, *Synthesis and Characterization of Nano-MnO₂ for Electrochemical Supercapacitor Studies*. Journal of The Electrochemical Society, 2008. **155**(1): p. A34-A40.
19. H.Y. Lee and J.B. Goodenough. J. Solid State Chem., p. 81.
20. Jeong, Y.U. and A. Manthiram, *Nanocrystalline Manganese Oxides for Electrochemical Capacitors with Neutral Electrolytes*. Journal of The Electrochemical Society, 2002. **149**(11): p. A1419-A1422.
21. Chen, S., et al., *Shape-Controlled Synthesis of One-Dimensional MnO₂ via a Facile Quick-Precipitation Procedure and its Electrochemical Properties*. Crystal Growth & Design, 2009. **9**(10): p. 4356-4361.
22. Beaudrouet, E., A. Le Gal La Salle, and D. Guyomard, *Nanostructured manganese dioxides: Synthesis and properties as supercapacitor electrode materials*. Electrochimica Acta, 2009. **54**(4): p. 1240-1248.
23. Ghaemi, M., et al., *Charge storage mechanism of sonochemically prepared MnO₂ as supercapacitor electrode: Effects of physisorbed water and proton conduction*. Electrochimica Acta, 2008. **53**(14): p. 4607-4614.
24. Wei, W.F., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. Chemical Society Reviews, 2011. **40**(3): p. 1697-1721.
25. Subramanian, V., et al., *Hydrothermal Synthesis and Pseudocapacitance Properties of MnO₂ Nanostructures*. The Journal of Physical Chemistry B, 2005. **109**(43): p. 20207-20214.
26. Xu, M., et al., *Hydrothermal Synthesis and Pseudocapacitance Properties of α -MnO₂ Hollow Spheres and Hollow Urchins*. The Journal of Physical Chemistry C, 2007. **111**(51): p. 19141-19147.
27. Wang, X., et al., *Sol-gel template synthesis of highly ordered MnO₂ nanowire arrays*. Journal of Power Sources, 2005. **140**(1): p. 211-215.

28. Yu, P., et al., *Solution-combustion synthesis of ϵ -MnO₂ for supercapacitors*. Materials Letters, 2010. **64**(1): p. 61-64.
29. V. Gupta, S.G.a.N.M.J.P.S., 175 (2008), p. 680.
30. Xu, M., et al., *Hydrothermal Synthesis and Pseudocapacitance Properties of α -MnO₂ Hollow Spheres and Hollow Urchins*. The Journal of Physical Chemistry C, 2007. **111**(51): p. 19141-19147.
31. Yan, J., et al., *Preparation and electrochemical properties of lamellar MnO₂ for supercapacitors*. Materials Research Bulletin, 2010. **45**(2): p. 210-215.
32. Ni, J., et al., *Low-Temperature Synthesis of Monodisperse 3D Manganese Oxide Nanoflowers and Their Pseudocapacitance Properties*. The Journal of Physical Chemistry C, 2008. **113**(1): p. 54-60.
33. Yu, P., et al., *Preparation and pseudo-capacitance of birnessite-type MnO₂ nanostructures via microwave-assisted emulsion method*. Materials Chemistry and Physics, 2009. **118**(2-3): p. 303-307.
34. Wang, X., A. Yuan, and Y. Wang, *Supercapacitive behaviors and their temperature dependence of sol-gel synthesized nanostructured manganese dioxide in lithium hydroxide electrolyte*. Journal of Power Sources, 2007. **172**(2): p. 1007-1011.
35. Yu, P., et al., *Solution-combustion synthesis of ϵ -MnO₂ for supercapacitors*. Materials Letters, 2010. **64**(1): p. 61-64.
36. S. C. Pang, M.A.A.a.T.W.C., J. Electrochem. Soc., 2000, 147, 444-450.
37. Chen, C.-Y., et al., *Electrophoretically deposited manganese oxide coatings for supercapacitor application*. Ceramics International, 2009. **35**(8): p. 3469-3474.
38. Broughton, J.N. and M.J. Brett, *Electrochemical Capacitance in Manganese Thin Films with Chevron Microstructure*. Electrochemical and Solid-State Letters, 2002. **5**(12): p. A279-A282.
39. Wei, W., et al., *Morphology evolution in anodically electrodeposited manganese oxide nanostructures for electrochemical supercapacitor applications, Effect of supersaturation ratio*. Electrochimica Acta, 2011. **56**(3): p. 1619-1628.
40. Wu, Z.S., et al., *Anchoring hydrous RuO₂ on graphene sheets for high-performance electrochemical capacitors*. Advanced Functional Materials, 2010. **20**(20): p. 3595-3602.
41. Rastogi, A.C. and K.S. Balakrishnan, *Monocrystalline CdTe Thin Films by Electrochemical Deposition from Aprotic Electrolytes*. Journal of the Electrochemical Society, 1989. **136**(5): p. 1502-1506.
42. Hill, S.C. and J.I.D. Alexander, *Modified diffusion-limited aggregation simulation of electrodeposition in two dimensions*. Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics, 1997. **56**(4): p. 4317-4327.

43. Babakhani, B. and D.G. Ivey, *Effect of electrodeposition conditions on the electrochemical capacitive behavior of synthesized manganese oxide electrodes*. Journal of Power Sources, 2011. **196**(24): p. 10762-10774.
44. Wei, W., et al., *Morphology evolution in anodically electrodeposited manganese oxide nanostructures for electrochemical supercapacitor applications* 鈣擡ffect of supersaturation ratio. Electrochimica Acta. **56**(3): p. 1619-1628.
45. Xu, C.-L., et al., *Highly ordered MnO₂ nanowire array thin films on Ti/Si substrate as an electrode for electrochemical capacitor*. Journal of Solid State Chemistry, 2006. **179**(5): p. 1351-1355.
46. Xu, C., et al., *Electrochemical properties of nanosized hydrous manganese dioxide synthesized by a self-reacting microemulsion method*. Journal of Power Sources, 2008. **180**(1): p. 664-670.
47. Yang, X.-h., et al., *Interfacial synthesis of porous MnO₂ and its application in electrochemical capacitor*. Electrochimica Acta, 2007. **53**(2): p. 752-757.
48. Yuan, C., et al., *Interface synthesis of mesoporous MnO₂ and its electrochemical capacitive behaviors*. Journal of Colloid and Interface Science, 2008. **322**(2): p. 545-550.
49. Jiang, R., et al., *A novel method to prepare nanostructured manganese dioxide and its electrochemical properties as a supercapacitor electrode*. Electrochimica Acta, 2009. **54**(11): p. 3047-3052.
50. Dong, B., et al., *Electrodeposition of mesoporous manganese dioxide films from lyotropic liquid crystalline phases*. Microporous and Mesoporous Materials, 2008. **112**(1,Äì3): p. 627-631.
51. Lee, C.W., et al., *Electrochemical synthesis of meso-structured lamellar manganese oxide thin film*. Microporous and Mesoporous Materials, 2010. **130**(1-3): p. 208-214.
52. Devaraj, S. and N. Munichandraiah, *High Capacitance of Electrodeposited MnO₂ by the Effect of a Surface-Active Agent*. Electrochemical and Solid-State Letters, 2005. **8**(7): p. A373-A377.
53. Devaraj, S. and N. Munichandraiah, *The effect of nonionic surfactant triton X-100 during electrochemical deposition of MnO₂ on its capacitance properties*. Journal of The Electrochemical Society, 2007. **154**(10): p. A901-A909.
54. Vittal, R., H. Gomathi, and K.J. Kim, *Beneficial role of surfactants in electrochemistry and in the modification of electrodes*. Advances in Colloid and Interface Science, 2006. **119**(1): p. 55-68.
55. Li, Y., et al., *Preparation and electrochemical performances of Å±-MnO₂ nanorod for supercapacitor*. Materials Letters, 2011. **65**(2): p. 403-405.

56. Khamis, E., et al., *Adsorption effect of cationic surfactants on corrosion inhibition of steel*. Materialwissenschaft und Werkstofftechnik, 1997. **28**(1): p. 46-50.
57. Hu, S., Y. Yan, and Z. Zhao, *Determination of progesterone based on the enhancement effect of surfactants in linear sweep polarography*. Analytica Chimica Acta, 1991. **248**(1): p. 103-108.
58. An, H.-J., et al., *Cationic surfactant promoted reductive electrodeposition of nanocrystalline anatase TiO₂ for application to dye-sensitized solar cells*. Electrochimica Acta, 2005. **50**(13): p. 2713-2718.
59. Khamis, E. and M. Atea, *Inhibition of Acidic Corrosion of Aluminum by Triazoline Derivatives*. Corrosion, 1994. **50**(2): p. 106-112.
60. Ghaemi, M., L. Khosravi-Fard, and J. Neshati, *Improved performance of rechargeable alkaline batteries via surfactant-mediated electrosynthesis of MnO₂*. Journal of Power Sources, 2005. **141**(2): p. 340-350.
61. Sun, X., et al., *Formation of manganite fibers under the directing of cationic surfactant*. Materials Science and Engineering: C, 2006. **26**(4): p. 653-656.
62. K, B., *Organic additives in zinc electroplating*. Electrodeposition and Surface Treatment, 1975. **3**(2): p. 77-95.
63. Maclean, L.A.H. and F.L. Tye, *Chemical hydrogen insertion into CMD exhibiting low microtwinning*. Journal of Materials Chemistry, 2001. **11**(3): p. 891-899.
64. Felhősi, I., et al., *Kinetics of self-assembled layer formation on iron*. Electrochimica Acta, 2002. **47**(13-14): p. 2335-2340.
65. Zhang, L.L., et al., *Manganese oxide carbon composite as supercapacitor electrode materials*. Microporous and Mesoporous Materials, 2009. **123**(1 鈥?): p. 260-267.
66. Li, J., Q.M. Yang, and I. Zhitomirsky, *Nickel foam-based manganese dioxide carbon nanotube composite electrodes for electrochemical supercapacitors*. Journal of Power Sources, 2008. **185**(2): p. 1569-1574.
67. Srinivasan, V. and J.W. Weidner, *Capacitance studies of cobalt oxide films formed via electrochemical precipitation*. Journal of Power Sources, 2002. **108**(1-2): p. 15-20.
68. Hu, Z.A., et al., *Synthesis of alpha-Cobalt Hydroxides with Different Intercalated Anions and Effects of Intercalated Anions on Their Morphology, Basal Plane Spacing, and Capacitive Property*. Journal of Physical Chemistry C, 2009. **113**(28): p. 12502-12508.
69. Li, Z., et al., *Electrostatic layer-by-layer self-assembly multilayer films based on graphene and manganese dioxide sheets as novel electrode materials for supercapacitors*. Journal of Materials Chemistry, 2011. **21**(10): p. 3397-3403.

70. Chen, S., et al., *Graphene Oxide–MnO₂ Nanocomposites for Supercapacitors*. ACS Nano, 2010. **4**(5): p. 2822-2830.

Chapter 4 NMP-assisted electrochemical deposition of α -cobalt hydroxide for supercapacitors

4.1. Introduction

We have discussed in chapter 2 that transition metal oxides deliver much higher energy density than carbon based materials and conducting polymers due to their multi-oxidation states and mass reversible redox reactions. We also discussed the improvement of supercapacitor performance of MnO_2 through the modification of its microstructure and morphology with the help of structure directing agent CTAB in chapter 3. It would be interesting to see how structure direction agent mediated synthesis will improve the morphology and supercapacitor performances of other materials. Among the various transition metal oxides used for supercapacitor application, cobalt hydroxide material has become prominent due to their layered structure with large interlayer spacing [1], which promises high surface area as well as fast ion insertion/desertion rate. Two possible reactions can occur during charge and discharge process, as expressed in equation 4.1 and 4.2:

Moreover, its high theoretical specific capacitance and the possibility of enhanced performance through different preparative methods [2-4] have further made cobalt hydroxide very competitive as supercapacitor electrode material. Recent technological development shows that structures or devices less than 100 nanometers in size, known as nanostructure or Nano devices, have exhibited characteristic properties or performances remarkably different from their bulk materials. This is because as the size of material enters into nanometer scale, electronic motion is restricted to a smaller space comparable to that of the mean free path of electrons, which leads to the stronger confinement of

electronic motion (spatial confinement) [5]. The quantization of electronic motion in metallic nanoparticles restricts them into discrete energy levels and makes the valence and conduction band no longer inseparable. As a result, materials exhibit properties not achievable from the bulk. Nevertheless, only a few papers touched on the modification of microstructure and their corresponding capacitive behavior of pure cobalt hydroxide [6]. It is also noted that in pseudo-capacitor, the charge storage mechanism is basically pseudocapacitor where surface or near surface faradic reactions happen during charge storage. Therefore, it is quite reasonable that crystal structure, grain size and surface morphology of electrode materials can strongly affect their capacitance performances [2-4], which is consistent with what we have discussed in chapter 3. As we have mentioned before, there have been many approaches adopted to prepare electrodes that have high conductivity, large specific surface area and proper crystal structures or morphologies that favor redox reactions [2, 4, 7-10]. Porous cobalt hydroxide nanoflake film prepared by galvanostatic electrodeposition on stainless steel mesh, has shown a high capacitance of 609 Fg^{-1} [6], other approach like microstructure modifications has also been carried on α -cobalt hydroxide, the resulted capacitance has shown an enhancement [9, 11]. Chou etc. recently reported a α -cobalt hydroxide film which was prepared by potentiostatically electrodeposition method, showed nanoflakes morphology and a high capacitance of 840 Fg^{-1} with potential window of 0.4 V [6]. These report again showed the tight relationship between morphology, microstructure and specific capacitance of electrode. As we have mentioned before, surfactant or organic solvent mediated fabrication of nanostructured materials have shown unique morphologies and performances[12]. Krasil'nikov etc. modified the synthesis of cobalt oxide with ethylene glycol and the as obtained cobalt oxide has a unique nanowiskers morphology [13]. The substitution of ethylene glycol molecules for two structure water molecules in the cobalt precursor resulted in complex super-molecules and unique nanowisker morphology upon heating. Xie [14] reported the

synthesis of nanorode-shaped cobalt hydroxycarbonate and oxide with the mediation of ethylene glycol, which acted as coordination agent and rate-controlling agent during crystal formation.

N-methylpyrrolidone (NMP) is a highly polar, aprotic, general-purpose organic solvent similar to ethylene glycol. It dissolves very well with a wide range of organic and inorganic compounds and is miscible with water at any temperatures. Other properties include high chemical and thermal stability. Its formula is C_5H_9NO and a schematic structure is shown in Figure 4.1. NMP has wide applications including process chemicals, engineering plastics, coatings, reaction medium in synthesis of active compounds and stabilizers etc. however few papers mentioned its ability to form complex super-molecules with metal ions such as cobalt and iron[15, 16], it would be interesting to investigate how the NMP would modify the morphology and nanostructure of cobalt during synthesis.

Figure 4.1 Schematic structure of NMP

There are many techniques to prepare $Co(OH)_2$ electrode, one of them is electrochemical deposition techniques which have attracted lots of attention because they can control the surface morphology and microstructure of deposited films relatively easy and accurate by just simply varying deposition parameters, such as electrolyte, deposition potential, deposition current, bathing temperature and so on [17], it also omit the use of polymer binders and conductive additives, which are needed for power form $Co(OH)_2$. Therefore, in this chapter, we intent to study the effect of N-Methylpyrrolidone (NMP) on the

synthesis of cobalt hydroxide and try to synthesis cobalt hydroxide with dense packed porous structure that promote supercapacitor performance.

4.2. Experimental procedures

Analytical grade chemicals $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, N-Methylpyrrolidone (NMP), 1 M KOH, and stainless steel (size $1\text{cm} \times 1\text{cm} \times 0.9\text{mm}$) were purchased from Sigma-Aldrich, Singapore. A typical three-electrode electrochemical cell was set up for electrochemical deposition purpose, with a platinum foil ($2\text{cm} \times 2\text{cm}$), Ag/AgCl (saturated KCl solution) and SS as counter electrode, reference electrode and working electrode respectively. The pre-deposition solutions for $\text{Co}(\text{OH})_2$ were prepared by adding different volume percent of NMP, 0%V, 10%V, 20%V and 30%V, in 0.1 M of $\text{Co}(\text{NO}_3)_2$ respectively. The potentiostatic deposition voltage was fixed at -1.0V, and 1.5C charges were allowed to pass through cathode. Following reactions were involved during the deposition of α -cobalt hydroxide on the stainless steel substrate: [18]:

After deposition, the as-obtained films were carefully washed with distilled water, followed by drying in air at 60°C for one day. The weights of the deposits were measured by using a micro-balance (Mettler Toledo, MT5) with an accuracy of 0.01 mg. The weights of all deposited films were around 0.74mg.

All of the as-prepared electrodes were characterized by field emission scanning electron microscopy (FE-SEM, JOEL, JSM-6340F) to study their surface morphologies. While X-ray diffractometer (XRD, RIGAKU, R1NT2100) with Cu $\text{K}\alpha$ radiation ($\lambda = 1.540\text{\AA}$) operating at 40kv and 30 mA, were used to obtain the XRD patterns. Besides, Fourier

transform infrared spectrometers (FTIR) of the cobalt hydroxide were obtained by using PerkinElmer Spectrum GX. Last but not least, the supercapacitor performances of as-prepared $\text{Co}(\text{OH})_2$ electrodes were characterized by using an AUTOLAB® machine (Eco Chemie, PGSTAT 30) in a three-electrode electrochemical cell with 1M KOH as electrolyte.

4.3. Results and discussion

4.3.1 Crystal structures and morphologies of $\text{Co}(\text{OH})_2$ synthesized in presence of NMP

Figure 4.2 shows the X-ray diffraction (XRD) pattern of the as-obtained $\text{Co}(\text{OH})_2$ nanostructures. The characteristic peaks at 10.46° , 22.58° , 33.74° , 38.14° and 59.08° were attributed to α - $\text{Co}(\text{OH})_2$, which is characteristic for electrochemical deposition obtained cobalt hydroxide. The peaks marked with asterisk (*) can be assigned to the characteristic peaks of the stainless steel substrate.

Figure 4.2 XRD pattern of the as-obtained α -Co(OH)₂ nanostructures

Fourier transform infrared spectroscopy (FTIR) is a technique to simultaneously collect an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of solid, liquid or gas. By shining a beam containing range of frequencies of light at once and measuring how much of that beam is absorbed by the solid sample surface, information about functional groups, and oxidation states and so on of the solid sample surface is obtained. In this study, FTIR technique is to examine the surface functional groups of Co(OH)₂. The FT-IR spectrums of the α -Co(OH)₂ electrode prepared with 20% V NMP and without NMP are shown in Figure 4.3, where the two spectrums showed similar shape. Characteristic peaks located at 3488 cm⁻¹ and 1651 cm⁻¹ were corresponding to the O-H stretching vibrations of interlayer water and free water molecules respectively. While the peak around 1347 cm⁻¹ was the characteristic

absorption peak of intercalated nitrate. As for the absorption peaks around 630 cm^{-1} and 523 cm^{-1} , they can be assigned to the $\delta(\text{Co-O-H})$ and $\nu(\text{Co-O})$ stretching vibrations [19, 20]. Last but not least, for cobalt hydroxide (20 vol.% NMP), obvious absorption peak at 1695 cm^{-1} that is related to C=O stretching in NMP was not observed. From the above analysis, we therefore concluded that the as-deposited cobalt oxides had high purity and were in hydrous form with plenty of structure water and NO_3^- ions intercalated.

Figure 4.3 FTIR spectrum of α -cobalt hydroxide and $\alpha\text{-Co(OH)}_2$ prepared under 20%V NMP concentration

Field emission scanning electron microscopy images of $\alpha\text{-Co(OH)}_2$ deposited with various NMP concentrations are presented in Figure 4.4a–f. All of the as-obtained cobalt

hydroxide films showed a typical layered structure. 3-D fibrous morphology was formed by randomly aligned α -Co(OH)₂ nanosheets. It is noteworthy that although all the films showed similar nanoporous structure, the interlayer distance was found to vary with the concentration of NMP in the pre-deposition solution. The densest structure with much more uniform distribution of α -Co(OH)₂ nanosheets as well as more smooth surface was obtained in the presence of 20% V NMP (Figure 4.4c). As mentioned earlier, the main capacitance contribution of Co(OH)₂ is pseudocapacitance achieved through surface or near surface faradic reactions, morphologies or structures that can enhance charge/ion transportation as well as redox reaction rate will definitely enhance the capacitive performance of the electrode. Therefore it is expected that nanostructures obtained in the presence of 20% V NMP, which has a dense, uniform structure with smooth surface, would provide much easier transportation path for charges and electrolyte ions [21-23] and as a result, better supercapacitor performance.

It is also noticed that nanolayer thickness of α -Co(OH)₂ prepared with 20vol.% NMP is thinner than that of pure α -Co(OH)₂ (Figure 4.4 f), 6 points were measured as show in Figure 4.4 e and f, the corresponding layer thickness for NMP modified α -Co(OH)₂ and pure α -Co(OH)₂ were 8nm (standard deviation is 1.5nm) and 14 nm (standard deviation is 5.3 nm) respectively. Moreover, sub-layers were observed for α -Co(OH)₂ prepared with NMP in the pre-deposition solution, which future reduced the layer thickness of cobalt hydroxide and increased specific surface area. Considering the layer thickness, interlayer distance and uniform morphology of all the prepared cobalt hydroxide films, it is therefore concluded that nanostructure synthesized in presence of 20vol.% NMP would have a high specific surface area and smoother diffusion path, which is same as that observed in CTAB modified manganese dioxide, and a higher specific capacitance is expected [21].

Figure 4.4 FESEM images of the α -cobalt hydroxides: (a) Co(OH)_2 (b) $\text{Co10vol.\% NMP}$ hydroxides (c) $\text{Co20vol.\% NMP}$ hydroxides (d) $\text{Co30vol.\% NMP}$ hydroxides (e) layer thickness of Co(OH)_2 (f) layer thickness of $\text{Co20vol.\% NMP}$ hydroxides

4.3.2 Influence of NMP on the synthesis of Co(OH)_2 electrode

It has been shown in Figure 4.4 that the obtained microstructures of Co(OH)_2 varied with different amount of NMP which were added into the pre-deposition solution. Before

exploring the mechanisms behind, the growth mechanism Co(OH)_2 in water without NMP is stated as follows: When the potentiostatic deposition of Co(OH)_2 starts, NO_3^- is reduced and large quantities of OH^- are produced at the cathode, Co^{2+} around cathode would react with these OH^- and form Co(OH)_2 precipitate. As the concentration of precipitate increases in the solution, some precipitates would attached to specific locations on the stainless steel substrate surface and act as nucleation center, excess Co(OH)_2 precipitates in the solution would follows these nucleation centers and finally growth into thin film with specific morphology and structure as we have shown in figure 4.4. The two nucleation and growth process would be affected by a number of factors such as substrate surface textual, pH concentration, structure direction agent and so on, as a result various morphologies and structures would be obtained by varying these experimental parameters. As has observed in Figure 4.4, different morphologies of Co(OH)_2 were obtained with different concentrations of NMP added. The reason may be attributed to the high polarity and dispersity of NMP surfactant in water that has resulted in the formation of a complex organic solvent/electrolyte system which provides smaller nucleation centers or faster growth rate for the Co(OH)_2 deposition. During the deposition, Co^{2+} will first reacts with OH^- to form Co(OH)_2 short-lived dimers, and the dimers and their arrangement may affected by the presence of NMP which has large hydrolytic group, as a result the nucleation and growth of the inorganic precipitates is affected by the presence and concentrations of NMP [24-27] add eventually leads to different morphologies of Co(OH)_2 . It is interesting to observe from Figure 4.4 that as the concentration of NMP increased, the thickness of nanosheets as well as the pore size formed by intercalation of nanosheets reduced accordingly, which may suggest higher nucleation rate due to the presence of NMP; at even higher NMP concentration (30% V), irregular morphology of Co(OH)_2 was obtained, this could be caused by too fast

nucleation, growth rate and overpotential, which is similar to what was observed in CTAB mediated synthesis of MnO_2 when high concentration of CTAB was added.

4.3.3 Supercapacitor performance of $\text{Co}(\text{OH})_2$ electrode

Supercapacitor performances of all as-prepared $\text{Co}(\text{OH})_2$ were characterized by cyclic voltammetry (CV) and galvanic charge-discharge characterization in 1M KOH aqueous solution. Figure 4.5 (a) shows the cyclic voltammetry curves of all $\text{Co}(\text{OH})_2$ films at a scan rate of 5 mVs^{-1} , with a potential window of -0.1V to 0.45V. As we have mentioned before, this potential window is limited by the intrinsic properties of the electrolyte solution and also cobalt hydroxide. Our studies indicated that when voltage was above than 0.45V, oxygen evolution reaction occurred and lots of bubbles were generated; while the voltage falls below -0.1V, there are no electrochemical reactions and no charges are stored. As observed in Figure 4.5(a), a pair of reversible redox peaks appeared in voltage range from -0.05 to 0.05, and 0.05 to 0.15 V. The corresponding surface faradic reaction of cobalt hydroxides can be described by following equation [24]:

The two distinct and symmetric humps and the non-rectangular shape of CV curves also indicated the fact that redox reactions occurred in the electrode and capacitance was generally pseudo-capacitance. Moreover, $\text{Co}(\text{OH})_2$ with 20vol.% NMP was observed to deliver the highest redox current (the height of hump). As we have mentioned before that at the same scan rate, the capacitance of electrode is directly proportional to the area included by the CV curve, therefore Figure 4.5 (a) suggested for $\text{Co}(\text{OH})_2$ prepared with 20vol.% NMP had the highest specific capacitance among all the as-prepared cobalt hydroxides in this study. Figure 4.5 (b) showed the discharge curves of $\text{Co}(\text{OH})_2$ electrode prepared with different concentration of NMP in 1M KOH electrolyte at 2 Ag^{-1}

with potential range between -0.1V and 0.45V. The shape of discharge curve showed the characteristic hump for pseudocapacitance instead of straight line for electric double layer capacitance, and the distinct hump can be directly related to the redox peaks in the CV curves. The specific capacitance of $\text{Co}(\text{OH})_2$ can be obtained from the discharge curve according to following equation [1],

$$C_m = C/m = (I \times \Delta t) / (\Delta V \times m) \quad (4.6)$$

where C_m (F/g) is the specific capacitance, I (A) is the discharge current, t (s) is the discharging time, V is the discharge potential and m (g) is the mass of active material within the electrode. The specific capacitances obtained were 473 Fg^{-1} , 571 Fg^{-1} , 651 Fg^{-1} and 473 Fg^{-1} for $\text{Co}(\text{OH})_2$ synthesized with 0 vol.%, 10 vol.%, 20 vol.% and 30 vol.% NMP in electrolyte, respectively. The manifest enhancement of capacitance was observed for $\text{Co}(\text{OH})_2$ prepared with 20vol.% NMP in electrolyte. Considering the structures and morphologies of $\text{Co}(\text{OH})_2$ prepared with different concentrations of NMP as we have discussed above, the enhancement may be attributed to the uniform and smooth nano-scale microstructure with thinner layer thickness of $\text{Co}(\text{OH})_2$ prepared with 20vol.% NMP than other cobalt hydroxides, which provided more electrode/electrolyte interfaces and shorter and smoother diffusion path for ions, therefore promoted the electrochemical reactions and resulted in higher capacitance.

Figure 4.4 (a) CV curves of Co(OH)_2 films at 5 mV s^{-1} and (b) Discharge curves of Co(OH)_2 films at 2 A g^{-1}

The supercapacitor performance of Co(OH)_2 (20vol.% NMP) was further analyzed and the results were presented in Figure 4.6(a), where Co(OH)_2 prepared with 20vol.% NMP were scanned at different cyclic voltammetry rate with a potential window of -0.1V to 0.45V. The corresponding specific capacitances at different scan rate were calculated to

be 604Fg^{-1} , 572Fg^{-1} , 527Fg^{-1} and 454Fg^{-1} at scan rate of 5 mVs^{-1} , 10 mVs^{-1} , 20 mVs^{-1} and 50 mVs^{-1} respectively, which means $\text{Co}(\text{OH})_2$ (20vol.% NMP) could still retain 75.17% of the capacitance when scan rate was 10 times faster. This result revealed a good rate capability performance of $\text{Co}(\text{OH})_2$ (20vol.% NMP), which is vital to practical supercapacitor application because we want to keep as much charge storage ability as possible even at high charge/discharge rate.

More information can be derived from the cyclic voltammetry curves of $\text{Co}(\text{OH})_2$ (20vol.% NMP). As we have done in the CTAB modified MnO_2 study, the anodic peak current i_p vs. V (voltage scan rate), and i_p vs. $V^{1/2}$, were plotted in Figure 4.6(b). if i_p vs. V shows a linear relationship regardless of the scan rates [19], then it is an absorption limited process. While, if i_p hold a linear relationship instead of with V but with $V^{1/2}$, then it is more likely to be a semi-infinite diffusion controlled process in liquid electrolytes [19]. It can be seen from Figure 4.6 that, i_p vs. V (black line) showed a nonlinear relationship, whereas i_p vs. $V^{1/2}$ (red line) showed a reasonably linear plot. Therefore, it is suggested that the redox reactions in $\text{Co}(\text{OH})_2$ (20vol.% NMP) were diffusion limited reaction, which also agreed with other reports in the literature [19].

Figure 4.7 shows the result of cyclic stability test of $\text{Co}(\text{OH})_2$ prepared with 20vol.% NMP. The as-prepared $\text{Co}(\text{OH})_2$ thin film was scanned at 50mVs^{-1} for 500 cycles in the potential range of $(-0.1\text{V}, 0.45\text{V})$. It is noticed that as the cycle number increases, the corresponding supercapacitor capacitance decreases slowly. Interestingly, most of the decrease of capacitance was made in the first 200 cycles. At the end of 500 cycles, 76 % of initial capacitance still remains. Few reasons may be responsible for the capacitance loss: (1) slow oxidation of $\text{Co}(\text{OH})_2$ to CoOOH owing to that Co^{3+} is more stable than Co^{2+} under alkali environment [28], and (2) another reason could be due to exfoliation of some active materials from electrode during long time cycling.

Figure 4.5 Cyclic voltammetry of Co(OH)₂ (20%NMP) at scan rate of 5 mVs⁻¹, 10 mVs⁻¹, 20 mVs⁻¹, 50 mVs⁻¹ and 100 mVs⁻¹ respectively (b) i_p vs. V^{1/2} and i_p vs. V plots of Co(OH)₂ (20%NMP)

Figure 4.6 Cyclic stability test of Cobalt hydroxide prepared in presence of 20vol.% NMP

Electrochemical impedance spectroscopy (EIS) study of all as-prepared $\text{Co}(\text{OH})_2$ electrodes were also carried on to explore the charge and ion transfer characteristics of electrodes. A DC voltage at 0.1V was applied to the 3-electrode cell and the frequency was set to from 10k Hz to 0.1 Hz. The obtained results were represented in well known Nyquist diagram as shown in Figure 4.7. The plots compose of approximately semi-circles at high and medium frequencies and a straight line along the imaginary axis (Z') at low frequencies. As we have mentioned before, the semicircle is related to Faradaic reactions and whose diameter represents interfacial charge transfer resistance (usually termed as Faradaic resistance); While the straight line is related to the transportation process of electrolyte ions and protons through the microstructure of electrodes. In Figure 4.8, diameters of the semicircles of $\text{Co}(\text{OH})_2$ prepared with NMP in electrolyte were smaller than that of $\text{Co}(\text{OH})_2$ prepared without NMP, which means $\text{Co}(\text{OH})_2$ prepared with NMP had smaller interfacial charge transfer resistances. The shape of all four curves was similar; all of them contained a semicircle at high frequency and straight line at low frequency indicating the resistor and capacitor nature of supercapacitor. However, the slope of the straight line at low frequency for $\text{Co}(\text{OH})_2$ prepared with NMP

were more steep than Co(OH)_2 prepared without NMP. The results showed that Co(OH)_2 samples prepared with NMP surfactant had lower reaction and diffusion resistance which means better electrolyte and proton diffusion properties in host electrode. All of these reasons resulted in higher specific capacitances of Co(OH)_2 prepared in NMP than those without any NMP added. It is also noticed that among the three Co(OH)_2 electrodes prepared in presence of NMP, Co(OH)_2 prepared in presence of 10% V showed the lowest interfacial charge transfer resistance and best electrolyte and proton transportation property, but it didn't deliver the highest capacitance, therefore other factors like thinner layer thickness, uniform morphology and smoother surface are reckoned to have significant effects on the electrochemical capacitance performances.

Figure 4.7 Nyquist plot of α - Co(OH)_2 prepared at different NMP concentrations

4.4 Conclusion

In conclusion, after the success of improving MnO₂ supercapacitor performance by modifying its nanostructure and morphology through the use of structure directing agent CTAB, a simple N-Methylpyrrolidone (NMP) assisted electrochemical route has been developed to modify the morphology of another very popular supercapacitor material layered Co (OH)₂. Results have shown that the surface morphology of Co (OH)₂ varied with different concentrations of NMP in the pre-deposition electrolyte solution. When 20 vol.% NMP surfactant was added into electrolyte solution, the resulted morphology showed much narrower interlayer spacing, thinner layer thickness as well as more uniform pore distribution, which can provide more active sites for electrochemical reactions. Electrochemical investigations showed that NMP mediated Co (OH)₂ had much higher redox peak currents and a capacitance increment as high as 37% is noted for Co (OH)₂ prepared in presence of 20% V NMP. Furthermore, EIS results also indicated that Co (OH)₂ synthesized with NMP have lower reaction and diffusion resistance. Cyclic stability test showed reasonable capacitance retention of 76% after 500 cycles of cyclic voltammetry test at 50mVs⁻¹. These results confirmed that microstructure plays a very important role in the property enhancement of supercapacitor, and an 20 vol.% NMP addition produces the layered Co(OH)₂ with best morphology and electrochemical performances in the present investigation.

4.5 References

1. Kamath, R.S.J.a.P.V., J. Mater. Chem.9, 1999: p. 961.
2. B.E. Conway, E.S.S.F.a.T.A., Kluwer, New York (1999).
3. Arico, A.S., et al., *Nanostructured materials for advanced energy conversion and storage devices*. Nature Materials, 2005. **4**(5): p. 366-377.
4. Simon, P. and Y. Gogotsi, *Materials for electrochemical capacitors*. Nat Mater, 2008. **7**(11): p. 845-854.
5. Sharma, J. and T. Imae, *Recent Advances in Fabrication of Anisotropic Metallic Nanostructures*. Journal of Nanoscience and Nanotechnology, 2009. **9**(1): p. 19-40.
6. S. L. Chou, J.Z.W., H. K. Liu, S. X. Dou, J. Electrochem. Soc. 155 (2008) A926.
7. Su, L.H., et al., *Improvement of the capacitive performances for Co-Al layered double hydroxide by adding hexacyanoferrate into the electrolyte*. Physical Chemistry Chemical Physics, 2009. **11**(13): p. 2195-2202.
8. Gupta, V., S. Gupta, and N. Miura, *Al-substituted alpha-cobalt hydroxide synthesized by potentiostatic deposition method as an electrode material for redox-supercapacitors*. Journal of Power Sources, 2008. **177**(2): p. 685-689.
9. Zhou, W.J., et al., *Electrodeposition of ordered mesoporous cobalt hydroxide film from lyotropic liquid crystal media for electrochemical capacitors*. Journal of Materials Chemistry, 2008. **18**(8): p. 905-910.
10. Choi, D., G.E. Blomgren, and P.N. Kumta, *Fast and Reversible Surface Redox Reaction in Nanocrystalline Vanadium Nitride Supercapacitors*. Advanced Materials, 2006. **18**(9): p. 1178-1182.
11. Casella, I.G. and M. Gatta, *Study of the electrochemical deposition and properties of cobalt oxide species in citrate alkaline solutions*. Journal of Electroanalytical Chemistry, 2002. **534**(1): p. 31-38.
12. Sun, D., et al., *Hexagonal nanoporous germanium through surfactant-driven self-assembly of Zintl clusters*. Nature, 2006. **441**(7097): p. 1126-1130.
13. Krasil'nikov, V., O. Gyrdasova, and G. Bazuev, *Ethylene glycol-modified cobalt and iron oxalates as precursors for the synthesis of oxides as extended microsized and nanosized objects*. Russian Journal of Inorganic Chemistry, 2008. **53**(12): p. 1854-1861.
14. Xie, X.W., et al., *Synthesis of Nanorod-Shaped Cobalt Hydroxycarbonate and Oxide with the Mediation of Ethylene Glycol*. Journal of Physical Chemistry C, 2010. **114**(5): p. 2116-2123.

15. Verma, S. and D. Pravarthana, *One-Pot Synthesis of Highly Monodispersed Ferrite Nanocrystals: Surface Characterization and Magnetic Properties*. Langmuir, 2011. **27**(21): p. 13189-13197.
16. Ding, K.Y., et al., *Coordination of N-methylpyrrolidone to iron(II)*. Journal of Organometallic Chemistry, 2009. **694**(26): p. 4204-4208.
17. Nelson, P.A., et al., *Mesoporous Nickel/Nickel Oxide Nanoarchitected Electrode*. Chemistry of Materials, 2002. **14**(2): p. 524-529.
18. Wang, X.F., Z. You, and D.B. Ruan, *A hybrid metal oxide supercapacitor in aqueous KOH electrolyte*. Chinese Journal of Chemistry, 2006. **24**(9): p. 1126-1132.
19. Hu, Z.A., et al., *Synthesis of alpha-Cobalt Hydroxides with Different Intercalated Anions and Effects of Intercalated Anions on Their Morphology, Basal Plane Spacing, and Capacitive Property*. Journal of Physical Chemistry C, 2009. **113**(28): p. 12502-12508.
20. Xu, Z.P. and H.C. Zeng, *Interconversion of Brucite-like and Hydrotalcite-like Phases in Cobalt Hydroxide Compounds*. Chemistry of Materials, 1998. **11**(1): p. 67-74.
21. Pell, W.G. and B.E. Conway, *Voltammetry at a de Levie brush electrode as a model for electrochemical supercapacitor behaviour*. Journal of Electroanalytical Chemistry, 2001. **500**(1-2): p. 121-133.
22. Zhang, L.L. and X.S. Zhao, *Carbon-based materials as supercapacitor electrodes*. Chemical Society Reviews, 2009. **38**(9): p. 2520-2531.
23. Meher, S.K. and G.R. Rao, *Ultralayered Co₃O₄ for High-Performance Supercapacitor Applications*. The Journal of Physical Chemistry C, 2011. **115**(31): p. 15646-15654.
24. Francesca, B., et al., *Hydrotalcite-Like Nanocrystals from Water-in-Oil Microemulsions*. European Journal of Inorganic Chemistry, 2009. **2009**(18): p. 2603-2611.
25. Brochette, P., C. Petit, and M.P. Pileni, *CYTOCHROME-C IN SODIUM BIS(2-ETHYLHEXYL) SULFOSUCCINATE REVERSE MICELLES - STRUCTURE AND REACTIVITY*. Journal of Physical Chemistry, 1988. **92**(12): p. 3505-3511.
26. Zulauf, M. and H.F. Eicke, *Inverted micelles and microemulsions in the ternary system water/aerosol-OT/isooctane as studied by photon correlation spectroscopy*. The Journal of Physical Chemistry, 1979. **83**(4): p. 480-486.
27. Pileni, M.P., *Mesostructured Fluids in Oil-Rich Regions: 鈥?Structural and Templating Approaches*. Langmuir, 2001. **17**(24): p. 7476-7486.

Chapter 5 Multilayer hybrid films consisting of alternating graphene and MnO₂ nanosheet for supercapacitor application

5.1 Introduction

In the studies of surfactant modified MnO₂ and cobalt hydroxide, it is found that reduction of layer thickness and increment of specific surface area can effectively promote surface redox reactions and as a result, lead to higher supercapacitor capacitances. From the literature review part, it is also learnt that two major approaches are often adopted to improve electrochemical performances of MnO₂. One approach is to modify manganese dioxide synthesis conditions to acquire desirable defect chemistry, crystal structure and morphology, which can provide large active surface area. The other strategy is to incorporate foreign metal elements [1, 2] or well designed electronic conducting architectures such as carbon nanofoams and mesoporous carbon template into MnO₂ [3], so as to improve internal electronic conductivity and facilitate ion diffusion in the whole electrode which helps to maintain structure integrity. Therefore in this study, we added foreign conducting agent into MnO₂ and were interested in how the conducting additive would affect the electrochemical performances of MnO₂. Among various porous carbonaceous materials used as intercalation agent, carbon nanotube (CNT) is very popular; it has good chemical stability and conductivity, plus large surface area. In addition, CNTs are usually strongly entangled, which provides an open mesoporous structure. Supercapacitors made of CNTs delivered capacitances ranging from 100 F/g to 200 F/g [4]. When CNTs are used as additives to improve the electrochemical performance of metal oxides or as deposition substrates for metal oxides, they also showed attractive synergetic effects [5]. In summary, the incorporation of CNT in MnO₂

for supercapacitor application has been broadly studied and have shown considerable improvement on the supercapacitor performance of MnO₂[6-8], and preparation techniques include electrochemical deposition [9], chemical co-deposition, and thermal decomposition. Recently, a new class of carbon material named graphene has caused wide interests. It is a two dimensional one-atom-thick planar sheet of sp² bonded carbon atoms, which can be used to build many other fullerene allotropic dimensionalities as shown in figure 5.1 below [10].

Figure 5.1 Schematic representation of graphene, which is the fundamental starting material for a variety of fullerene materials; buckyballs, carbon nanotubes, and graphite [8]

The graphene sheet can either be “wrapped” into zero-dimensional spherical balls, “rolled” into one dimensional CNTs or can be “stacked” into three-dimensional graphite (generally with more than ten graphene layers). The unique structure of graphene enables it to have many great properties for energy storage application. The theoretical surface area of graphene is 2630 m²g⁻¹ [11], surpassing that of graphite (~10 m²g⁻¹) and is two times larger than that of CNT (1315m²g⁻¹). Additionally, the electronic conductivity of graphene has been calculated to be ~64 mScm⁻¹, which is approximately 60 times more than that of single wall carbon nanotube [12]. Furthermore, its conductivity remains stable over a great range of temperatures [13], which is essential for reliability within

many applications. All of these properties make graphene a very promising candidate for supercapacitor [14, 15]. Graphene oxide (GO) is one of the most important derivatives of graphene. It is graphene layer with oxygen functional groups located on the basal planes and edges. These extra function groups enable GO to be hydrophilic and highly dispersive in water [16], which makes it much more processable than pure graphene nanosheet. Therefore, graphene oxide is often used as precursor material for the preparation of graphene oxide based or graphene nanosheet (GNS) based hybrid material after reduction. The reduction process of GO could be achieved by e.g. H₂ reduction at high temperature or reduction by N₂H₂ at room temperature [17, 18]. The properties and applications of graphene and graphene oxide composite have interested researchers a lot since the first isolation of graphene in 2004. They have been found very useful in solar cell, sensor and supercapacitor fields owing to its extraordinary electronic conductivity, high specific area, superior mechanical properties and good electrochemical stability [19-22]. In the tremendous study for supercapacitor application, graphene has shown capacitance as high as 205 Fg⁻¹ with excellent cyclic stability and a power density of 10 kW kg⁻¹, energy density of 28.5 Wh kg⁻¹, plus 90% of the capacitance remained after 1200 cycles [23]. Moreover via using of ionic electrolyte, the operating voltage window of graphene can be extended up to 3.5V, a specific capacitance of 75 Fg⁻¹ and extraordinary high energy density of 31.9 Wh kg⁻¹ can be reached [24]. However, it is showed that the full potential of graphene is not achieved. Therefore great efforts have be dedicated to fabrication of graphene based hybrid materials, which make use of its outstanding high surface area and high conductivity [25]. In these studies [26-28], graphene showed potential to outperform its counterparts as a capacitor material. Yan et

al. [26] reported polyaniline(PANI)/graphene composite synthesized through in situ polymerization, which exhibited a high specific capacitance of 1046 Fg^{-1} compared to 115 Fg^{-1} for individual PANI, 463 Fg^{-1} for single wall CTN/PANI, and 500 Fg^{-1} for multiwall CNT/PANI, and the polyaniline(PANI)/graphene composite showed an attractive power density of 70 kW kg^{-1} and an energy density of 39 Wh kg^{-1} . These improvements in capacitance are believed not only come from enhanced surface area but also ascribed to the increment in lattice defect density and interlayer spacing of graphene [29]. Studies [30, 31] showed that increment in the inter-planar spaces between graphene sheets and available edge plane sites could promote supercapacitor performance [10]. The supercapacitor performance of graphene-based hybrids is also affected by how the graphene is mixed with other material, close contact or chemical anchoring are beneficial and desired for higher capacitance [31]. After the review of the properties and performances of graphene and graphene based composites, it is reckoned that the combination of MnO₂ with graphene is able to provide superior electronic conductivity as well as large accessible surface area for hydrate ions transportation; as a result a improved supercapacitor performances is expected for graphene/ MnO₂ composite. However, to date, only few papers reported the graphene/MnO₂ nanocomposites electrodes for supercapacitor application [19-22]. One reason could be that the harsh preparation conditions and poor disparity of graphene in water limit its application. Most of the reports involved a complicated preparation process to synthesize graphene/MnO₂ composite and they had poor control of the MnO₂ crystal structures and morphologies. Moreover, most of the as-prepared graphene/MnO₂ nanocomposite are in powder form and have to be further mixed up with other conducting additives like carbon black and

polymer binders before using as an electrode, which not only increases the charge transfer resistance within the electrodes but also degrades electrochemical performances. More recently, An et al [32] reported a simple route to prepare stable, homogeneous and loose graphene thin film on stainless steel substrate by simultaneously electrophoretic deposition and reduction of graphene oxide, which eliminates tedious preparation work and provides an alternative way of graphene application.

Therefore in this work, for the first time we have developed a facile approach to prepare graphene/MnO₂ porous multilayer hybrid film by sequentially layer by layer electrophoretic deposition/reduction of graphene oxide and potentiostatic deposition of MnO₂. The merits of this approach are: (1) it creates a multilayered nano-architecture with homogeneous and orderly distribution of graphene and MnO₂ for an enhanced supercapacitor performance; (2) layer by layer deposition technique allows an easy control of the crystal structure, morphology and composition of MnO₂ and graphene by varying their respective deposition conditions, which opens up a great possibilities of multilayer hybrid composites for supercapacitor application; (3) in addition, this complete electrochemical deposition method allows direct growth of graphene and MnO₂ on the substrates without any “binders” or “glues”. As a result, internal resistances can be reduced and supercapacitor performance is improved.

5.2 Experiment setup and procedures

Materials and electrochemical deposition setup

Analytical grade Manganese nitrite (Mn (NO₃)₂·6H₂O) and sodium sulfate (Na₂SO₄) were purchased from Sigma-Aldrich and used without further purification. All other

chemicals and solvents were of analytical grade. Ultra pure water from a Milli-Q reagent water system at a resistivity $> 18\text{M}\Omega\text{ cm}$ was used throughout the experiment. A three-electrode electrochemical cell was set up for electrochemical deposition and electrochemical characterization purpose, with a platinum foil ($2\text{cm}\times 2\text{cm}$), Ag/AgCl (KCl-saturated) as counter electrode and reference electrode, respectively. For working electrode, a few types of substrate were prepared including stainless steel plate, stainless steel foam, indium tin oxide (ITO) and graphite paper. Before the deposition, stainless steel plates (size $2\text{cm}\times 1\text{cm}\times 0.9\text{ mm}$) were polished with emery paper to a rough finish, then washed with ethanol and distilled water, followed by drying in oven, for other three types of substrates, they were also washed with ethanol and distilled water followed by drying in oven before deposition.

Synthesis of graphene/ MnO₂ multilayer hybrid film

In a typical synthesis process, a porous MnO₂ layer was first potentiostatically deposited onto various substrates from 0.1 M manganese nitrate solution at 1 V for 45 seconds, after that, the electrode was washed with distilled water and dried in oven at 60°C. Then the substrates coated with porous MnO₂ layer was subjected to graphene deposition through simultaneous electrophoretic deposition and anodic reduction in 1mg ml^{-1} graphene oxide colloidal solution as reported by An et al [32] at 10 V for 60 seconds. the graphene oxide colloidal suspension used here was prepared by dispersing 30 mg graphene oxide, which was synthesized from purified natural graphite by the modified Hummers method [33] followed by purification through filtration and dialysis, into 30 ml distilled water and then ultrasonicated for 2 hours at room temperature. The electrode was then washed with distilled water and dried for MnO₂ deposition again. The above

process was repeated for three times to achieve a uniform multilayer hybrid film of MnO₂ and graphene. Finally, the obtained multilayer hybrid film was heated at 100°C for 1 hour to remove moistures and enhance graphene conductivity [32]. For comparison, a pure porous MnO₂ film was also deposited under the same conditions using potentiostatic method at 1V for 150 seconds.

Characterization of graphene/ MnO₂ multilayer hybrid film

The morphology and microstructure of the as-prepared graphene/ MnO₂ multilayer hybrid films (GMHF) were characterized via field emission scanning electron microscopy (FE-SEM, JOEL, JSM-6340F) and X-ray sequence spectrometer (Bruker AXS, Germany) with Cu K α radiation ($\lambda = 1.5406\text{\AA}$) operating at 40kv and 40 M α .

Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge experiments, as well as electrochemical impedance spectra measurement were performed to evaluate the electrochemical performances of the graphene/ MnO₂ multilayer hybrid film. The electrochemical performances of pure MnO₂ were also evaluated for comparison. All of the above electrochemical measurements were carried out in 1 M Na₂SO₄ electrolyte solution with a potential window of -0.1V to 0.9V by using a three-electrode electrochemical system as described above on AUTOLAB® machine (Eco Chemie, PGSTAT 30).

5.3 Results and discussion

Graphene/MnO₂ multilayer hybrid films (GMHF) were deposited on top of stainless steel plates, stainless steel foam, ITO, and graphite paper by same experiment procedures.

It was found that very little hybrid films were deposited onto ITO probably due to the

surface affinity of ITO to MnO₂ and graphene is very poor; while for graphite paper, strong affinity between graphene and graphite caused massive deposition of graphene, and the high deposition voltage at 10 volt induced strong water decomposition reaction which destroyed the graphite substrate. For stainless steel foil and stainless steel mesh, uniform deposition of graphene and MnO₂ was achieved without substrate damage, however, hybrid films on stainless steel mesh showed much smaller specific capacitance than hybrid films on stainless steel foil, thus in this chapter, the graphene/MnO₂ multilayer hybrid films used for morphology characterization and electrochemical analysis were all deposited on stainless steel foil.

5.3.1 Crystal structures and morphologies of graphene/MnO₂ multilayer hybrid film

Fig. 5.2a shows the X-ray diffraction (XRD) pattern of the as-prepared graphene/MnO₂ multilayer hybrid film (GMHF). A clear view of the graphene peaks is shown in figure 5.2b, The low and broad (002) diffraction peak detected at 2θ between 20 and 30° and the (100) diffraction peak at 43.7° confirmed a marginal disordered stacking of graphene sheets [34], which indicated the successful reduction and deposition of graphene oxide through electrophoretic deposition (EPD) method. While peaks at $2\theta=51^\circ$ (411) and 64.7° (002) indexed to α -MnO₂ (JCPDS NO.44-0141), showed the good crystallinity of α -MnO₂ in the composite. Peak located at 44.5° which is marked with * came from the reflection of stainless steel substrate. Figure 5.2c shows the X-ray diffraction (XRD) pattern of graphene oxide, the sharp and intensive peak at 11.7° is corresponding to the (001) reflection. The disappearance of this peak in GMHF

confirmed the regular stacks of graphene oxide are exfoliated.

Figure 5.2 XRD pattern of the graphene/ MnO_2 multilayer hybrid film (a), enlarge view of graphene XRD diffraction peaks(b), XRD pattern of graphene oxide (c)

Figure 5.3 shows the image of an electrophoretic deposited graphene on stainless steel surface at 10 volt for 180s, fuzzy stainless steel surface was observed beneath the semi-transparent layer, and the wrinkles on graphene surface indicated a disordered stacking of graphene sheets.

Figure 5.3 SEM image of electrophoretically deposited graphene thin layer (a) and thick layer (b)

Fig. 5.4 presents the FESEM images of GMHF, where Fig. 5.4a shows MnO₂ layer above graphene layer, and Fig. 5.4b shows graphene layer deposited on top of MnO₂ layer. As seen in Fig. 5.4a, the α -MnO₂ showed continuous three-dimensional (3-D) fibrous network morphology. For supercapacitor electrode material, 3-D mesoporous and ordered/periodic architectures are beneficial for the penetration of electrolyte and reactants into the entire electrode matrix, therefore as-prepared MnO₂ with a porous architecture has not only a high surface area but good ionic conductivity [35]. The MnO₂ layer thickness was measured to be around 10 nm thick according to SEM image. While in Fig. 5.4b, graphene layer is observed to be a uniform and semi-transparent thin film. A blurry image of porous MnO₂ layer can be observed to lie beneath the graphene layer, which confirmed the multilayer hybrid structure and close contact between graphene and MnO₂. This morphology is believed to benefit electronic conductivity improvement [36], because close contact between graphene and MnO₂ is important to ensure fast electronic and ionic transportation plus maximization of the synergetic effects between them. Besides, the multilayer hybrid structure of graphene and MnO₂ prevents the aggregation of graphene sheets and allows a uniform distribution of graphene sheets inside the entire MnO₂ composite. Figure 5.4 (c) gives the side-view of the film, exhibiting a layered structure with a uniform thickness of about 1.5 μ m.

Figure 5.4 FESEM images of (a) MnO_2 and (b) graphene/ MnO_2 multilayer hybrid film (c) side-view of and graphene/ MnO_2 multilayer hybrid film

5.3.2 Supercapacitor performance of graphene/ MnO_2 multilayer hybrid film

To evaluate the electrochemical performance and quantify the specific capacitance of manganese dioxide, graphene and as-prepared graphene/ MnO_2 multilayer hybrid film, cyclic voltammetry (CV) measurements were performed at a scan rate of 100 mVs^{-1} in $1 \text{ M Na}_2\text{SO}_4$ aqueous solution with a potential window of $-0.1 - 0.9 \text{ V}$. As shown in Fig. 5.5, the CV curve of graphene was close to be rectangular shape; indicating a typical electrical double layer capacitance nature, the tail at voltage close to 0.9 could be attributed to hydrogen evolution reaction. While for both MnO_2 and GMHF, their CV curves exhibited a symmetric but slightly distorted rectangular shape, symmetric CV shape is desired for supercapacitor electrode, as it is sign of undergoing highly reversible redox reactions and good cyclic stability. The ideal CV curve of MnO_2 should be

rectangular like that of ruthenium oxide as we have review in chapter 2, the distortion of the CV curve can be explained by following reasons: (1) Faradaic reactions take place during the sweep process [37] (2) the raise of internal resistance of electrode material and (3) the diffusion limitation of Na⁺ in the electrode [38]. It is also noticed that the CV curve of GMHF expanded more in the vertical direction and approached closer to a ideal rectangular shape than that of MnO₂, suggesting improved electronic conductivity in GMHF than MnO₂ [19]. In other word, it indicates that the electrical conductivity of MnO₂ was effectively improved by developing graphene and MnO₂ into multilayer hybrid film. Moreover, since the average areas of CV curve is proportional to the specific capacitance of electrodes [39], the GMHF CV curve expanded more in the vertical direction also showed that it had much larger CV area than those of as grown graphene and manganese dioxide, which indicated larger specific capacitance. It is therefore reasonable to conclude that the synergetic effects of multilayer hybrid structure of graphene/MnO₂ composite had improved electronic conductivity and promoted more electrochemical reactions inside composite and eventually resulted higher specific capacitance.

Figure 5.5 CV curves of graphene, MnO_2 and GMHF in 1 M Na_2SO_4 solution at scan rate of 100 mVs^{-1}

To further investigate the capacitive behavior of GMHF electrode, galvanostatic charge/discharge measurements were carried out in 1 M Na_2SO_4 solution between -0.1 and 0.9 V at different current densities, as shown in Figure 5.6. The electrodes were passed through a positive fixed current until its potential reached the maximum cut-off potential at 0.9 V, after that a negative fixed current with same magnitude was applied until it reached the minimum cut off potential at -0.1 V. The y-axis, which indicates potential, is plotted with x-axis, which records the charge/discharge time. In Figure 5.6, the charge/discharge curves of GMHF at all current densities exhibited a symmetric and slightly curving shape, indicating the good reversibility of electrochemical reactions and the presence of pseudo-capacitance along with double layer capacitance. The negligible voltage drop at the tip of charge/discharge curves reveals small equivalent series resistance (ESR) and good electrical conductivity of GMHF. The specific capacitances C_s are calculated based on the discharge curves according to $C_s = I * \Delta t / (\Delta V * m)$ [19], where I is the constant discharge current, Δt is the discharge time, and ΔV is the potential

drop during discharge stage [20]. The calculated Cs of GMHF at various current densities 1, 2, 5, 10 and 20 A g^{-1} were 396, 321, 249.5, 207 and 172 F g^{-1} respectively. These values are much higher than those of manganese dioxide (297 F g^{-1} at 1 A g^{-1}) prepared for comparison, and other reported manganese dioxide/graphene composites [20, 40], which showed the remarkable performances of graphene/ MnO_2 multilayer hybrid film structure. These findings were in good agreement with result indicated by CV.

Figure 5.6 Galvanostatic charge/discharge curves of GMHF at 1, 2, 5, 10, 20 A g^{-1}

Rate performance is important in evaluating supercapacitor electrode for practical application, it indicates the electrochemical reaction rate in electrode and determines how fast the electrode can be charge or discharged. In this study, the rate performance of the GMHF and MnO_2 was evaluated by comparing their specific capacitances at different charge/discharge current densities. The results were presented in Figure 5.7, it is interesting to note that GMHF and MnO_2 performed similar to each other at low current densities (below 2 A g^{-1}), however with increasing current densities, GMHF performed

much better with higher capacitance retention, which means better rate performance. This can be explained as follows: in GMHF and MnO_2 the charge storages were mainly based on faradic redox reactions, which are limited by how fast the electrons and ions can transfer or diffuse into the electrode/electrolyte interface. At low current density, low concentration polarization has enough time for ion diffusion and complete the charging process [41], while at high current densities; the limited time restricts ion diffusion and allows only part of the active electrode materials to complete charging process, so specific capacitance is reduced compared with that at low current density. The better rate performance of GMHF at high current densities indicates that the synergetic effect of graphene/ MnO_2 multilayer hybrid structure promoted electrochemical reactions within the electrode material. This finding was also evidenced by the investigation of electrochemical impedance spectroscopy (EIS).

Fig. 5.7 Capacitance retention of MnO_2 and GMHF at different charge/discharge current densities

Electrochemical impedance spectroscopy (EIS) is a complementary technique to cyclic voltammetry. It provides more information about the electrochemical frequency behavior of electrodes and therefore it is usually used to characterize electrochemical systems. Electrical impedance measures the frequency response of an electrical circuit to the passage of a current when a voltage is applied. Quantitatively, it is a complex ratio of the voltage to the alternating current and can be expressed as:

$$Z = |Z|e^{j\theta} \quad (5.1)$$

Where the magnitude $|Z|$ represents the ratio of the voltage difference amplitude to the current amplitude, and the argument θ gives the phase difference between voltage and current, j is the imaginary unit. EIS measures the impedance of a system over a range of frequencies. Analysis of the system response contains information about the interface, structure of electrode and electrochemical reactions taking place. Based on the response information, an equivalent circuit could be derived from the impedance data to show some important physical properties of the complex electrochemical system. The equivalent circuit is composed of ideal resistors (R), capacitors (C), and inductors (L). In real systems of supercapacitor, two more factors are added to complete the modeling: generalized constant phase element (CPE) and Warburg element (Z_W), which represent the diffusion or mass transport impedances of the cell. One typical equivalent circuit of a supercapacitor electrode is shown below:

Figure 5.8 Typical equivalent circuits for supercapacitor electrode

In the equivalent circuit, resistors represent the transfer resistance for ion and electron. For supercapacitor, the resistance could come from the ion transport of the electrolyte, electron transport from conductor to active material and the charge transfer process at the electrode surface. While the capacitors and inductors shown in the curve are related to space-charge polarization regions, such as the electrochemical double layer, and adsorption/desorption processes at an electrode/electrolyte interface. The data obtained by EIS is often expressed in Nyquist plot, which plots the imaginary impedance which represents the capacitive and inductive character of the cell, versus the real impedance of the cell. In Nyquist plot, a unique impedance arc arising at intermediate frequency region represents the activation controlled process with distinct time constant. The shape of the arc carries information about the possible mechanism or governing phenomena.

In this study, the Nyquist plots of GMHF and MnO_2 were obtained after 500 cycles of charge/discharge test in the frequency range of 0.1 Hz to 10 kHz in 1 M Na_2SO_4 solution at a DC bias of 0V. As shown in Fig. 5.9, the intercepts of Nyquist plots with the real axis at high frequency, which represent the combined resistance coming from the capacitive film, electrolyte and electrical substrate of GMHF and MnO_2 , were 5.0 Ω and 6.9 Ω respectively, indicate that the multilayer film was less resistive than the pure MnO_2 film.

It should be noted that this estimation is based on the reasonable assumption that the

resistances of stainless steel substrate and the Na₂SO₄ electrolyte were the same in both experiments. The improvement in conductivity is highly due to the conductive contribution from the graphene, however it also should not be forgot that the reduced resistance of the composite film may be also due to the increased surface area of the porous composite structure [42]. The semicircle in the intermediate frequency range, which is related to Faradic reactions and the diameter of which represents interfacial charge transfer resistance, is also quite different for GMHF and MnO₂. It can be clearly observed that GMHF exhibited much smaller semicircle than MnO₂, indicating smaller charge transfer resistance. The respective charge transfer resistances were about 20 Ω for GMHF and nearly 96 Ω for MnO₂. It is therefore reasonable to reckon that the incorporated graphene layers with high conductivity were responsible for the significantly improved charge transfer resistance. The transition point between the semicircle and oblique straight line is called “knee” [43], and the knee frequency denotes the maximum frequency at which capacitive behaviors is dominant [44]. Read from the plot, the knee frequencies of GMHF and MnO₂ were 24 Hz and 3 Hz respectively, which means that GMHF started capacitive behavior faster than MnO₂. Furthermore, the linear part of the Nyquist plot at low frequency range is related to the ion diffusion/transportation process within electrode. Both GMHF and MnO₂ exhibit a oblique line with slope close to 45° which is the Warburg-type impedance response and typical in porous structure electrode, it indicated the slow ion migration process in the electrolyte solution the whole electrochemical reactions were limited by the electrolyte ion diffusion [45].

Figure 5.9 Nyquist plots of MnO_2 and GMHF

In order to evaluate the cycling stability of the as-prepared GMHF composite in high load condition as in practical application, 500 galvanostatic charge-discharge cycles were performed at a current density as high as 4 A g^{-1} between -0.1 and 0.9 V in $1 \text{ M Na}_2\text{SO}_4$ electrolyte solution. The result is shown in Fig. 5.10. It is noted that the as-prepared composite reached the highest capacitance after about 25 charge/discharge cycles; this may be due to electrolyte needs some time to fully penetrate through the composite and reaches the highest material utilization ratio. After that capacitance declined, possible reasons could be: dissolution of active materials into electrolyte and deformation of structure caused by long time cyclic test. It is noteworthy that about 75% of the initial capacitance remained after 500 cycles and most of the capacitance reduction happened in the initial 250 cycles (18.3% loss), after that only 6.7% was lost, indicating the capacitive film was becoming stable as cyclic test went on. Considering the fact that the higher charge/discharge current, the more rigorous requirements for the structure stability of capacitive film, the cycling stability of GMHF was reasonably good at the high

charge-discharge current density of 4 A g^{-1} .

Fig. 5.10 Cycle performance of the GMHF with a voltage of 1.0 V at a current density of 4 A g^{-1}

5.4 Conclusion

In conclusion, a new and facile approach has been developed to produce multilayer hybrid film of graphene and MnO_2 On various substrates for supercapacitor application. Their microstructure and supercapacitor performance are systematically investigated. The results can be concluded as follows:

- (1) The facile approach of sequentially layer-by-layer potentiostatic deposition of MnO_2 and electrophoretic deposition/reduction of graphene oxide, leads to well-designed multilayer hybrid architecture. Besides, the proposed method eliminates the use of any binders or mediators that may increase the internal charge transfer resistance and degrade the electrochemical performances, which is a big merit this technique in constructing hybrid film.

- (2) The as-prepared multilayer graphene/ MnO₂ hybrid composite showed excellent electrochemical performances with capacitance as high as 396 F g⁻¹ at 1 A g⁻¹, and better rate capability than individual MnO₂ or graphene electrode. These improvements may be attributed to the presence of highly conductive graphene sheets and synergetic effects of graphene/MnO₂ multilayer hybrid structure as indicated by cyclic voltammetry test and electrochemical impedance study.
- (3) Moreover, the synthesis and application of graphene has always been a challenge and interest of researchers, the proposed graphene/ MnO₂ multilayer hybrid film construction technique in this study is an facile method and can be readily generalized to build many other graphene incorporated transition metal oxide hybrid films, which will be promising materials for a large spectrum of applications such as sensor, battery and so on.

5.5 Reference

1. Chen, Y.-S. and C.-C. Hu, *Capacitive Characteristics of Binary Manganese-Nickel Oxides Prepared by Anodic Deposition*. Electrochemical and Solid-State Letters, 2003. 6(10): p. A210-A213.
2. Nakayama, M., et al., *Electrodeposition of Manganese and Molybdenum Mixed Oxide Thin Films and Their Charge Storage Properties*. Langmuir, 2005. 21(13): p. 5907-5913.
3. Sharma, R.K., et al., *Carbon-supported, nano-structured, manganese oxide composite electrode for electrochemical supercapacitor*. Journal of Power Sources, 2007. 173(2): p. 1024-1028.
4. Ma, S.-B., et al., *Electrochemical properties of manganese oxide coated onto carbon nanotubes for energy-storage applications*. Journal of Power Sources, 2008. 178(1): p. 483-489.
5. Raymundo-Pinero, E., et al., *Performance of manganese oxide/CNTs composites as electrode materials for electrochemical capacitors*. Journal of the Electrochemical Society, 2005. 152(1): p. A229-A235.
6. Chou, S.L., et al., *Electrodeposition of MnO_2 nanowires on carbon nanotube paper as free-standing, flexible electrode for supercapacitors*. Electrochemistry Communications, 2008. 10(11): p. 1724-1727.
7. Fan, Z., et al., *Preparation and characterization of manganese oxide/CNT composites as supercapacitive materials*. Diamond and Related Materials, 2006. 15(9): p. 1478-1483.
8. Ko, J.M. and K.M. Kim, *Electrochemical properties of MnO_2 /activated carbon nanotube composite as an electrode material for supercapacitor*. Materials Chemistry and Physics, 2009. 114(2-3): p. 837-841.
9. Wang, Y., et al., *Manganese dioxide-carbon nanotube nanocomposites for electrodes of electrochemical supercapacitors*. Scripta Materialia, 2009. 61(11): p. 1079-1082.
10. Brownson, D.A.C., D.K. Kampouris, and C.E. Banks, *An overview of graphene in energy production and storage applications*. Journal of Power Sources, 2011.

- 196(11): p. 4873-4885.
11. Pumera, M., *Electrochemistry of graphene: new horizons for sensing and energy storage*. The Chemical Record, 2009. 9(4): p. 211-223.
12. Liu, C., et al., *Membraneless enzymatic biofuel cells based on graphene nanosheets*. Biosensors and Bioelectronics, 2010. 25(7): p. 1829-1833.
13. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nat Mater, 2007. 6(3): p. 183-191.
14. Stankovich, S., et al., *Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide*. Carbon, 2007. 45(7): p. 1558-1565.
15. Stankovich, S., et al., *Graphene-based composite materials*. Nature, 2006. 442(7100): p. 282-286.
16. Jeong, H.K., et al., *Evidence of graphitic AB stacking order of graphite oxides*. Journal of the American Chemical Society, 2008. 130(4): p. 1362-1366.
17. Wu, Z.S., et al., *Anchoring hydrous RuO₂ on graphene sheets for high-performance electrochemical capacitors*. Advanced Functional Materials, 2010. 20(20): p. 3595-3602.
18. Wang, D., et al., *Ternary self-assembly of ordered metal oxide-graphene nanocomposites for electrochemical energy storage*. ACS Nano, 2010. 4(3): p. 1587-1595.
19. Li, Z., et al., *Electrostatic layer-by-layer self-assembly multilayer films based on graphene and manganese dioxide sheets as novel electrode materials for supercapacitors*. Journal of Materials Chemistry, 2011. 21(10): p. 3397-3403.
20. Chen, S., et al., *Graphene Oxide-MnO₂ Nanocomposites for Supercapacitors*. ACS Nano, 2010. 4(5): p. 2822-2830.
21. Wang, H.L., et al., *Mn₃O₄-Graphene Hybrid as a High-Capacity Anode Material for Lithium Ion Batteries*. Journal of the American Chemical Society, 2010. 132(40): p. 13978-13980.
22. Manga, K.K., et al., *Multilayer Hybrid Films Consisting of Alternating Graphene and Titania Nanosheets with Ultrafast Electron Transfer and Photoconversion Properties*. Advanced Functional Materials, 2009. 19(22): p. 3638-3643.

23. Wang, Y., et al., *Supercapacitor devices based on graphene materials*. Journal of Physical Chemistry C, 2009. 113(30): p. 13103-13107.
24. S.R.C. Vivekchand, C.S.R., K.S. Subrahmanyam, A. Govindaraj and C.N.R. Rao. J. Chem. Sci., 120 (2008), p. 9.
25. Yan, J., et al., *Preparation of graphene nanosheet/carbon nanotube/polyaniline composite as electrode material for supercapacitors*. Journal of Power Sources. 195(9): p. 3041-3045.
26. Wang, H., et al., *Graphene oxide doped polyaniline for supercapacitors*. Electrochemistry Communications, 2009. 11(6): p. 1158-1161.
27. Lu, T., et al., *Electrochemical behaviors of graphene, ZnO and graphene, SnO₂ composite films for supercapacitors*. Electrochimica Acta, 2010. 55(13): p. 4170-4173.
28. Zhang, Y., et al., *Capacitive behavior of graphene, ZnO composite film for supercapacitors*. Journal of Electroanalytical Chemistry, 2009. 634(1): p. 68-71.
29. Du, X., et al., *Graphene nanosheets as electrode material for electric double-layer capacitors*. Electrochimica Acta, 2010. 55(16): p. 4812-4819.
30. Goh, M.S. and M. Pumera, *Multilayer graphene nanoribbons exhibit larger capacitance than their few-layer and single-layer graphene counterparts*. Electrochemistry Communications, 2010. 12(10): p. 1375-1377.
31. Pan, D., et al., *Li Storage Properties of Disordered Graphene Nanosheets*. Chemistry of Materials, 2009. 21(14): p. 3136-3142.
32. An, S.J., et al., *Thin Film Fabrication and Simultaneous Anodic Reduction of Deposited Graphene Oxide Platelets by Electrophoretic Deposition*. Journal of Physical Chemistry Letters, 2010. 1(8): p. 1259-1263.
33. Hummers, W.S. and R.E. Offeman, *Preparation of Graphitic Oxide*. Journal of the American Chemical Society, 1958. 80(6): p. 1339-1339.
34. Qian, Y., S.B. Lu, and F.L. Gao, *Synthesis of manganese dioxide/reduced graphene oxide composites with excellent electrocatalytic activity toward reduction of oxygen*. Materials Letters, 2011. 65(1): p. 56-58.
35. Wei, W., et al., *Manganese oxide-based materials as electrochemical*

- supercapacitor electrodes*. Chemical Society Reviews. 40(3): p. 1697-1721.
36. Wu, Z.-S., et al., *High-Energy MnO₂ Nanowire/Graphene and Graphene Asymmetric Electrochemical Capacitors*. ACS Nano, 2010. 4(10): p. 5835-5842.
37. Zhang, L.L., et al., *Manganese oxide carbon composite as supercapacitor electrode materials*. Microporous and Mesoporous Materials, 2009. 123(1 鈇?): p. 260-267.
38. Li, J., Q.M. Yang, and I. Zhitomirsky, *Nickel foam-based manganese dioxide carbon nanotube composite electrodes for electrochemical supercapacitors*. Journal of Power Sources, 2008. 185(2): p. 1569-1574.
39. Srinivasan, V. and J.W. Weidner, *Capacitance studies of cobalt oxide films formed via electrochemical precipitation*. Journal of Power Sources, 2002. 108(1-2): p. 15-20.
40. Hou, Y., et al., *Design and Synthesis of Hierarchical MnO₂ Nanospheres/Carbon Nanotubes/Conducting Polymer Ternary Composite for High Performance Electrochemical Electrodes*. Nano Letters, 2010. 10(7): p. 2727-2733.
41. Zhang, J.T., J.W. Jiang, and X.S. Zhao, *Synthesis and Capacitive Properties of Manganese Oxide Nanosheets Dispersed on Functionalized Graphene Sheets*. Journal of Physical Chemistry C, 2011. 115(14): p. 6448-6454.
42. Hughes, M., et al., *Electrochemical capacitance of a nanoporous composite of carbon nanotubes and polypyrrole*. Chemistry of Materials, 2002. 14(4): p. 1610-1613.
43. Niu, C., et al., *High power electrochemical capacitors based on carbon nanotube electrodes*. Applied Physics Letters, 1997. 70(11): p. 1480-1482.
44. Della Santa, A., D. De Rossi, and A. Mazzoldi, *Performance and work capacity of a polypyrrole conducting polymer linear actuator*. Synthetic Metals, 1997. 90(2): p. 93-100.
45. Lu, L., et al., *Carbon titania mesoporous composite whisker as stable supercapacitor electrode material*. Journal of Materials Chemistry, 2010. 20(36): p. 7645-7651.

Chapter 6 Graphene / $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film for supercapacitor application

6.1 Introduction

It is well known that the two major limitations in the application of MnO_2 as supercapacitor electrode are its poor electrical conductivity and low accessible surface areas. Research efforts are dedicated to synthesis MnO_2 or MnO_2 composites, which can provide large specific surface area, smooth, and fast charge/ion transfer tunnels, so that high supercapacitor performances can be achieved [1].

In chapter 3, we have successfully synthesized MnO_2 in the presence of surfactant CTAB, and it is found that MnO_2 prepared in the presence of 1 wt. % CTAB showed a uniform and smooth morphology with extreme thin layer thickness, its large pore size also provided large accessible surface area for redox reactions and high way for ion transportation. The highest obtained capacitance was 359 F g^{-1} at a charge/discharge current density of 1 A g^{-1} . Moreover, the cyclic stability of MnO_2 electrode prepared with 1 wt. % CTAB is significantly improved, with no capacitance loss after 1000 cycles. This remarkable improvement may come from the structure strengthen effects of surfactant CTAB that prevents the loss of active material, and also stable mesoporous structure, which facilitates the charge transfer and increases structure tolerability. In the latter approach of incorporating graphene into MnO_2 and formation of multilayer hybrid films for supercapacitor application in chapter 5, the hybrid film composite showed excellent electrochemical performances with capacitance as high as 396 F g^{-1} at 1 A g^{-1} , and better rate capability than individual MnO_2 and graphene electrode. These improvements may be attributed to the presence of highly conductive graphene sheets and synergetic effects due to the formation of graphene/ MnO_2 multilayer hybrid structure.

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With the discoveries and understanding on the MnO₂ supercapacitor performance improvement from the previous chapters, in this chapter, we aim to further improve the supercapacitor performance of MnO₂ by developing a multilayer hybrid film consisting CTAB mediated MnO₂ and graphene. The morphology and electrochemical performance of the hybrid film will be investigated through FESEM, Cyclic voltammetry, charge/discharge test and EIS to evaluate how these two approaches that have effectively improve MnO₂ supercapacitor performance, work together.

6.2 Experimental procedure

Materials and electrochemical deposition setup

Analytical grade Manganese nitrite (Mn(NO₃)₂·6H₂O), cetyltrimethylammonium bromide (CTAB) and sodium sulfate (Na₂SO₄) were purchased from Sigma-Aldrich and used without further purification. All other chemicals and solvents were of analytical grade. Ultra pure water from a Milli-Q reagent water system at a resistivity > 18MΩ cm was used throughout the experiment. A three-electrode electrochemical cell was set up for electrochemical deposition and electrochemical characterization purpose, with a platinum foil (2cm×2cm), Ag/AgCl (KCl-saturated) and Stainless steel (SS) as counter electrode, reference electrode and working electrode, respectively. The distance between working electrode and counter electrode was fixed at 2 cm. Before the deposition, stainless steel plates (size 2cm×1cm×0.9 mm) were polished with emery paper to a rough finish, then washed with ethanol and distilled water, followed by drying in oven at 60°C, after that back side of the SS film is covered with parafilm to prevent deposition of MnO₂. To prepare the precursor solution for MnO₂ deposition, 1wt. % CTAB powder was added into 0.1 M manganese nitrate solution by stirring at 40°C for one night.

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Synthesis of graphene/ MnO₂CTAB multilayer hybrid film

In a typical synthesis process, a porous MnO₂ layer prepared in presence of 1wt. % CTAB (denoted as MnO₂CTAB) was firstly potentiostatically deposited onto stainless steel substrate from 0.1 M MnO₂CTAB precursor solution at 1 V for 40 seconds. After that, the electrode was washed with ethanol and distilled water followed by drying in oven at 60°C. Then the substrates coated with porous MnO₂CTAB layer was subjected to graphene deposition through simultaneous electrophoretic deposition and anodic reduction in 1mg ml⁻¹ graphene oxide colloidal solution as reported by An et al [2] at 10 V for 45 seconds. The graphene oxide colloidal suspension used here was prepared by dispersing 30 mg graphene oxide, which was synthesized from purified natural graphite by the modified Hummers method [3] followed by purification with filtration and dialysis, into 30 ml distilled water and then ultrasonicated for 2 hours at room temperature. The electrode was then washed with distilled water and dried for MnO₂ deposition again. The above process was repeated for three times to achieve a uniform multilayer hybrid film of MnO₂CTAB and graphene. Subsequently, the electrode was washed in 70°C ethanol for 2 hours and then in distilled water for 1 hour, this washing cycle was repeated for 2 days, followed by drying at 60°C in oven overnight. Finally, the obtained multilayer hybrid film was heated at 100°C for 1 hour to remove moistures and enhance graphene conductivity [2].

Characterization of graphene/ MnO₂CTAB multilayer hybrid film

The morphology and microstructure of the as-prepared graphene/ MnO₂CTAB multilayer hybrid films were characterized via field emission scanning electron microscopy (FE-SEM, JOEL, JSM-6340F) and X-ray sequence spectrometer (Bruker AXS, Germany) with Cu K α radiation ($\lambda = 1.5406\text{\AA}$) operating at 40kv and 40 Ma.

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Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge experiments, as well as electrochemical impedance spectra measurement were performed to evaluate the electrochemical performances of the graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film. All of the above electrochemical measurements were carried out in 1 M Na_2SO_4 electrolyte solution with a potential window of -0.1V to 0.9V by using a three-electrode electrochemical system as described above on AUTOLAB® machine (Eco Chemie, PGSTAT 30).

6.3 Results and discussion

6.3.1 Morphology characterization of MnO_2 , $\text{MnO}_{2\text{CTAB}}$, graphene/ MnO_2 and graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film

Fig. 6.1 presents the FESEM images of MnO_2 , $\text{MnO}_{2\text{CTAB}}$, graphene/ MnO_2 composite, and graphene/ $\text{MnO}_{2\text{CTAB}}$ composite, where Fig. 6.1(a) and (b) show MnO_2 and $\text{MnO}_{2\text{CTAB}}$ layer only without the disposition of graphene layers, and Fig. 6.1(c) and (d) shows graphene/ MnO_2 and graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid films with graphene layer deposited on top. In Fig. 6.1(a) and (b), it clearly shows that the $\text{MnO}_{2\text{CTAB}}$ layer had a continuous three-dimensional (3-D) fibrous network morphology with thinner layer thickness and larger pore sizes which were formed by interconnected nanosheets than those of MnO_2 . It is already known that for supercapacitor electrode material, 3-D mesoporous and ordered/periodic architectures are desirable for the penetration of electrolyte and reactants into the entire electrode matrix, therefore as-prepared $\text{MnO}_{2\text{CTAB}}$ with a porous architecture that showed much thinner layer thickness and pore size, would have higher specific surface area for redox reactions and also improved ionic conductivity [4]. While in Fig. 6.1 (c) and (d), both of the multilayer hybrid films showed

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a uniform and semi-transparent graphene thin film on the top, where a blurry image of porous MnO_2 layer lied beneath. This morphology confirmed the multilayer hybrid structure and close contact between graphene and MnO_2 . The close contact not only ensures fast electronic and ionic transportation but also prevents the aggregation of graphene sheets and allows a uniform distribution of graphene sheets inside the entire composite. In summary, in graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film, $\text{MnO}_{2\text{CTAB}}$ had much thinner layer thickness, larger pore size and also uniform morphology; other than that, it closely contacted with graphene and formed a multilayer hybrid structure, therefore a better capacitive performance than individual $\text{MnO}_{2\text{CTAB}}$ or graphene/ MnO_2 is expected.

Figure 6.1 FESEM images of (a) MnO_2 , (b) $\text{MnO}_{2\text{CTAB}}$, (c) Graphene/ MnO_2 multilayer hybrid film and (d) Graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film

6.3.2 Supercapacitor performance characterization of MnO_2 , $\text{MnO}_{2\text{CTAB}}$, graphene/ MnO_2 and graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film

The electrochemical performance of as prepared graphene/ $\text{MnO}_{2\text{CTAB}}$ multilayer hybrid film was investigated through cyclic voltammetry test.

Figure 6.2 (a) presents the cyclic voltammetry curves of graphene/ MnO_2 , $\text{MnO}_{2\text{CTAB}}$ and graphene/ $\text{MnO}_{2\text{CTAB}}$ obtained at scan rate of 100 mVs^{-1} . All of the three curves exhibited characteristic rectangular shape of MnO_2 supercapacitor electrode in Na_2SO_4 , no distinct redox peaks were observed. Since at the same scan rate, the capacitance is proportional to the area enclosed by CV curves, it could be concluded from the curve that graphene/ $\text{MnO}_{2\text{CTAB}}$ had the highest capacitance followed by graphene/ MnO_2 , and $\text{MnO}_{2\text{CTAB}}$. Figure 6.2 (b) shows the CV curves of graphene/ $\text{MnO}_{2\text{CTAB}}$ at different scan rates, the characteristic shapes of CV curves are observed not change significantly with the increase of scan rate, which indicates the fast redox reaction rate and good rate capability. The CV characteristics of graphene/ $\text{MnO}_{2\text{CTAB}}$ electrode were further investigated by plotting the anodic peak current i_p (measured at 0.4 V) vs. V (voltage scan rate) as shown in Figure 6.2(c). As we have explained in the chapter 3 that in a typical absorption process, i_p vs. V is expected to give a linear relationship regardless of the scan rates [5]. In figure 6.2(c), i_p vs. V shows a reasonably linear plot, indicating an ideally capacitive behavior and absorption process dominated electrochemical reactions.

Figure 6.2 (a) CV curves of MnO_2 , $\text{MnO}_{2\text{CTAB}}$, and Graphene/ $\text{MnO}_{2\text{CTAB}}$ in 1 M Na_2SO_4 solution at scan rate of 100 mVs^{-1} , (b) CV curves of $\text{MnO}_{2\text{CTAB}}/\text{Graphene}$ in 1 M Na_2SO_4 solution at scan rate of 10 mVs^{-1} , 20 mVs^{-1} , 50 mVs^{-1} , 100 mVs^{-1} (c) i_p vs. V plot of Graphene/ $\text{MnO}_{2\text{CTAB}}$

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The electrochemical performances of graphene/ MnO_{2CTAB} were further characterized by using the charge/discharge test, which was carried out in 1 M Na₂SO₄ solution between -0.1 and 0.9 V at different current densities, as shown in Figure 6.3.

Figure 6.3 Charge/discharge curves of graphene/MnO_{2CTAB} at current density of 2 Ag⁻¹, 5 Ag⁻¹, 10 Ag⁻¹ and 20 Ag⁻¹

It is observed that the charge/discharge curves of graphene/ MnO_{2CTAB} multilayer hybrid film at all current densities of exhibited a symmetric and slightly curving shape as we have obtained for other MnO₂ electrodes in this study, which indicated the presence of pseudo-capacitance along with double layer capacitance and good reversibility of electrochemical reactions. Besides, there was no significant voltage drop at the tip of charge/discharge curves revealing small equivalent series resistance (ESR) and good electronic conductivity. The specific capacitances C_s are calculated based on the discharge curves according to $C_s = I * \Delta t / (\Delta V * m)$ [6], where I is the constant discharge current, Δt is the discharge time, and ΔV is the potential drop during discharge stage [7]. The calculated C_s of graphene/ MnO_{2CTAB} at various current densities 2, 5, 10 and 20 A g⁻¹ are 403, 297, 248, and 216 F g⁻¹ respectively. This value was much higher than those of MnO₂, MnO_{2CTAB}, and similar to graphene/ MnO₂, which we have prepared in this

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study, indicating the combination of two capacitance enhancement mechanisms through morphology modification and electronic conductivity improvement, has successfully promoted the supercapacitor performance of MnO₂ to a higher level. The increased capacitance may be contributed from two aspects (1) the CTAB modified MnO₂ possessed increased surface area because of the had ultra thin interconnected nanosheets and enhanced ionic transfer due to much larger pore size; (2) the uniform distribution of graphene inside MnO₂CTAB electrode reduced the internal resistance and at the same owned a synergetic effect on the capacitive performances of MnO₂CTAB due to the formation of multilayer hybrid structure. However, it is also noticed that the capacitance enhancement is not simply adding up the two mechanisms together. The capacitive performance of graphene/MnO₂CTAB may not be fully achieved. This may be attributed to that there were some conflicts between the two enhancement mechanisms, like the enhanced ionic transportation due to larger pore size of MnO₂CTAB might be blocked by the intercalated graphene sheets; similarly the much increased MnO₂CTAB surface area corresponded to fixed graphene nanosheets surface area would degrade the degree of electronic conductivity enhancement. As a result, the full potential of the capacitance enhancement approaches cannot be realized and led to a less competitive capacitance performance. It is also noticed during the experiment that the capacitive performances of graphene/ MnO₂CTAB hybrid film were greatly affected by the degree of washing. This may be caused by that since it is not easy to remove CTAB completely due to the blocking effects of graphene, therefore residual CTAB in the composite would increase internal resistance and block ionic transportation, as a result the capacitance dropped.

Electrochemical impedance spectroscopy (EIS) is a complementary technique to cyclic voltammetry and provides more information about the electrochemical frequency behavior of electrodes. The EIS measurement of graphene/ MnO₂CTAB was carried out in

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the frequency range of 0.1 Hz to 10 kHz in 1 M Na₂SO₄ solution at a DC bias of 0V and results are presented in figure 6.4. The EIS data of MnO₂CTAB and graphene/ MnO₂ were also presented for comparisons. In Figure 4, all of the EIS curves were composed of an arc at high frequency and a straight sloping line at low frequency range. As have illustrated in previous chapters, the intercept of Nyquist plots with the real axis at high frequency represents the combined resistance coming from the capacitive film, electrolyte and electrical substrate. It could be read from the curve that all of the three samples had very small resistance; especially graphene/ MnO₂CTAB had the smallest resistance. It should be noted that this estimation is based on the reasonable assumption that the resistances of stainless steel substrate and the Na₂SO₄ electrolyte were the same for all three electrodes. The improvement in conductivity may be contributed from the conductive additive graphene or the increased surface area of the porous composite structure [8]. The semicircle in the intermediate frequency range is related to Faradic reactions and the diameter of which represents interfacial charge transfer resistance. It can be clearly observed that all of the three samples have quite small interfacial charge transfer resistance; especially graphene-incorporated electrodes had even smaller resistance, which indicated that the presence of graphene improved the electronic conductivity. Moreover, at low frequency range, where the linear part of the Nyquist plot is presented and related to the ion diffusion/transportation process within electrode, MnO₂CTAB had a slope more close to a vertical line, which was a typical ideal capacitive behavior and indicated that electrochemical reactions were mainly limited by the absorption process [9]. While the graphene/ MnO₂ had slope close to 45° which was the Warburg-type impedance response and typically observed in porous structure electrode, this behavior indicated slow ion migration process in the solution pores and electrochemical reactions were limited by electrolyte diffusion process [10]. As for

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graphene/ $\text{MnO}_{2\text{CTAB}}$, it had a slope between $\text{MnO}_{2\text{CTAB}}$ and graphene/ MnO_2 , indicating it behaved between the two types of electrode, which was consisted with the hybrid structure of graphene/ $\text{MnO}_{2\text{CTAB}}$.

Figure 6.4 Nyquist plots of MnO_2 , $\text{MnO}_{2\text{CTAB}}$, and Graphene / $\text{MnO}_{2\text{CTAB}}$ in 1 M Na_2SO_4 solution

The cyclic stability of the as-prepared graphene/ $\text{MnO}_{2\text{CTAB}}$ composite was investigated at high load condition, 1250 galvanostatic charge-discharge cycles were performed at a current density as high as 10 A g^{-1} between -0.1 and 0.9 V in 1 M Na_2SO_4 electrolyte solution. The result is shown in Fig. 6.5 with the charge/discharge curves of the first 10 cycles and the last 10 cycles displayed. It was calculated that 97% of the initial capacitance was retained after 1250 cycles. In comparison, in the chapter 3, we have shown that for $\text{MnO}_{2\text{CTAB}}$ 100% of the initial capacitance remained after 1000 cycles and for graphene/ MnO_2 composite, 75% of the initial capacitance remains after 500 cycles. So it may suggested that the improved cyclic stability of graphene/ $\text{MnO}_{2\text{CTAB}}$ composite may come from the excellent stable $\text{MnO}_{2\text{CTAB}}$ structure due to the structure stabilization

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effect of CTAB and increased structural tolerance, and the 3% capacitance loss after 1250 cycles may come from the structure degradation of the multilayer hybrid film during long time charge/discharge cycles. Overall, 97% capacitance retention after 1250 cycles at 10 A g^{-1} is excellent cyclic stability.

Figure 6.5 The first 10 cycles and the last 10 cycles charge/discharge curves of graphene/ $\text{MnO}_{2\text{CTAB}}$ in a 1250 cycles stability test

6.4 Conclusion

In this chapter, the two-capacitance enhancement mechanisms of MnO_2 through modification of morphology as well as electronic conductivity have been combined to prepare a multilayer hybrid film containing MnO_2 and graphene. The resulted composite consisting alternating graphene layer and $\text{MnO}_{2\text{CTAB}}$ layer, has been investigated as supercapacitor electrode. The results can be concluded as follows:

- (1) The capacitive performances of as-prepared graphene/ $\text{MnO}_{2\text{CTAB}}$ electrode showed the highest capacitance of 403 F g^{-1} at 2 A g^{-1} , which is much

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larger than individual MnO₂CTAB and graphene/MnO₂ multilayer film with capacitances of 286 F g⁻¹ and 321 F g⁻¹, respectively. The improved capacitive performances may be attributed to that MnO₂CTAB provided thinner layer thickness and large pore size while graphene reduced internal charge transfer resistance, which promoted fast electrochemical redox reactions at the electrode/electrolyte interface.

(2) In addition, the cyclic stability of graphene/MnO₂CTAB electrode showed excellent performance, with 97% capacitance retention after 1250 cycles at 10 Ag⁻¹ charge/discharge rates. This improvement may come from the stabilized MnO₂CTAB structure, which effectively stopped active material loss, facilitated the electrolyte ion penetration and increased structure tolerability.

(3) Although the supercapacitor performance of graphene/MnO₂CTAB was improved by combining the two capacitance enhancement mechanisms, it is also noticed that the two mechanisms may inhibit each other during charge storage. The enhanced ionic transportation due to larger pore size may be blocked by the intercalated graphene sheets and the much increased MnO₂CTAB surface area corresponded to fixed graphene nanosheets surface area would degrade the degree of electronic conductivity enhancement. Other than that, the removal of CTAB from the multilayer hybrid film may be more difficult due to the presence of graphene layer and residual CTAB may increase the internal resistance and degrades supercapacitor performance. As a result, the full potential of the capacitance enhancement approaches cannot be realized and leads to a less competitive capacitance performances.

6.5 Reference

1. Wei, W.F., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. Chemical Society Reviews, 2011. **40**(3): p. 1697-1721.
2. An, S.J., et al., *Thin Film Fabrication and Simultaneous Anodic Reduction of Deposited Graphene Oxide Platelets by Electrophoretic Deposition*. Journal of Physical Chemistry Letters, 2010. **1**(8): p. 1259-1263.
3. Hummers, W.S. and R.E. Offeman, *Preparation of Graphitic Oxide*. Journal of the American Chemical Society, 1958. **80**(6): p. 1339-1339.
4. Wei, W., et al., *Manganese oxide-based materials as electrochemical supercapacitor electrodes*. Chemical Society Reviews. **40**(3): p. 1697-1721.
5. Hu, Z.A., et al., *Synthesis of alpha-Cobalt Hydroxides with Different Intercalated Anions and Effects of Intercalated Anions on Their Morphology, Basal Plane Spacing, and Capacitive Property*. Journal of Physical Chemistry C, 2009. **113**(28): p. 12502-12508.
6. Li, Z., et al., *Electrostatic layer-by-layer self-assembly multilayer films based on graphene and manganese dioxide sheets as novel electrode materials for supercapacitors*. Journal of Materials Chemistry, 2011. **21**(10): p. 3397-3403.
7. Chen, S., et al., *Graphene Oxide– MnO_2 Nanocomposites for Supercapacitors*. ACS Nano, 2010. **4**(5): p. 2822-2830.
8. Hughes, M., et al., *Electrochemical capacitance of a nanoporous composite of carbon nanotubes and polypyrrole*. Chemistry of Materials, 2002. **14**(4): p. 1610-1613.
9. Chen, W.C., T.C. Wen, and H.S. Teng, *Polyaniline-deposited porous carbon electrode for supercapacitor*. Electrochimica Acta, 2003. **48**(6): p. 641-649.
10. Lu, L., et al., *Carbon titania mesoporous composite whisker as stable supercapacitor electrode material*. Journal of Materials Chemistry, 2010. **20**(36): p. 7645-7651.

Chapter 7 Conclusions

7.1 Conclusions

In summary, we have focused on the charge storage mechanism and capacitive performance enhancement of transition metal oxides; two of very popular transition metal oxides: cobalt hydroxide and manganese dioxide were carefully studied in this study. CTAB mediated MnO_2 , NMP mediated cobalt hydroxide, graphene/ MnO_2 multilayer hybrid film, and graphene/ CTAB mediated MnO_2 multilayer hybrid film have been electrochemically deposited on stainless steel substrates for supercapacitor application. The as-prepared materials were used as supercapacitor electrodes directly. Their morphologies, crystal structure and various electrochemical performances have been systematically studied and compared with bare cobalt hydroxide and manganese dioxide. In addition, the organic solvent and surfactant working mechanisms as well as the capacitance enhancement mechanisms have been bravely proposed and the importance of morphology modification and electronic conductivity improvement has been proved. The major conclusions of present work could be drawn as follows:

- I. Structural directing agent CTAB was observed to change the morphology of MnO_2 significantly; the presence of CTAB changed the inner boundary of the diffuse layer as well as double layer characteristics and electrokinetics during electrochemical deposition. As a result, MnO_2 electrode with a uniform mesoporous structure formed by extremely thin interconnected nanosheets was formed when 1 wt. % CTAB is added. Higher concentration of CTAB (5 wt. %), however caused electrode overvoltage and led to an irregular morphology that resulted in smaller capacitance.
- II. With the success of CTAB on MnO_2 supercapacitor performance improvement, Organic solvent NMP was found to be able to influence the nucleation and growth

process of cobalt hydroxide, and proper concentration of NMP could result in cobalt hydroxide with much narrower interlayer spacing, thinner layer thickness as well as more uniform pore size distribution, which can therefore provide more active sites for electrochemical reactions and higher capacitance. A capacitance increment as high as 37% is observed.

III. The capacitive performances of as-prepared MnO_2 electrodes prepared with different CTAB concentrations were investigated by using various techniques. MnO_2 electrodes prepared with 1 wt. % CTAB showed the highest capacitance of 359 F g^{-1} at 1 A g^{-1} , which was larger than those of MnO_2 and MnO_2 (5 wt. % CTAB) with capacitances of 297 F g^{-1} and 309 F g^{-1} , respectively. The improved capacitive performances may be attributed to the thinner layer thickness, which results in larger accesable surface area for electrochemical redox reactions and larger pore size that allows easy electrolyte ion transportation. Other than that, the cyclic stability of MnO_2 electrodes prepared with 1 wt. % CTAB showed remarkable improvement, e.g. with no capacitance loss after 1000 cycles. The reason for this could be due to the structural strengthening effect of CTAB, which prevents the loss of active material and also the mesoporous structure with larger pore size that facilitates the ion transfer and increases structure tolerability.

IV. The capacitance enhancement of MnO_2 through reducing internal electronic transfer resistance has also been investigated. A well-designed multilayer hybrid film consisting of MnO_2 and graphene has been fabricated through sequential layer-by-layer potentiostatic deposition of MnO_2 and electrophoretic deposition/reduction of graphene oxide.

V. The morphology, crystal structure and supercapacitor performance of the graphene/ MnO_2 multilayer hybrid film have been studied carefully. It showed that MnO_2 layer and graphene layer organized alternatively and uniformly in the composite

and with tight contact between them. The as-prepared multilayer hybrid film showed a lower interfacial charge transfer resistance as indicated by EIS and also a high specific capacitance of 396 F g^{-1} at 1 A g^{-1} , plus a better rate capability than individual MnO_2 or graphene electrode has been obtained. These improvements may be attributed to the presence of highly conductive graphene sheets and synergetic effect of graphene/ MnO_2 multilayer hybrid structure.

VI. The capacitance enhancement mechanisms through modification of the morphology as well as improvement of the electronic conductivity have been combined to prepare a multilayer hybrid film consisting of alternating graphene layer and $\text{MnO}_{2\text{CTAB}}$ layer. The as prepared film was investigated as supercapacitor electrode and compared with individual $\text{MnO}_{2\text{CTAB}}$ and graphene/ MnO_2 electrodes.

VII. The graphene/ $\text{MnO}_{2\text{CTAB}}$ electrodes showed the highest capacitance of 403 F g^{-1} at 2 A g^{-1} , which is larger than that of $\text{MnO}_{2\text{CTAB}}$ (e.g. 286 F g^{-1}) and graphene/ MnO_2 multilayer film (e.g. 321 F g^{-1}). The improved capacitive performances may be attributed to the following reasons: $\text{MnO}_{2\text{CTAB}}$ provided thinner layer thickness and large pore size while graphene reduced internal charge transfer resistance which promoted effective electrochemical redox reactions at the electrode/electrolyte interface. Moreover, the graphene/ $\text{MnO}_{2\text{CTAB}}$ showed an excellent cyclic stability performance, with 97% capacitance retention after 1250 cycles at a charge/discharge current density of 10 Ag^{-1} . This improvement may be due to the stabilized $\text{MnO}_{2\text{CTAB}}$ layer that has excellent cyclic stability, while the little loss may come from the structure deformation of multilayer hybrid film during cycling.

VIII. It is also noticed that the two capacitance improvement mechanisms MnO_2 may inhibit each other during charge storage. The intercalated graphene sheets may block the enhanced ionic transportation, which is caused by larger pore size of $\text{MnO}_{2\text{CTAB}}$, and on the other hand the much-increased $\text{MnO}_{2\text{CTAB}}$ surface area would degrade the degree of

electronic conductivity enhancement. Other than that, the removal of CTAB from the multilayer hybrid film may be more difficult due to the presence of graphene and residual CTAB will increase internal resistance and degrade supercapacitor performance. As a result, the potential of the capacitance enhancement approaches cannot be fully realized and results a less competitive capacitance performances.

7.2 Main scientific contributions

The main scientific contributions of the present work can be summarized as following:

- It is the first time to use surfactant CTAB to synthesis MnO_2 for supercapacitor application. The effects of surfactant concentrations on the morphology, crystal structure, and electrochemical performances are systematically investigated.
- MnO_2 synthesized with mediation of CTAB showed very attractive supercapacitor performances. Morphology of ultra thin layer thickness as well as large pore size is responsible for the capacitance enhancement. It is also found that CTAB mediated MnO_2 had an excellent cyclic stability with no capacitance loss in 1000 cycles which is very rare for MnO_2 electrode due to the CTAB stabilization effect and increased structural tolerability.
- This work also for the first time used organic solvent NMP during cobalt hydroxide synthesis for morphology modification purpose. The presence of NMP influences the nucleation and growth process of Co(OH)_2 and results in Co(OH)_2 with smaller interlayer spacing, thinner layer thickness and uniform pore size, which are found in favor of higher supercapacitor capacitances.
- It is found that different surfactants/organic solvents work for different material systems, CTAB works well on manganese dioxide and NMP works well on cobalt hydroxide.
- A new and facile technique has been developed in this work to fabricate graphene/ MnO_2 multilayer hybrid film through electrochemical layer by layer deposition

method without tedious preparation work of graphene and any binders than may increase internal resistance.

- It is found that the graphene/MnO₂ showed enhanced supercapacitor performances in such a hybrid structure. The enhancement mechanism has been also discussed.
- It is the first time to develop CTAB modified MnO₂ with graphene into a multilayer hybrid film structure and its supercapacitor performances are carefully studied.
- Although graphene/MnO_{2CTAB} showed significant capacitance enhancement, it is found that there are some conflicts between the two capacitance enhancement mechanisms, more work needs to be done to fully realize the potential of this graphene/MnO_{2CTAB} hybrid structure.

Chapter 8 Future work

8.1 Future work

In the present work, we have synthesized and systematically studied the effect of morphology, specific surface area and electronic conductivity on the capacitive performances of transition metal oxides. Cobalt hydroxide, manganese dioxide and graphene/manganese dioxide composite with unique morphologies and structures have been successfully fabricated with improve supercapacitor performance. However during the studying process, it is also realized that some mechanisms still remain unclear and there are more room for the further development of these transition metal oxide based supercapacitor electrode material, therefore the following future work is proposed.

Firstly, CTAB mediated synthesis of MnO_2 has shown remarkable capacitive improvement by forming thinner layer thickness, uniform morphology and larger pore size. When CATB was extended to cobalt hydroxide synthesis, CTAB mediated cobalt hydroxide has shown typical porous structure with interconnected nanosheets and also larger pore size, the capacitance observed was as high as 731 Fg^{-1} , higher than that modified with NMP (604 Fg^{-1}). However, its performances varied a lot with experiment conditions, like deposition potential, CTAB concentration and so on. Thus more work is needed to study the roles of CTAB and the ideal experiment conditions for cobalt hydroxide synthesis. Besides that, since cobalt hydroxide in this study was obtained through cathodic deposition, therefore removal of the residual cationic surfactant CTAB in the as prepared electrode could be more difficult, but it also provides an opportunity to improve supercapacitor performances.

Secondly, graphene in the graphene/ MnO_2 multilayer hybrid composite is noted to be responsible for the enhancement of electronic conductivity and the synergetic effect between graphene and MnO_2 that promoted electrochemical performances. It is worth to

investigate how the number and thickness of layers as well as the content of graphene in the multilayer hybrid films, which determines the interaction and distribution of graphene and MnO_2 , would affect the supercapacitor performances. This could further facilitate the understanding of capacitance enhancement mechanism of graphene/transition metal oxide multilayer hybrid films.

Thirdly, the method developed during the synthesis of graphene/ MnO_2 multilayer hybrid film could be very attractive to be extended to synthesis other supercapacitor electrode materials that have poor electronic conductivity, such as V_2O_5 , Fe_3O_4 and SnO_2 etc. The improved electronic conductivity as well as synergetic effects by developing graphene/transition metal oxide multilayer hybrid film could promote their supercapacitor performances to a new level.

Last but not least, in the study of developing CTAB mediated MnO_2 and graphene into a multilayer hybrid structure to achieve higher supercapacitor performance, although an attractive capacitance of 403 F g^{-1} at 2 A g^{-1} was achieved, the full potential of the two supercapacitor performance enhancement mechanism by improving surface morphology and electronic conductive, was not brought out, because they interfere with each other. More work on the synthesis procedurals or $\text{MnO}_{2\text{CTAB}}$ /graphene arrangements needs to be done in the future to maximize their supercapacitor performance.

Appendix

Publication list

Journal papers

1. **T. Zhao**, H. Jiang, and J. Ma, "Surfactant-assisted electrochemical deposition of α -cobalt hydroxide for supercapacitors," *Journal of Power Sources*, vol. 196, pp. 860-864, 2011.
2. **T. Zhao.**, H. Jiang, and J. Ma, "Multilayer hybrid films consisting of alternating graphene and MnO_2 nanosheet for supercapacitor application." *The Journal of physical chemistry c*.(Major revision)
3. **T. Zhao.**, H. Jiang, and J. Ma, "CTAB modified MnO_2 for supercapacitor application", submitted, 2012
4. H. Jiang, **T. Zhao**, C. Li, and J. Ma, "Hierarchical self-assembly of ultrathin nickel hydroxide nanoflakes for high-performance supercapacitors," *Journal of Materials Chemistry*, vol. 21, pp. 3818-3823, 2011.
5. H. Jiang, **T. Zhao**, J. Ma, C. Yan, and C. Li, "Ultrafine manganese dioxide nanowire network for high-performance supercapacitors," *Chemical Communications*, vol. 47, pp. 1264-1266, 2011.